New routes to highly fluorinated ethers

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NEW ROUTES TO HIGHLY FLUORINATED ETHERS

Submitted by

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To Gillian

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MEMORANDUM

The work described in this thesis was carried out at the University of Durham between October 1982 and September 1985 and is original except where acknowledged by reference. This work has not previously been submitted, either wholly or in part for a degree at this or any other university.

NEW ROUTES TO HIGHLY FLUORINATED ETHERS

by

PETER T. TELFORD

The aim of this research project was to devise a viable synthetic route to perfluoropolyethers. Current commercial processes are elaborate but inefficient and hence are limited in application by cost.

The approach undertaken in this project consisted of essentially two steps; (1) the free radical addition of a polyether to a fluorinated olefin and (2) the direct fluorination of the polyadducts derived from the addition process (scheme i)

$$CH_3O(CH_2CH_2O)_nOCH_3 + \text{F-alkene} \xrightarrow[\text{or } b]{a} RfCH_2O(CH_2\underset{\displaystyle Rf}{\underset{|}{C}}HO)_nOCH_2Rf \xrightarrow{F_2} Rf'CF_2O(CF_2\underset{\displaystyle Rf'}{\underset{|}{C}}FO)_nOCF_2Rf'$$

a = peroxide, heat

b = gamma rays

(scheme i)

(Rf = polyfluoroalkyl, Rf' = perfluoroalkyl)

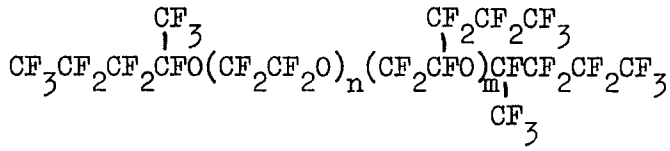
The research work was carried out in two phases. The initial investigation examined the free radical addition of simple mono-, di-, and poly-ethers to various fluorinated olefins. The participation of a 1,5 hydrogen transfer process was found to have a major influence on the production of poly-adducts.

The second phase of the process involved the development of techniques for the further fluorination of the simple adduct systems. Fluorination was achieved using cobalt trifluoride for volatile systems but the approach was limited by fragmentation of the substrate as the molecular weight of the adduct increased.

Techniques for direct fluorination have been developed and a

range of simple ether adducts were successfully fluorinated producing the corresponding perfluoroethers.

The findings from the model compound studies were applied to polyethylene glycol diethyl ether (av. molecular weight 456). Addition of the polyether to hexafluoropropene, followed by fluorination of the resulting polyadduct with elemental fluorine, produced a perfluoroether with the following structural features in good yield:



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CHAPTER ONE

INTRODUCTION

CHAPTER ONE

A. BACKGROUND

Organofluorine compounds possess many desirable properties and find applications in various facets of industry,[1,2] such as polymers, anaesthetics, blood substitutes, drugs, herbicides, refrigerants and lubricants.

The unique properties of fluorocarbon compared to hydrocarbon systems are due mainly to two factors, (1) the difference in electronegativity of fluorine and hydrogen, and (2) the influence of the non-bonded electron pairs of the fluorine atom on the fluorine-containing molecule. Several excellent books have been published discussing organofluorine chemistry in some detail.[1,2,3,4,5,6]

The work described in this thesis concerns the synthesis of a particular type of organofluorine compound, perfluoropolyethers (PFPE). PFPE are extremely important as vacuum diffusion pump oils and high performance lubricants due to their exceptional chemical and thermal stability. Recently P.F.P.E. are produced on an industrial scale using elaborate but inefficient techniques.

A major part of our synthetic strategy to this class of compounds has involved a new perfluorination process and so it has been valuable to review previous work in this field.

1B. Fluorination using elemental fluorine

1. Discovery and Generation of Fluorine

Fluorine was originally isolated in significant quantities by the French Scientist Moissan[7,8] who generated it by the electrolysis of a dilute solution of potassium fluoride in anhydrous hydrogen fluoride. In order to prevent loss of hydrogen fluoride by evaporation it was necessary to operate the cell at -25°C.

Today, laboratory scale production of fluorine is still *via* electrolysis. However, an electrolyte with the composition KF.2HF is used as this has a convenient melting point of around 89°C.

There are several designs of fluorine cell available both for laboratory and industrial scale production. These designs have been comprehensively reviewed by Rudge.[9]

2. Theory and Mechanism

It was understood during some of the earliest attempts[10] of direct fluorination that the process occurred by some kind of radical chain mechanism similar to that observed for the photochlorination of hydrocarbons (Scheme 1).

$$F_2 \longrightarrow 2F^{\bullet} \quad \left.\vphantom{x}\right) \text{initiation}$$

$$F^{\bullet} + RH \longrightarrow R^{\bullet} + HF \quad \left.\vphantom{x}\right)$$

$$R^{\bullet} + F_2 \longrightarrow RF + F^{\bullet} \quad \left.\vphantom{x}\right) \text{propagation}$$

$$F^{\bullet} + R^{\bullet} \longrightarrow RF \quad \left.\vphantom{x}\right)$$

$$R^{\bullet} + R^{\bullet} \longrightarrow RR \quad \left.\vphantom{x}\right) \text{termination}$$

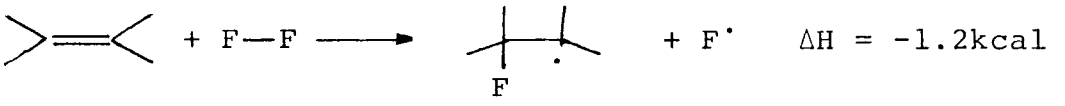
Scheme 1

As the reaction was known to proceed in the dark and at lower temperatures the initiation of the process was not clearly understood. It was suggested that, although fluorine was known to be minimally dissociated at room temperature ($F_2 \rightleftharpoons 2F^{\cdot}$ $K \approx 10^{-20}$)[4] this small abundance of fluorine atoms was enough to initiate the free radical process. An alternative, plausible theory put forward by Miller *et al*[11] postulated the reaction between a fluorine molecule and a hydrocarbon to produce a fluorine atom, hydrogen fluoride and an alkyl radical as the initial step (eqn. 1)

$$R - H + X_2 \longrightarrow R^{\cdot} + HX + X^{\cdot} \qquad \text{(eqn. 1)}$$

Comparison of the heats of reaction for equation (1) for the halogens F_2, $\Delta H \sim +4.1$ kcal; Cl_2, $\Delta H \sim +53.9$ kcal; Br_2 $\Delta H = +67.6$ kcal; immediately shows that the mechanism is feasible in the case of fluorine and extremely unlikely in the case of the other halogens.

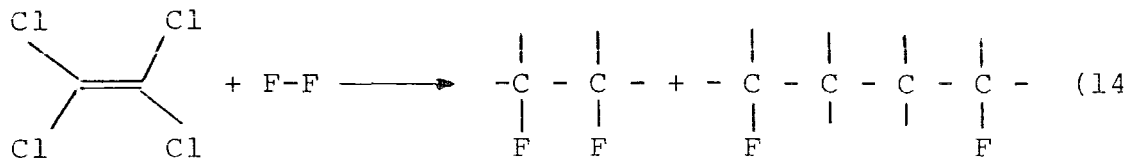
Little experimental evidence was available to conclusively support Miller's proposal but recent experiments at extremely low temperatures in cryogenic reactors,[12] where fluorination still occurs, give the mechanism strong support. In the case of olefins the reaction with fluorine is even more likely



(*cf.* Cl_2, $\Delta H = +22.5$ kcal; Br $\Delta H = +23$ kcal)

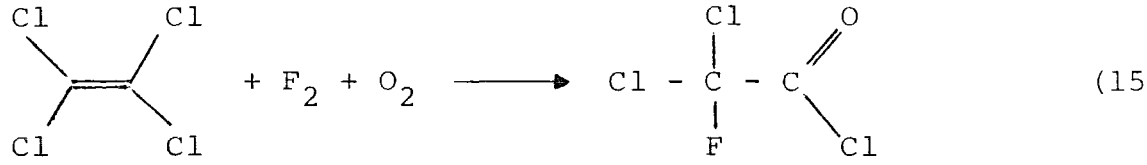
Supportive evidence for this mechanism is fairly well documented. It is known that fluorine will act as a free radical initiator in the dimerisation and halogenation of perhalo-olefins.[13,14]

$$Cl_2 + CCl_2{=}CCl_2 \xrightarrow[\text{trace}]{F_2} CCl_3{-}CCl_3 \ (80\%) \qquad (13)$$



(14)

Also fluorine sensitised oxidation reactions have been noted.[15]



(15)

3. Site selectivity in free radical halogenation

Table 1a illustrates the relative selectivities of fluorine, chlorine, and bromine radicals when abstracting a hydrogen atom from a primary, secondary, or tertiary site of a hydrocarbon.

TABLE 1a.[16]

Radical	Temp.	Rel. rate of abstraction		
		$-CH_3$	$-CH_2-$	$-\overset{\vert}{C}-H$
$F^{\cdot}$	27	1	1.2	1.4
$Cl^{\cdot}$	27	1	3.9	5.1
$Br^{\cdot}$	127	1	82	1600

As can be seen in the case of the more reactive radicals $F^{\cdot}$ and $Cl^{\cdot}$ little selectivity is shown in hydrocarbon molecules. However when polar groups are introduced into the

substrate selectivity is observed. For example Bochemüller[17] observed the following reactions

$$CH_3CH_2CH_2C(=O)-OH \xrightarrow[-78^{o}C]{F_2/N_2} CH_2FCH_2CH_2COOH + CH_3CHFCH_2CO_2H$$

$$(CH_3)_2CHCH_2CO_2H \xrightarrow[-78^{o}C]{F_2/N_2} (CH_3)_2CFCH_2COOH \qquad (17)$$

Also, in the case of propionic acid the relative rates of abstraction from the α and β sites by methyl radicals and chlorine atoms has been compared[18], (Table 1b).

TABLE 1b

Radical	Rel. Sel. in H· abstraction	
	CH_3 -	CH_2 - COOH
CH_3·	1	7.8
Cl·	1	0.03

Moreover, the reaction between 1-fluorobutane and the halogens gives similar results (Table 2).

TABLE 2.[19]

Halogen	Temp. °C	Relative selectivity at each position			
		FCH_2 -	CH_2 -	CH_2 -	CH_3
F·	20	<0.3	0.8	1.0	1
Cl·	35	0.8	1.6	3.7	1
Br·	146	10	9	8.2	1

These polar effects are not surprising as halogen atoms are electrophilic radicals and will therefore prefer to attack positions where there is high electron density.

Perhaps the best rationalisation of these observations is given by the Hammond Postulate[20] which states "the

geometry of the transition state for that step resembles the side to which it is closest in free energy", *i.e.*

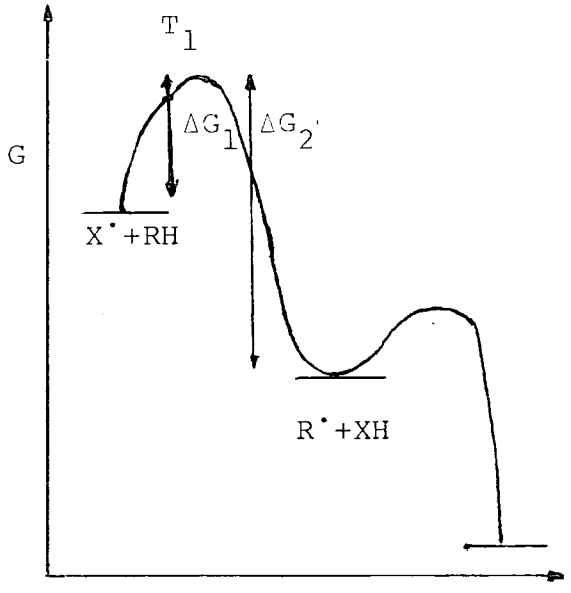


Diagram 1. X = Cl or F.

For example considering diagram 1 it is clear that $\Delta G_1 < \Delta G_2$ and therefore it would be expected that the geometry of transition state T_1 would closely resemble that of the starting materials. It follows that polar characteristics of the starting material will be important in the abstraction of the hydrogen atom. The energy profile in diagram1 is a good model for reactive systems like fluorine atoms and chlorine atoms, and as it is observed these two radicals are most affected by polar effects in substrates.

To consider another possibility examine diagram 2.

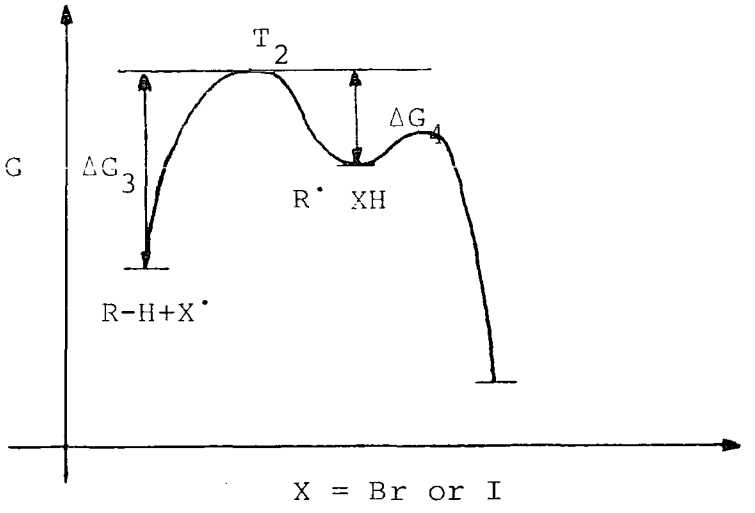


Diagram 2.

This diagram is a good model for an endothermic process such as free radical bromination or iodination. In this instance $\Delta G_3 > \Delta G_4$ and by Hammond's Postulate it would be expected that transition state T_2 should resemble the intermediate radical R· in geometry. Hence the stability of R· should be the major factor governing the site of hydrogen atom abstraction and not the polarity of the starting materials.

4. Development of direct fluorination techniques

Most early attempts to control the extreme reactivity of elemental fluorine with organic molecules involved some form of dilution technique and included a method of heat dissipation. Usually the reactions were carried out at elevated temperatures in the vapour phase, as lower temperature reactions had resulted in the formation of polymeric material[21]

and surprisingly, a higher proportion of fragmentation products. In each case both the fluorine and substrate vapour were heavily diluted with an inert carrier gas such as helium or nitrogen. There were many early reactor designs of this type all of which incorporated some, if not all of the aforementioned features. The actual construction detail of these reactors has been amply covered in some excellent reviews on the subject[22,23,24] and so will not be dealt with in depth here.

One of the more successful designs was the jet-reactor[25] of Bigelow and Tyzcowski; this reactor used no packing but favoured a short contact time between the fluorine and the substrate before quickly quenching the products in a liquid air trap. Using this technique a range of aliphatic alicyclic, aromatic, and functionalised hydrocarbons were directly fluorinated with interesting results (Table 3).

Other reactor designs utilized a divided metal packing as a heat sink. These metals, however, had such an effect on the reaction that they were suspected of having a catalytic function. As the reaction between the substrate and the fluorine is carried out over the surface of the metal, the fluorine may react, in part, preferentially with the metal forming a higher valency fluoride. The high valency metal fluoride may then react with the organic substrate, replacing a hydrogen in the substrate with fluorine and itself reverting to its normal valency fluoride (Scheme 2).

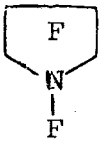
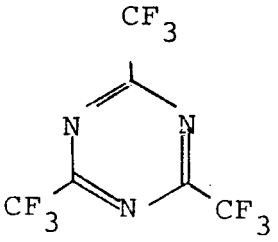
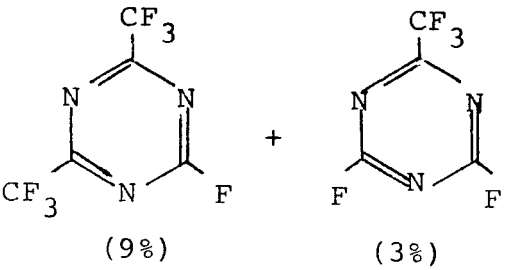
i.e.

$$Ag + F_2 \xrightarrow{\Delta} AgF_2 \qquad \text{step 1}$$

$$2AgF_2 \longrightarrow AgF + F_2$$
$$R\text{-}H + F_2 \longrightarrow R\text{-}F + HF \qquad \text{step 2.}$$

Scheme 2.

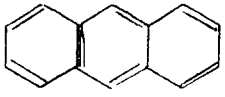
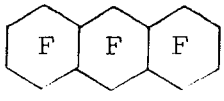
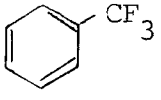
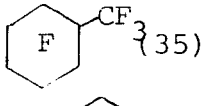
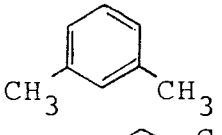
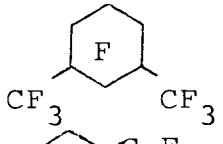
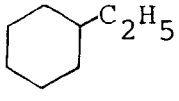
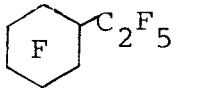
TABLE 3

Substrate	Reaction Temp °C	Product (% Yield)	Reference
C_2H_6	100-175	C_2F_6 (87)	26
nC_4H_{10}	100-175	nC_4F_{10} (89)	26
$(CH_3)_3CF$	100-175	$(CF_3)_3CF$ (88)	26
$(CH_3)_2CO$	80	$(CF_3)_2CO$ (10)	27
$CH_3\overset{O}{\overset{\|}{C}}C_2H_5$	100	$CF_3\overset{O}{\overset{\|}{C}}C_2F_5$ (15)	28
	120	C_6F_{12} (a)	29
CH_3NH_2	200	CF_3NF_2, CHF_3, CF_3NFCHF_2 (a)	30
$CF_2(CN)_2$	175	$NF_2(CF_2)_3NF_2$ (15)	31
$(CF_2CN)_2$	175	 (20)	31
	240	 (9%) + (3%)	32

(a) No yields given.

Among others gold[33,34,35] and silver[36,37] plated copper catalysts were perhaps the most effective. Using this "catalytic" fluorination technique several organic compounds were fluorinated to give the desired products, the results of these reactions are summarised in Table 4.

TABLE 4

Substrate	Conditions ^{o}C.	Product (% Yield)	Reference
C_6H_6	265	C_6F_{12} (58)	36
n heptane	135	C_7F_{16} (62)	36
$C_6H_5CF_3$	200	C_7F_{14} (85)	36
$C_6H_4(CF_3)_2$	200	C_8F_{16} (87)	36
	300		36
	280	 (40)	37
	200	 (35)	37
	200 Au/Cu	 (40)	33
	200 Au/Cu	 (21)	33

Although these techniques were invaluable contributions to the development of direct fluorination the resulting products were often in minor yield, and contained in mixtures difficult to separate.

It was also a regular feature that extensive fragmentation of the substrate molecule occurred.

5. Recent approaches to direct fluorination

Modern applications of direct fluorination have developed in three main areas:

a. Exhaustive fluorination of both functionalised and non-functionalised hydrocarbons;

b. direct fluorination of hydrocarbon polymers;

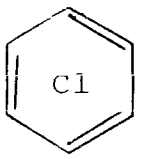
c. selective replacement of one or two hydrogen atoms in a molecule.

As previously outlined fluorine has many problems associated with its handling and extreme reactivity with hydrocarbon molecules. It is not surprising, therefore, that each of the above categories requires different approaches for successful fluorination and so it would be appropriate to consider each application in turn although some overlap of techniques is inevitable.

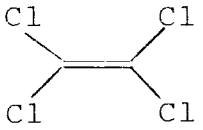
a. Exhaustive fluorination of organic molecules

Until recently the use of elemental fluorine for the purpose of producing organo-fluorine compounds has largely been avoided. It has often been considered a crude approach and the use of milder fluorinating agents, such as high valency metal fluorides,[38] main group fluorides,[39] and electrochemical fluorination[40] has generally been favoured.

Although some direct fluorination techniques were developed using either low temperatures and/or inert solvents,[41,42] there was no general method that could be applied to a range of functionalised organic compounds.



$$\xrightarrow[\substack{CFCl_2-CF_2Cl \\ 20^{o}C}]{F_2/N_2} \quad C_6F_6Cl_6 \text{ (average)} \quad 90\% \qquad (41)$$



$$\xrightarrow[0^{o}C]{F_2/N_2} \quad CFCl_2\text{-}CFCl_2 + C_2FCl_5 \qquad (42)$$

The recent report describing the LaMar[43] direct fluorination process, however, suggests that it is a generally applicable technique. After subsequent developments[44] to the original design the process has been used to successfully fluorinate hydrocarbon polymers, perfluoropolyethers, branched hydrocarbons,[45] functionalised hydrocarbons,[46,47,48] metal alkyls ($M[R]_n$)[49] and inorganic compounds.[50] Lagow and Margrave, the inventors of this process, approached the problem of direct fluorination from a theoretical aspect[27] and in doing so, attempted to establish the feasibility of direct fluorination and gauge the required experimental conditions by consideration of the thermochemistry involved. This approach has enhanced the scientific interest in direct fluorination and is outlined below:

1. Thermochemistry of direct fluorination reactions

Table 5 details the thermodynamic data for the direct fluorination of methane.[27]

The limiting factor of a successful direct fluorination process is the weakest bond contained within the reactant compound. It may be suggested from the thermodynamic data that, although the overall process (step 7, Table 5) is exothermic enough (ΔG_{298} = -103.4 kcal mol^{-1}) for carbon-carbon

TABLE 5[27] Thermodynamic Data for steps in fluorination of CH_4

Step	Reaction	ΔH_{298} kcal mol^{-1}	ΔH_{598} kcal mol^{-1}	ΔG_{298} kcal mol^{-1}	ΔG_{598} kcal mol^{-1}
1. Initiation	$F_2 \rightarrow F^{\cdot}$	+37.7	+38.5	+29.5	+20.9
2.	$F_2+RH \rightarrow R^{\cdot}+HF+F^{\cdot}$	+3.9	+5.1	-5.84	-18.9
3. Propagation	$RH+F^{\cdot} \rightarrow R^{\cdot}+HF$	-33.8	-33.4	-36.2	-35.5
4.	$R^{\cdot}+F_2 \rightarrow RF+F^{\cdot}$	-69.1	-69.5	-68.1	-64.1
5. Termination	$R^{\cdot}+F^{\cdot} \rightarrow RF$	-106.8	-108.0	-97.5	-85.0
6.	$R^{\cdot}+R^{\cdot} \rightarrow R-R$	-83.8	-83.0	-70.3	-57.5
7. Overall Reaction	$R-H+F_2 \rightarrow RF+HF$	-102.9	-102.9	-103.4	-103.9

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bond fission (C-C b.d.e. 84-88 kcal mol^{-1}) to occur, each individual step of the reaction is not, except termination step 5. Hence if the concentration of atomic fluorine could be kept to a minimum, thus avoiding reaction step 5, direct fluorination should be feasible, from a thermodynamic viewpoint, without extensive fragmentation occurring. The polymerisation problem, step 6, may also be overcome by limiting the mobility of the alkyl radicals, *e.g.* in a crystaline state.

2. Kinetic control of direct fluorination reactions

In order to produce the conditions outlined in the thermochemical argument the Lamar system used high dilution of fluorine with helium initially and gradually approached one atmosphere of fluorine. Using the dilution technique at room temperature was sufficient to fluorinate hydrocarbon polymers successfully. In the case of more volatile compounds,[44]

however, the substrate was maintained in the solid state by cooling in solid carbon dioxide. This limited the free movement of alkyl radicals so inhibiting coupling reactions and also lowered the concentration of fluorine atoms relative to fluorine molecules. Often reactors employing several different temperature zones[44] were used

The successful increase in fluorine concentration in the Lamar process may be understood from steric factors. As a hydrocarbon becomes progressively fluorinated the fluorine atom substituents sterically protect the carbon skeleton. This is perhaps best illustrated by Figure 1 showing the helicle arrangement of the fluorine atoms in polytetrafluoroethylene (PTFE). The electron cloud associated with these fluorine atoms will tend to repel any approaching fluorine molecules from the carbon skeleton. It is, therefore, possible to allow the relative number of collisions between the hydrocarbon and fluorine molecule to increase as the reaction proceeds.

As previously mentioned a diverse set of compounds both organic and inorganic have been successfully fluorinated using the LaMar process. The results of these are outlined in Tables 6, 7 and 8.

Although the application of the LaMar[43] technique and the improved variations[44] are diverse and the yields apparently high, there are considerable drawbacks associated with the process. For example the LaMar process is only applicable to solid polymers, the products of these reactions, as detailed in Section 5b, are only idealised structures and substantial cross-linking, oxygen incorporation, and carbon-

FIGURE 1

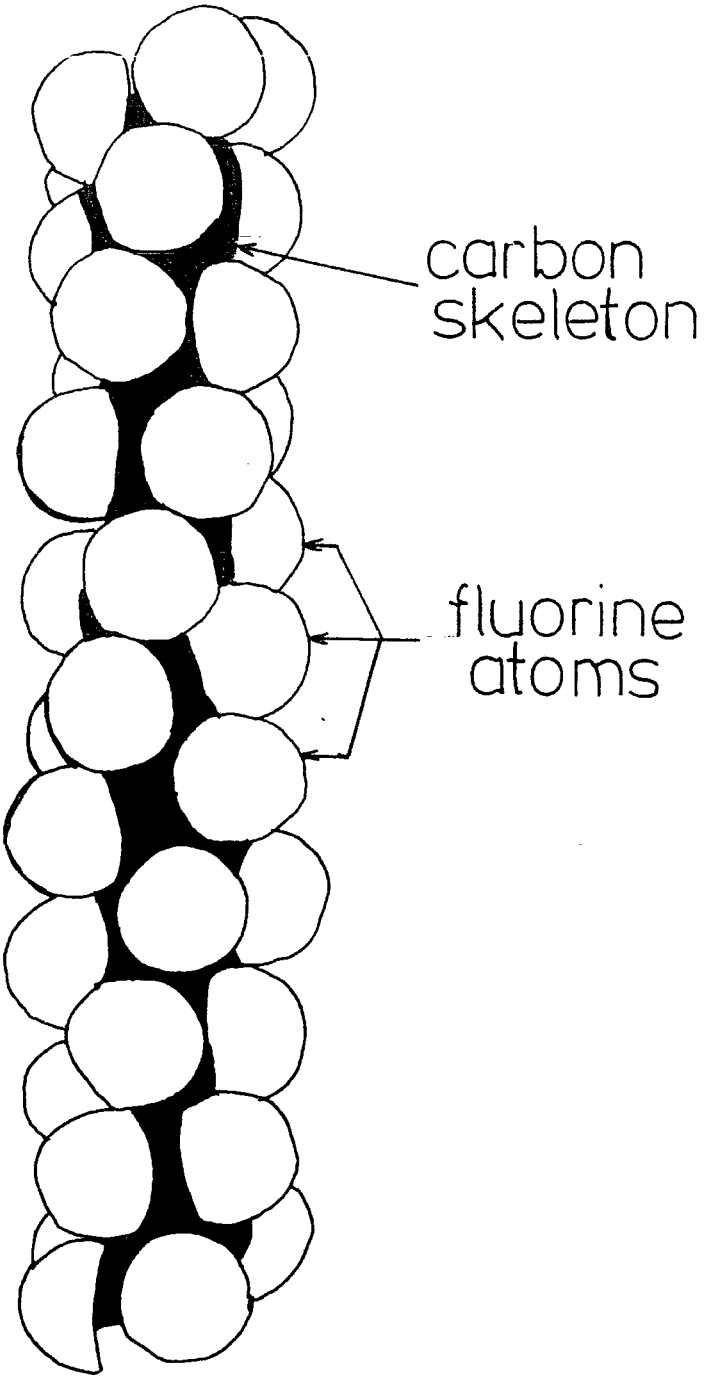


TABLE 6. LaMar Fluorination of Hydrocarbons

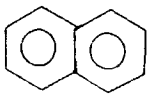
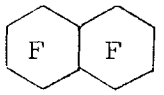
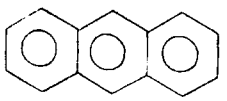
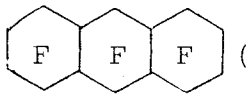
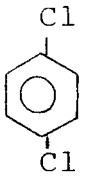
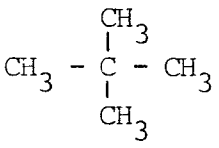
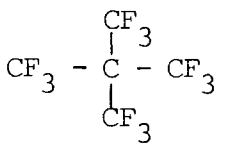
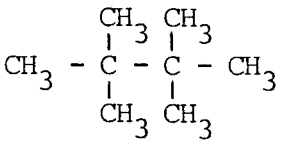
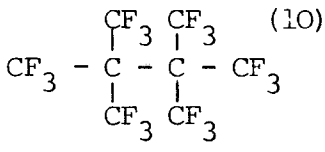
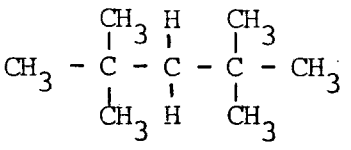
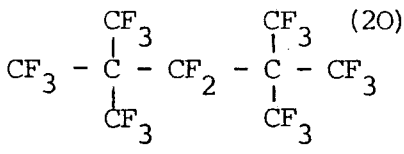
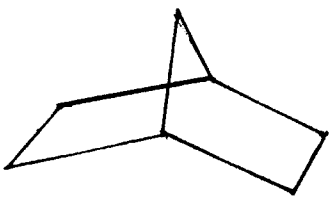
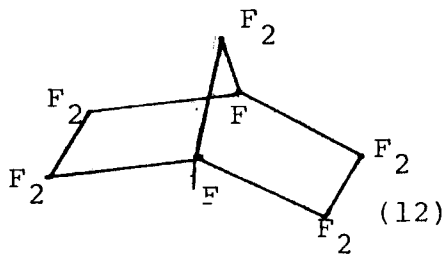
Substrate	Initial Temperature °C	Product (Yield)	Ref.
	20	 (60)	
	20	 (60)	
	20	 (60)	
	-78	 (10)	
	-78	 (10)	45
	-78	 (20) [+ 3 hydro (60%)]	51
	-78	 (12)	45

TABLE 6 (contd.)

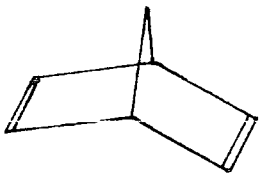
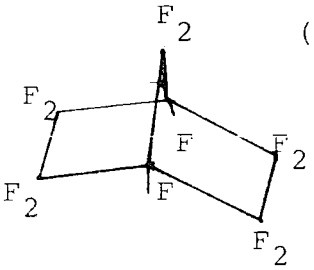
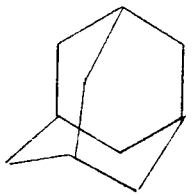
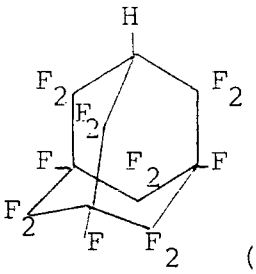
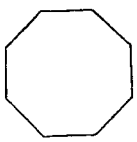
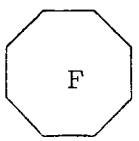
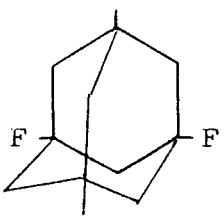
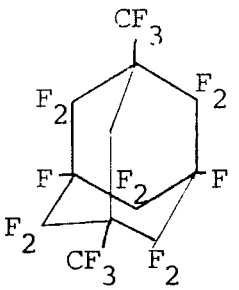
Substrate	Initial Temperature °C	Product (Yield)	Ref.
	-78	 (8)	45
 adamantane	-78	 (4) 1-hydro	45
	-78	 (6)	45
	-78	 (26)	52

TABLE 7. LaMar Fluorination of Functionalised Hydrocarbons

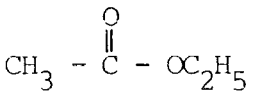
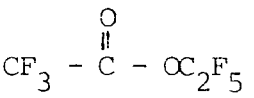
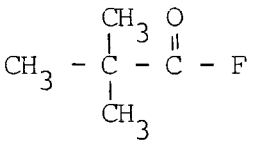
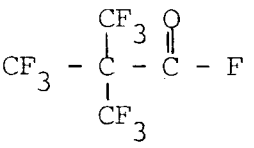
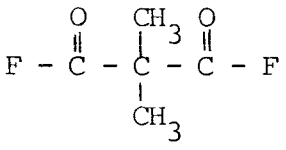
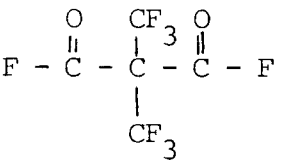
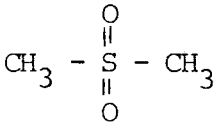
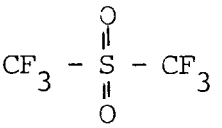
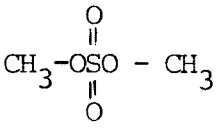
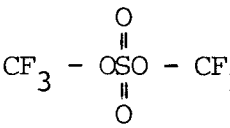
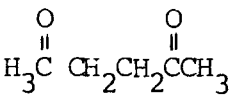
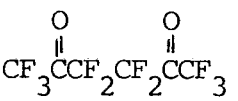
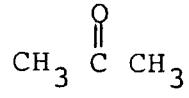
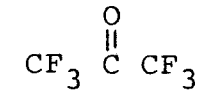
Substrate	Starting Temperature	Products (Yield)	Ref.
	-100	 (5)	47
	-78	 (52)	47
	-78	 (14)	46
	-100	 (20)	48
	-100	 (20)	48
	-78	 (5)	44
	-130		44

TABLE 7 (contd.

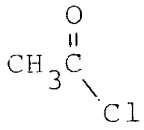
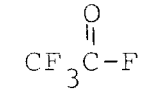
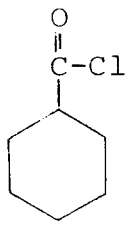
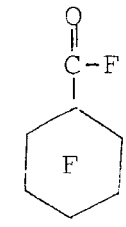
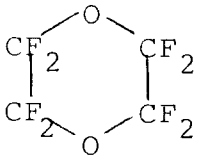
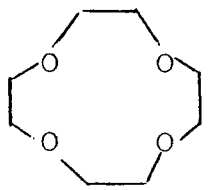
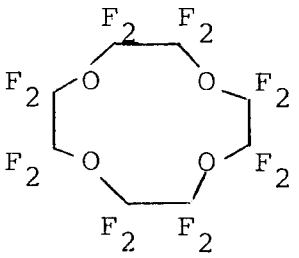
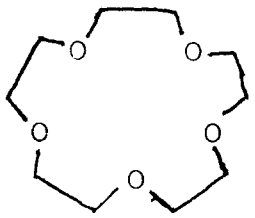
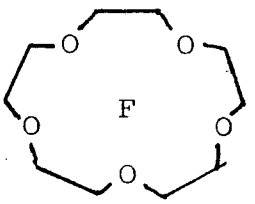
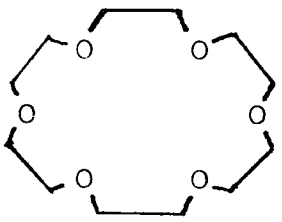
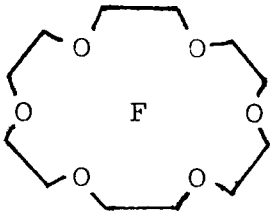
Substrate	Starting Temperature	Products (Yield)	Ref
	-78	 (50)	44
$NC(CH_2)_3CN$	-78	$F_2N(CF_2)_5NF_2$	44
	-78		44

TABLE 8. LaMar Direct Fluorination of Hydrocarbon Ethers

Substrate	Starting Temperature °C	Product (Yield %)	Ref.
$CH_3OCH_2CH_2OCH_3$	-78	$CF_3OCF_2CF_2OCF_3$ (21)	53,54,55
$CH_3(OCH_2CH_2)_2OCH_3$	-78	$CF_3O(CF_2CF_2O)_2CF_3$ (16)	53,54,55
$C_2H_5(OCH_2CH_2)OC_2H_5$	-78	$C_2F_5O(CF_2CF_2O)C_2F_5$ (20)	53,54
 1,4 dioxane	-78	 (40)	47
$[(CH_3)_3CCH_2\dagger_2O$	-80	$[(CF_3)_3CCF_2\dagger_2O$	56
$[(CH_3)_2CH\dagger_2O$	-80	$[(CF_3)_2CF\dagger_2O$	56
$[(CH_3)_2CHCH_2\dagger_2O$	-80	$[(CF_3)_2CFCF_2\dagger_2O$	56
$[(CH_3)_2CHCH_2CH_2\dagger_2O$	-80	$[(CF_3)_2CFCF_2CF_2\dagger_2O$	56
	-78	 (30)	57
	-78	 (30)	57
	-78	 (30)	57

carbon bond fission is suspected to occur. The improved LaMar technique[44] is only applicable to compounds which have appreciable vapour pressures when in the crystalline state in order to allow mobility between the various temperature zones in the reactor. Most important of all is the long reaction times required for complete fluorination, often in excess of 200 hrs is used for polymers and 100 hrs for smaller molecules, leading to inefficient use of the fluorine reagent gas. The reaction scale is usually of the order of a few grammes and is a batch process.

These disadvantages are considerable and the process cannot be seriously considered as a potential industrial process.

The most recent general direct fluorination process has been developed by Adcock *et al*[58,59]. The process described involves the direct fluorination of an aerosol suspension of the substrate. The aerosol medium is generally sodium fluoride and the carrier gas, which also acts as a diluent, is helium. The hydrocarbon substrate is condensed onto the surface of the sodium fluoride particles thus exposing a large surface area to the fluorine. The aerosol medium supporting the hydrocarbon substrate is then passed into the reactor, which contains several temperature zones, and several gas inlets to admit fluorine of various concentrations. Hence as the substrate gradually passes through the reactor it meets progressively higher temperatures and increasing fluorine concentrations. To obtain perfluorinated products a photochemical step is often used as the final stage of the reaction.

In summary the technique maintains the substrate in a condensed or crystalline state, while allowing good mobility between reactor zones, and uses large exposed surface areas with low initial temperatures and fluorine concentrations.

The process has been successful in producing perfluoro compounds from a range of hydrocarbon substrates. The results are summarised in Tables 10, 11 and 12.

TABLE 10

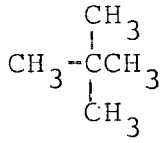
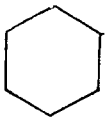
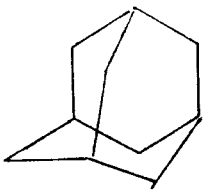
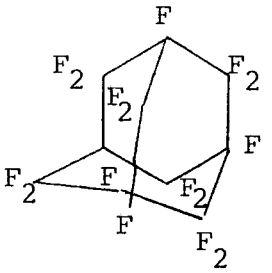
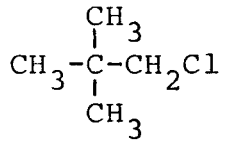
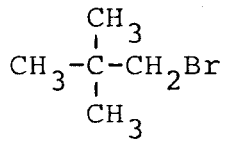
Substrate	Conditions	Products (Yield)	Ref.
 neopentane	$-60^{o} \rightarrow 0^{o}$, 3hr u.v.	$C(CF_3)_4$ (10)	58
	$-60 \rightarrow 0^{o}C$, 4hr u.v.	 (30)	59
	$-30 \rightarrow 10^{o}C$, 7hr u.v.	 (28)	60
	low temp. 3hr. u.v.	$(CF_3)_3CCF_2Cl$ (74)	64
	low temp. 3hr. u.v.	$(CF_3)_2CFCF_2CF_3$ (62) $(CF_3)_2CFCF_3$ (10)	64

TABLE 11. Aerosol Fluorination of Ethers

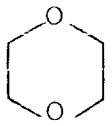
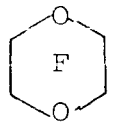
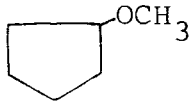
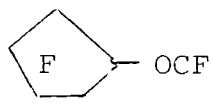
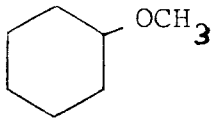
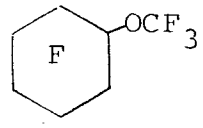
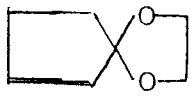
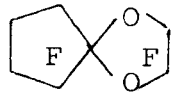
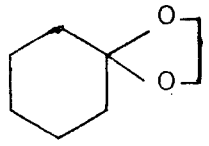
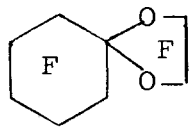
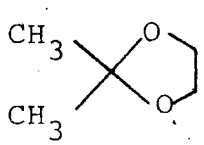
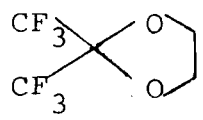
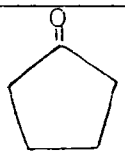
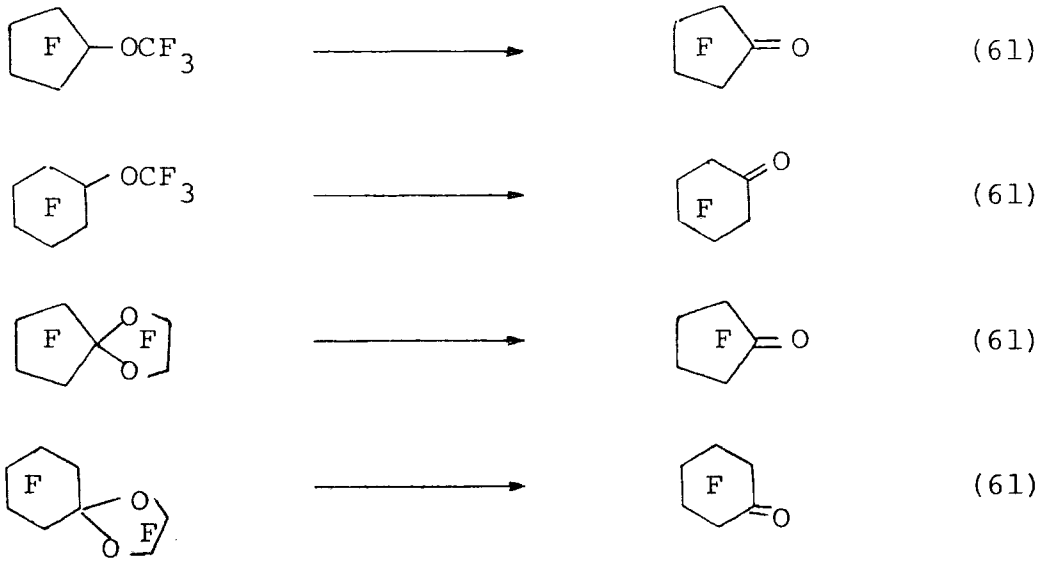
Substrate	Conditions	Products (% Yield)	Ref.
	-60→0°C u.v.3 hrs.	 (50)	59
$CH_3OCH_2CH_2OCH_3$	-40→0°C u.v. 4hrs	$CF_3OCF_2CF_2OCF_3$ (36)	60
$CH_3O(CH_2CH_2O)_2CH_3$	-40→0°C u.v. 4hrs.	$CF_3O(CF_2CF_2O)CF_3$ (22)	60
$CH_3O(CH_2CH_2O)_3CH_3$	-40→0°C u.v. 4hrs.	$CF_3O(CF_2CF_2O)_3CF_3$ (20)	60
$CH_3O(CH_2CH_2O)_4CH_3$	-40→0°C u.v. 4hrs.	$CF_3O(CF_2CF_2O)_4CF_3$ (15)	60
	-60→0 u.v. 3hrs.	 (22)	61
	-60→0 u.v. 3 hrs.	 (32)	61
	-60→0 u.v. 3 hrs.	 (10)	61
	-60→0 u.v. 3 hrs.	 (9)	61
	-60→0°C, 3 hrs. u.v.	 (50)	59

TABLE 12. Aerosol Direct Fluorination or Ketones

Substrate	Conditions	Products (% Yield)	Ref.
$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$	-20→10°C, 4hr. u.v.	$CF_3CF_2\overset{O}{\overset{\|}{C}}CF_2CF_3$ (13)	62
$CH_3CH_2CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$	-30→10°C, 4hr. u.v.	$nC_3F_7\overset{O}{\overset{\|}{C}}nC_3F_7$ (23)	62
	-40→0°C, 4hr. u.v.	$nC_4F_9C(=O)F$ (13)	62
$CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_2CH_3$	-30→10°C, 4hr. u.v.	$C_2F_5\overset{O}{\overset{\|}{C}}C_3F_7$	62
$CH_3\overset{O}{\overset{\|}{C}}C(CH_3)_3$	-30→10°C, 4hr. u.v.	$CF_3\overset{O}{\overset{\|}{C}}C(CF_3)_3$ (12)	63
$(CH_3)_3C\overset{O}{\overset{\|}{C}}C(CH_3)_3$	-30→10°C, 4hr. u.v.	$(CF_3)_3C\overset{O}{\overset{\|}{C}}CF_2CF(CF_3)_2$	63

Some interesting observations from these results include the formation of perfluoroalkyl chlorides producing a perfluorinated molecule containing a predetermined reactive site. In the case of neopentyl bromide however significant rearrangement of the carbon skeleton occurred which, although not fully understood, was attributed to the formation of an intermediate carbocation.[64]

The attempt to produce perfluorocyclic ketones was also unsuccessful with ring opening occurring to produce the corresponding aliphatic acid fluoride. Perfluorocyclic ketones were prepared by a more indirect route, by hydrolysis of the corresponding ketals or methyl ethers in 100% sulphuric acid.[61]



The technique has illustrated an interesting approach to the direct fluorination of various hydrocarbons and functionalised derivatives. However there are obviously limitations to the process. For example, the substrate must have physical properties which will not affect the aerosol properties of the sodium fluoride. Although the process is a flow system, recovery from the reactor may be as little as 30%, the remaining

substrate being deposited, unreacted, on the walls of the reactor. The technique is also essentially a small scale process only a few grammes of substrate used over several hours.

b. Direct Fluorination of Hydrocarbon Polymers

Fluorocarbon polymers have found a wide range of uses[65] and so have become increasingly important industrial compounds. Unfortunately the preparation of perfluorinated polymers is, in many cases, not as facile as the hydrocarbon analogue. For example polypropylene is a well known commercial product, hexafluoropropene, however will polymerise only under forcing conditions using free radical initiation. The difficulty involved here has been attributed to the large steric requirements of the trifluoromethyl group in a polymer chain. It may also be the case that perfluorinated monomers are difficult if not impossible to make or may be prohibitively expensive. Once formed problems of moulding the perfluoropolymers, *e.g.* (PTFE) to produce finished articles may arise, in these cases the polymer must be "machined" or extruded, limiting the application of the materials.

One technique that has emerged to combat the problems involved in producing perfluoropolymers has been to convert the corresponding hydrocarbon polymer to the perfluorinated analogue by direct fluorination.

Two approaches to the direct fluorination of polymers may be adopted (1) a perfluoropolymer may be prepared by direct fluorination of polymer particles of small mesh sizes (12 mesh max) allowing diffusion of the fluorine into the pores of the

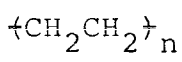
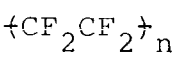
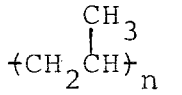
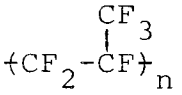
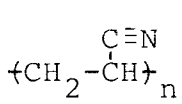
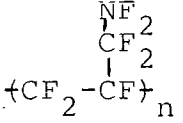
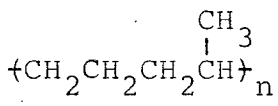
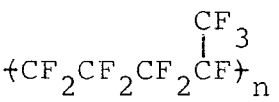
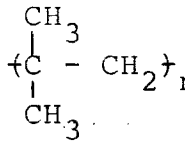
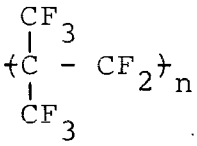
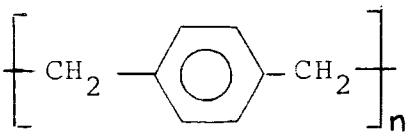
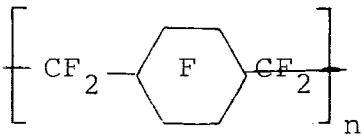
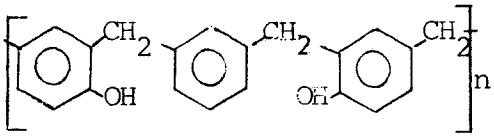
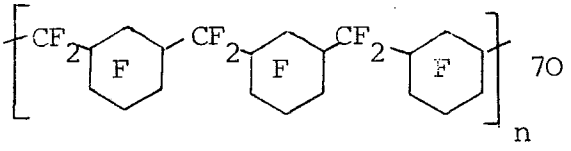
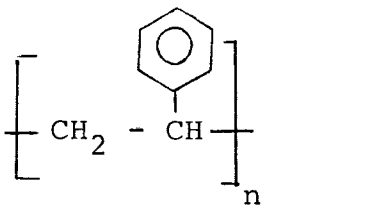
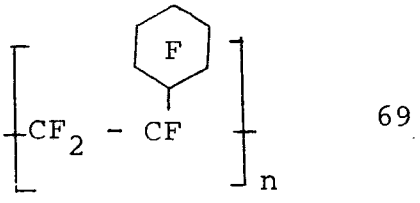
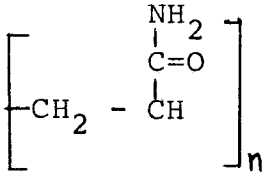
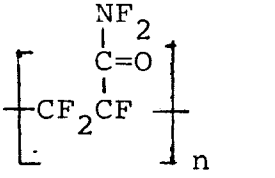
polymer, (2) a finished article, formed from a hydrocarbon polymer (*e.g.* a chemical beaker, fuel tanks, sealing rings), may be directly fluorinated imparting to the surface of the article the desired properties of the relevant fluoropolymer, *i.e.* wettability, chemical and thermal stability, and increased strength. In this case the internal bulk of the material remains unchanged.

The initial work carried out on the direct fluorination of a polymer surface was by Rudge *et al*[66] who successfully fluorinated the surface of polyethylene. Subsequent work by Okada and Makuuchi[67] noted a vigorous reaction between polyethene particles and fluorine which often ignited. In this case the only guide to fluorine incorporation into the polymer was by weight increase, a fairly crude technique.

Japanese workers[68] have directly fluorinated PVF (polyvinyl fluoride) films substituting 65% of the surface hydrogen atoms with fluorine. Perfluorination was not achieved using this technique and carbon carbon bond fission as well as surface oxidation reactions were prevalent.

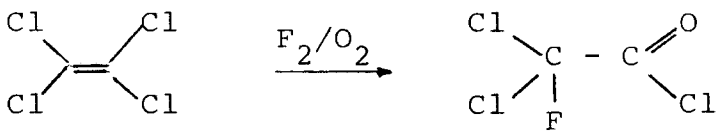
With the development of the LaMar[47] technique a fairly extensive study of the fluorination of hydrocarbon polymers[69] was made. The process has been described in detail earlier. The reactions were carried out at ambient ($20^{o}C$) temperature using considerable reaction times, typically 100 hrs. Several hydrocarbon polymers have been successfully fluorinated in the form of small particles allowing diffusion of fluorine into the core of the polymer. The results are summarised in Table 9. The products indicated are idealised structures only, it was accepted that some cross-linking and oxidation of the surface had occurred.

TABLE 9

Substrate	Conditions °C	Product	Ref.
	20		69
	20		69
	20		69
	20		69
	20		70
	20		70
	20		70
	20		69
	20		69

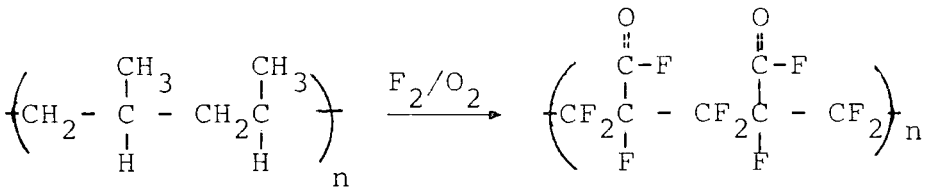
Perfluorination of the hydrocarbon polymers was suggested in each case but subsequent workers[71] refute this claim. The process has been applied to finished articles[69] made of polyethene or polypropene, such as chemical beakers, fibres, films, fabric, and rope, to produce items with a "fluorinated skin" of up to 0.2mm thick. It was noted however that although the chemical and thermal stability desired was imparted to these objects, they often became quite brittle due to the cross-linking process.

A problem that is associated with the direct fluorination of polymer surfaces is the incorporation of labile oxygen in the system. The abstraction of a proton from the partially fluorinated polymer results in a relatively stable hydrofluoroalkyl radical. This radical may be long lived and subsequently react with the diradical species oxygen. It is, therefore, necessary if a fluorocarbon polymer analogous to the hydrocarbon polymer is required, that precautions are taken to exclude oxygen from the system. This oxidation process has, however, been used to advantage to introduce functionality into a polymer.[72,73] The technique was a variation of the LaMar process and was used to incorporate between 5% and 60% of acid fluoride groups w.r.t. monomer units into a polymer. The process was named "oxy-fluorination", a similar technique was concurrently reported by Manley.[74] Fluorine sensitised oxidations were first reported by Miller,[15] who reacted tetrachloroethene with a fluorine oxygen mixture to yield 1-fluorodichloroacetyl chloride.



(15)

The introduction of acid fluoride groups *via* the LaMar oxyfluorination process was suspected to occur *via* oxidation of pendant methyl groups or alkyl groups rather than carbon carbon bond fission of the polymer backbone, *i.e.*

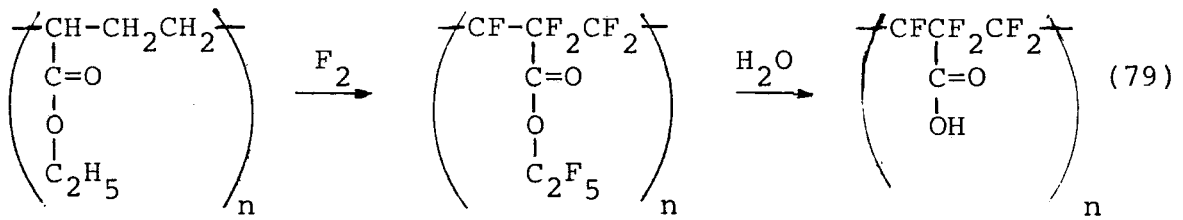


(75)

This proposal was based on the observation that little functionality could be incorporated into low density linear polyethene.

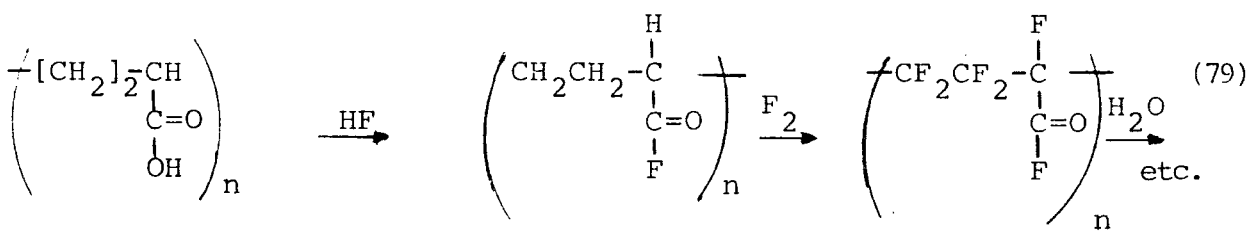
The process has been applied to more volatile molecules such as neopentane.[76]

Chemically inert polymers that incorporate functional groups such as sulphonic acid groups, (NAFION[77]) or carboxylic acid groups (FLEMION[78]) are industrially important materials employed as membranes in ion exchange devices and chloro-alkali cells. Further developments in the LaMar process have led to the successful fluorination of functionalised polymers[79] such as copolymers of acrylate esters or acrylic acid with ethene.



(79)

or with polymers with pendant carboxylic acid groups



(79)

Lagow *et al* have also applied their technique successfully to the preparation of perfluoropolyethers[80,81] by the direct fluorination of polyethylene oxide at ambient temperature and then at elevated temperature to promote fragmentation.

$$\text{+CH}_2\text{CH}_2\text{-O+}_m \xrightarrow[\text{ambient}]{He/F_2} \text{+CF}_2\text{CF}_2\text{-O+}_m \xrightarrow[\Delta]{F_2} R_f(OCF_2CF_2)OR_f \quad (80)$$

polyethylene oxide $R_f = CF_3,\ C_2F_5$

$$\text{+CH}_2\text{-O+}_n \xrightarrow{F_2/He} COF_2 + \text{Fluoroethers.} \quad (81)$$

polymethylene oxide

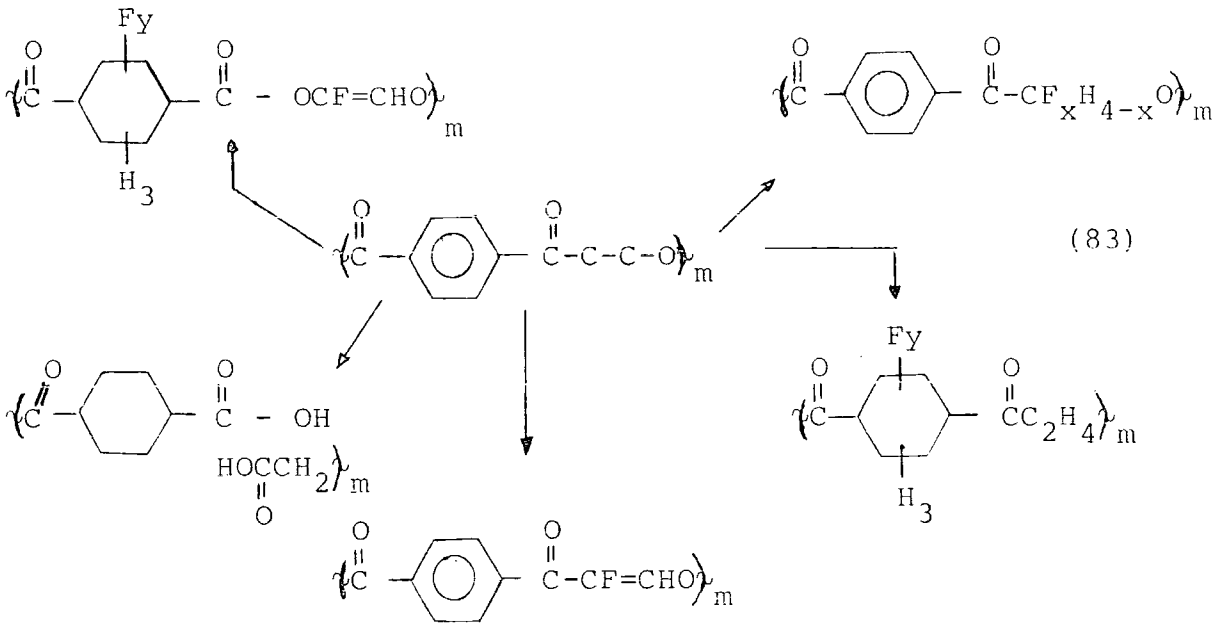
$$\text{+CH}_2\text{CH(CH}_3\text{)-O+}_p \xrightarrow[(2)\ \text{heat}]{(1)\ He/F_2,\ \text{ambient}} Rf\ O(CF_2CF_2O)_nRf \quad (81)$$

$R_f = CF_3, C_2F_5, nC_3F_7$

polypropylene oxide

The synthesis of this important class of compounds is discussed in more detail in Chapter Two.

Partial fluorination of polymer surfaces may also impart desirable properties to the material. For example better soil release, soil anti-deposition and better wettability are some of the characteristics obtained on partial fluorination of a polymer. A commercial process has been developed by Hayes and Dixon[82] monopolising these effects. The process involves exposing the polymer, *e.g.* polyester (polyethylene terephthalate)[83] to a dilute mixture of fluorine in nitrogen (typically 1:10, F_2:N_2) for a short time period of between one and fifteen minutes at room temperature. Various reactions were proposed to occur (Scheme 3).



(83)

Scheme 3

A maximum of three per cent incorporation of fluorine was detected. The process was also applied to polyamides,[84] polyethene, and polypropene.[85]

The direct fluorination of graphite in various forms has resulted in fluorinated compounds ranging from $(CF_{0.68})_x$[87] and $(C_4F)_x$[87] to $(C_2F)_x$[86] and $(CF)_x$[86]. The formation of carbon monofluoride $(CF)_x$ is favoured at elevated temperatures *ca.* 600°C and that of dicarbon monofluoride $(C_2F)_x$ at 350-400°C.[86] Interest in carbon monofluoride has arisen from its application as cathode material in high energy lithium batteries.

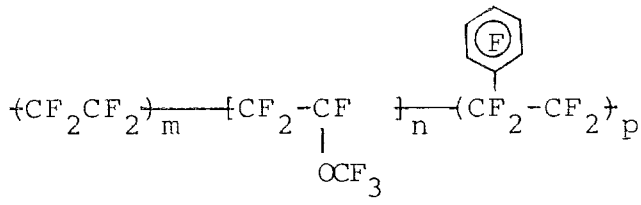
The perfluorination of a polymer surface using a cold plasma discharge to initiate the reaction has, more recently, been reported.[88] In the report it is claimed that ESCA studies[89] have revealed that previous direct fluorination attempts on polymers resulted in carbon carbon bond fission and oxygen incorporation. The reaction between a polymer

surface, *e.g.* low density (l.d.) polyethene, and fluorine is considerably accelerated by the formation of active species such as ions and radicals generated in the cold plasma discharge. The fluorinating species arise not only from fluorine, but also from carbon tetrafluoride (CF_4), hexafluoroethane (C_2F_6) or sulphur hexafluoride (SF_6). The plasma generates a high density of fluorine atoms and other ionic or radical species derived from the "inert diluent gas", and the polymer surface.

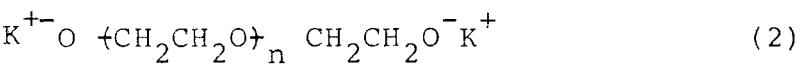
Using this technique a perfluorinated layer to a depth of 60Å may be obtained in the case of l.d.polyethene film. The limiting factor to the depth of fluorination tends to be the competing etching process of the polyethylene surface by cations in the plasma. Distinct advantages of this technique over other methods is the much shorter reaction times, *ca.* 30 minutes as opposed to 3 days for the LaMar process. There is, also, little if no incorporation of oxygen into the polymer surface. It remains to be seen however how generally applicable the technique will be.

The exact mechanism of the reaction is not well understood but kinetic studies[90] have been carried out and the influence of the ultra violet radiation, generated by the plasma, investigated.[91]

The use of direct fluorination in the preparation of perfluoroelastomers from fluorohydroelastomers has appeared in the patent literature.[92] Usually the terpolymer (1) of tetrafluoroethylene, perfluorophenylethylene and perfluoromethyl vinyl ether is cross-linked with a difunctional hydrocarbon unit, *e.g.* dipotassium salt of polyethylene oxide (2).



(1)



(2)

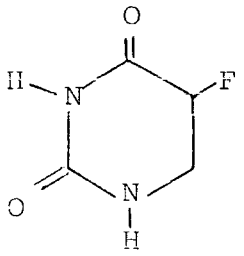
The resulting elastomer exhibits good performance up to 600°C. This may be improved however by reaction of the cross-linked polymer with fluorine diluted in helium or nitrogen at ambient temperature. The result is an essentially perfluorinated elastomer.

c. Selective Fluorinations of Organic Molecules

The selective fluorination of complex organic molecules using elemental fluorine is becoming an increasingly important technique. Although not directly related to the topic of this thesis, it is valuable to draw the reader's attention to the degree of control that is possible in reactions involving elemental fluorine and hydrocarbon derivatives. The efforts of other workers, outlined in this section, is not a comprehensive review of the subject, but rather, a brief summary of the results possible in this field.

There is considerable interest in the preparation of partially fluorinated organic molecules due to the high biological activity that may result. Partially fluorinated molecules find uses particularly in the pharmaceutical and agro-chemical industries,

e.g.

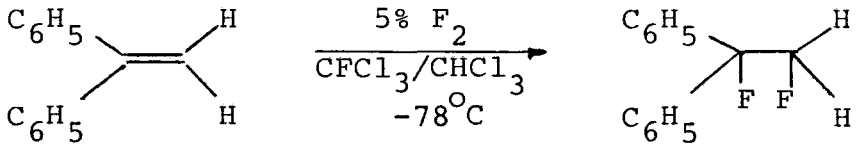


5-Fluorouracil[93]
anti cancer agent

Despite the extreme reactivity of fluorine in free radical reactions with hydrocarbon derivatives, it has been shown that great selectivity is possible without degradation of the carbon skeleton of the molecule, or polysubstitution at several sites.

The first instance of selective fluorination to be observed was the direct fluorination of n-butyric acid by Bochemüller,[18] previously discussed in Section B3 , the selectivity in this case may be attributed to the polar nature of the substrate.

The reaction of elemental fluorine with unsaturated molecules in general results in simple *cis* addition products. For example the addition of molecular fluorine to 1,1-diphenyl-ethene carried out by Merrit *et al.*[94]



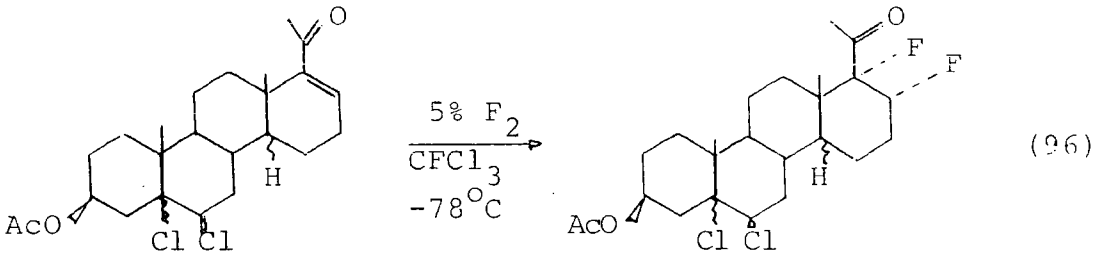
(94)

and in the case of alkynes, tetrafluoro-compounds result.

$$C_6H_5C{\equiv}CR \xrightarrow[\text{solvent}]{5\%\ F_2,\ -78^{\circ}C} C_6H_5CF_2CF_2R \qquad (95)$$

R = C_6H_5, CH_3, H

This simple reaction has been applied to the synthesis of more complex molecules such as steroids to give high yields of the difluoroderivative



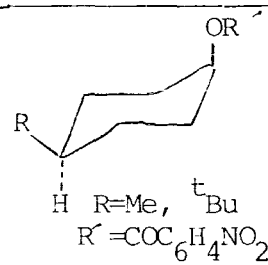
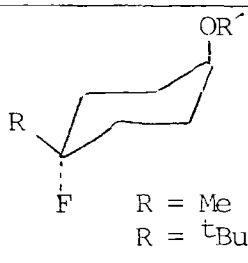
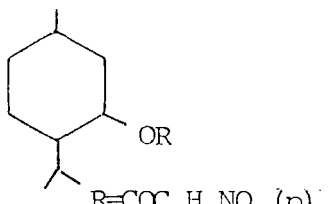
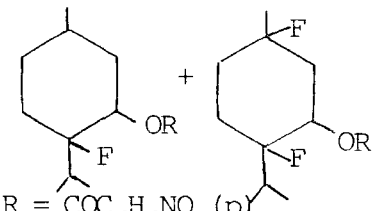
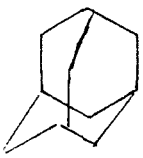
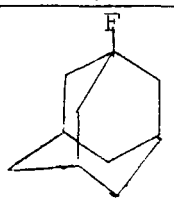
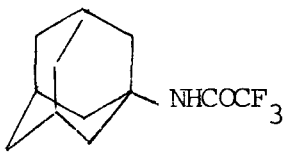
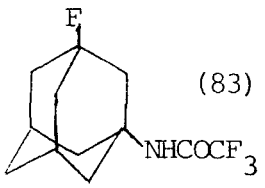
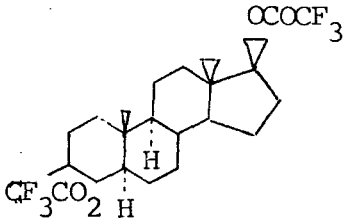
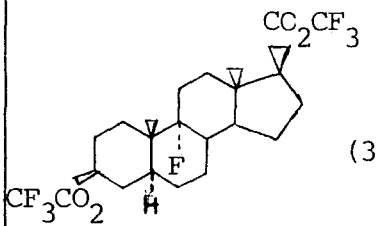
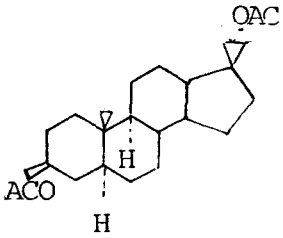
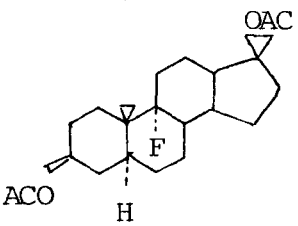
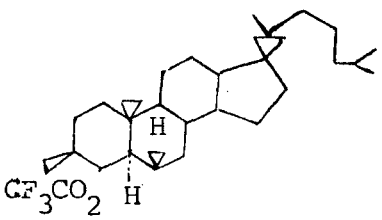
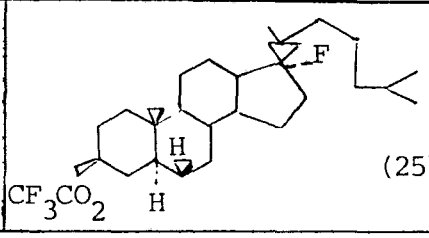
(96)

The mechanism is electrophilic in nature and is carried out at low temperatures in the presence of radical scavangers (*e.g.* nitrobenzene) to inhibit the side reaction of random poly-substitution of hydrogen atoms in the molecule. Yields are noted to be increased in the presence of polar solvents such as trichloromethane and ionic mechanisms[102,103] have been suggested for the reaction.

Selective fluorination at a saturated carbon is perhaps a more surprising phenomenon. Selective fluorination at a tertiary carbon in a molecule containing no carbon carbon unsaturated bonds is possible. The reaction is stereo-selective and usually occurs at the site most removed from an electron withdrawing centre.

Examples of these reactions are contained in Table 13.

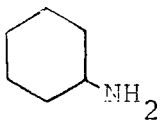
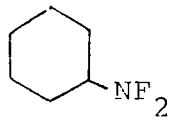
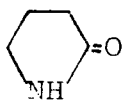
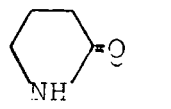
TABLE 13 Selective Fluorination of Saturated Hydrocarbon Derivatives

Substrate	Conditions	Product (Yield)	Ref.
 H R=Me, ^{t}Bu R´=$COC_6H_4NO_2$(p)	5%F_2,in $CHCl_3$ $CFCl_3$, -70°C	 R = Me (65) R = ^{t}Bu(83)	97
 R=$COC_6H_4NO_2$(p)	5% F_2, in $CHCl_3$ $CFCl_3$, -70°C	 R = $COC_6H_4NO_2$(p)	97
	5% F_2 in N_2 in $CFCl_3$, -78°C	 (84)	98
	5% F_2 in N_2, in $CFCl_3$, -78°C	 (83)	98
	5% F_2 $CFCl_3$ -78°C	 (34)	99
	5% F_2 $CFCl_3$ -78°C	 (50)	99
	5% F_2 $CFCl_3$ -78°C	 (25)	99

An extensive study[100] on the substitution of hydrogen by fluorine in various aromatic compounds has suggested, from the products observed, that an electrophilic substitution mechanism occurs. The yields quoted are extremely high but conversions are so low as to render the technique synthetically unimportant.

Aqueous phase fluorinations of primary amines to yield N-N-difluoroamines[101,102] have been carried out, carbamamates[103] may also yield N,N-difluoro derivatives but under these conditions hydrolysis may occur to give the difluoroamine compound, (Table 14).

TABLE 14 Aqueous phase fluorinations of Amines + Carbamamates

Substrate	Conditions	Products (Yield %)	Ref.
	30% F_2 in N_2 0°C	 (66)	102
$nC_4H_9NH_2$	30% F_2 in N_2 0°C	$nC_4H_9NF_2$ (25)	102
	30% F_2 in N_2 5°C	 (16) $NF_2(CH_2)_3COOH$	103
CH_3NHCHO	30% F_2 in N_2 -30°C (no solvent)	CH_3NHCHO, (31) CH_3NF_2	103

Other polar solvents such as trifluoroacetic acid have also been frequently used, perhaps the most important discovery being the D.F. of uracil to produce 5-fluorouracil,[93,104] the reaction occurring in either H_2O, or CF_3COOH.

The mechanism in these polar solvents is suspected to occur *via* an intermediate hypofluorite, *e.g.* CF_3COOF generated *in situ* of the substrate.

CHAPTER TWO

PREPARATION OF PERFLUOROPOLYETHERS (P.F.P.E.)

IIA. Introduction

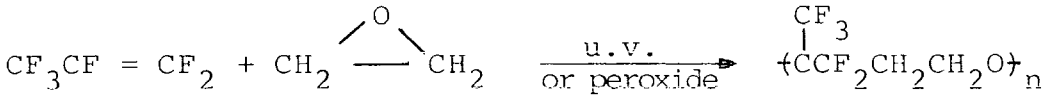
Perfluoropolyethers are perhaps the most important class of fluoropolymers to be produced on an industrial scale in recent years. The importance of P.F.P.E. arises from the exceptional thermal and chemical stability that they display and that they remain liquid over large temperature ranges. Thermally P.F.P.E. are known to withstand temperatures in excess of 350^{o}C without suffering substantial fragmentations or decomposition. Chemically P.F.P.E. are extremely inert and have been shown to be stable in the presence of liquid oxygen. The only known reaction of P.F.P.E. is with aluminium chloride at elevated temperatures which results in cleavage of the carbon oxygen bond or replacement of α fluorine atoms with chlorine. The thermal and chemical stability of P.F.P.E. has been the subject of several studies.[105,106] This exceptional stability makes P.F.P.E. suitable for many important applications such as lubricants, diffusion pump fluids, inert fluids and heat exchange fluids.

It is not surprising, therefore, that the preparation of P.F.P.E. has been the subject of intensive industrial research in the past decade. Early work in this field was centred on polyfluoroethers rather than the more important perfluorinated analogues. Many of these early approaches have been adequately reviewed[107] and will only be summarised here.

IIB1. Preparation of highly fluorinated ethers by polymerisation processes

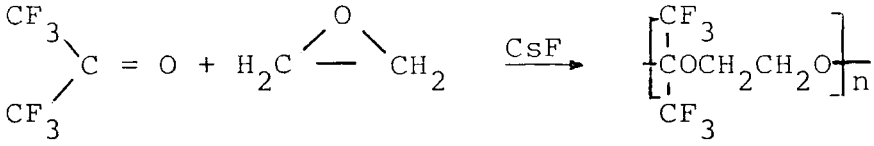
The first example of a highly fluorinated polyether was produced by the free radical induced polymerisation of

hexafluoropropene with ethylene oxide.[108]



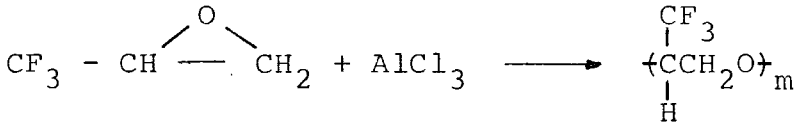
(108)

Subsequent reactions with various olefin epoxides have produced more interesting polymers. For example the polymerisation of perfluoroacetone and ethylene oxide in the presence of caesium fluoride yields crystalline products.[109]



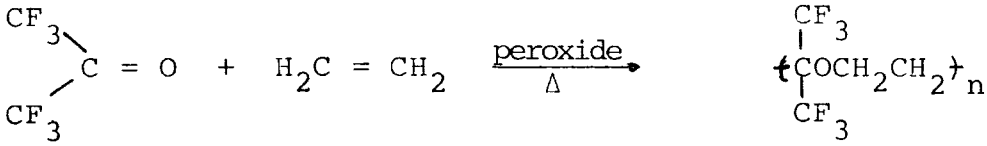
(109)

Homopolymers of highly fluorinated epoxides may be produced using a Lewis acid as the initiator.[110]



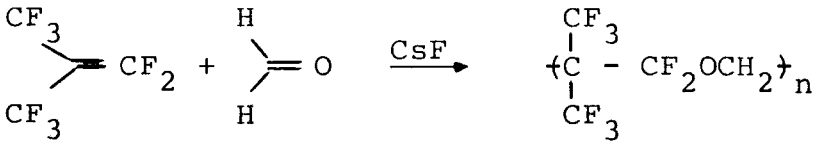
(110)

Hexafluoroacetone forms low molecular weight polyethers when copolymerised with ethylene under free radical conditions.[111]



(111)

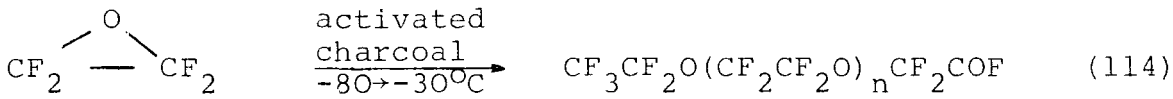
Finally formaldehyde is known to copolymerise with fluorinated olefins in the presence of caesium fluoride.[112]



(112)

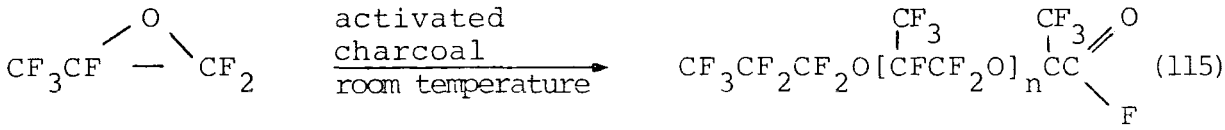
The partially fluorinated polyethers do not possess the same thermal and chemical stability as the perfluorinated analogues and so their application is, comparatively, somewhat limited.

Preparation of perfluoropolyethers was made possible by the discovery and preparation of perfluoroolefin epoxide monomers.[113] Several patents have appeared in the literature concerning the polymerisation process. An early example involved the polymerisation of tetrafluoroethylene oxide over an activated charcoal catalyst.[114]



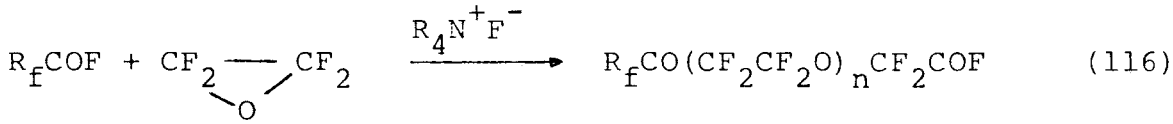
$$CF_2(O)CF_2 \xrightarrow[-80\rightarrow-30^{\circ}C]{\text{activated charcoal}} CF_3CF_2O(CF_2CF_2O)_nCF_2COF \qquad (114)$$

A similar process for hexafluoropropene oxide was reported also.[115]



$$CF_3CF(O)CF_2 \xrightarrow[\text{room temperature}]{\text{activated charcoal}} CF_3CF_2CF_2O[CF(CF_3)CF_2O]_nCC(=O)F \qquad (115)$$

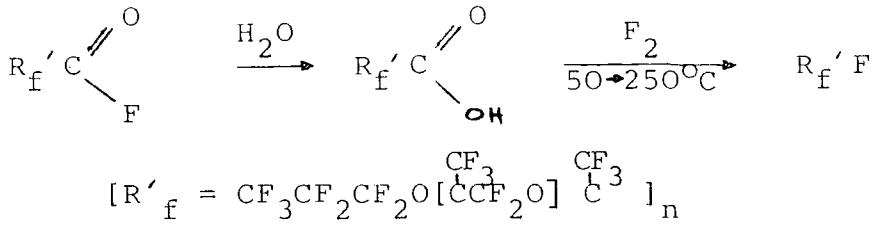
Later examples revealed that the polymerisation could be effected by a perfluoroalkoxy anion generated from an acid fluoride.[116]



$$R_fCOF + CF_2(O)CF_2 \xrightarrow{R_4N^+F^-} R_fCO(CF_2CF_2O)_nCF_2COF \qquad (116)$$

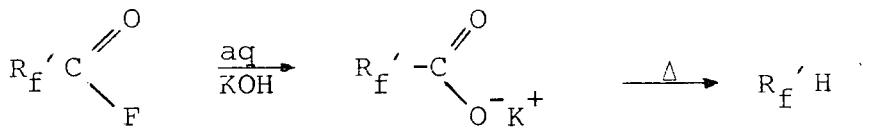
$[R_f = CF_3(CF_2)_n \quad n = 1\rightarrow10]$

The resulting P.F.P.E.s from these processes were exceptionally stable materials but it was found that this stability could be improved further by removal of the acid fluoride end groups. Several techniques have been employed to "cap" the polymers. For example the acid fluoride may be hydrolysed and the resulting carboxylic acid simultaneously fluorinated and decarbonylated by passing fluorine through the liquid polymer at elevated temperatures.[115]



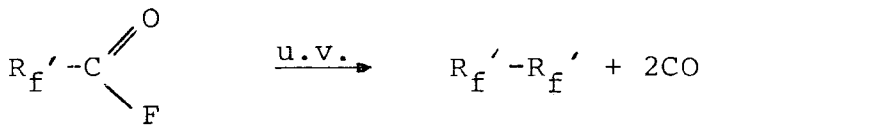
$$[R'_f = CF_3CF_2CF_2O[\overset{CF_3}{\overset{|}{C}}CF_2O]\overset{CF_3}{\overset{|}{C}}]_n$$

An alternative technique is hydrolysis of the acid fluoride, with subsequent pyrolysis of the potassium salt of the resulting carboxylic acid.[117]



$$[R_f' = CF_3CF_2CF_2O[\overset{CF_3}{\overset{|}{C}}CF_2O]_n\overset{CF_3}{\overset{|}{C}}-]$$

Finally, photolysis of the acid fluoride results in a coupling, decarbonylation reaction.[118]



$$[R_f' = CF_3CF_2CF_2O[\overset{CF_3}{\overset{|}{C}}CF_2O]_n\overset{CF_3}{\overset{|}{C}}-]$$

A second industrial synthesis of PFPE has been reported which involves the photopolymerisation of fluorinated olefins in the presence of oxygen.[119] The resulting PFPE are known as the "FOMBLIN"† range of fluids (MONTEFLUOS company). For example the copolymerisation of hexafluoropropene and tetrafluoroethylene in the presence of oxygen.[120]

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† FOMBLIN is a registered trade name of the Montefluos group of companies.

$$CF_3CF = CF_2 + CF_2 = CF_2 + O_2 \xrightarrow[-100^{o}C \rightarrow 25^{o}C]{h.\nu.}$$

$$R_f(C_2F_4O)_o(C_2F_4O_2)_q(C_3F_6O)_n(C_3F_6O_2)_m\underset{\displaystyle CF_3}{\overset{\displaystyle |}{C}}FCOF$$

(III)

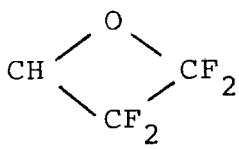
Unstable linkages such as the peroxide groups and the acid fluoride end groups are removed by heat treatment of (III) and subsequent direct fluorination.

$$(III) \xrightarrow[or\ \Delta]{h.\nu.} CF_3O\{C_2F_4O\}_q\{C_3F_6O\}_r\underset{\displaystyle CF_3}{\overset{\displaystyle |}{C}}FCOF$$

$$\Delta \downarrow F_2$$

$$CF_3O(C_2F_4O\ \}_q\{C_3F_6O\ \}_rCF_2CF_3$$

The most recent industrial process for the production of PFPE has been reported by Japanese workers.[121] This process, a ring opening polymerisation of 2,2,3,3,tetrafluoro-oxetane, produces a highly fluorinated polyether.



$$\xrightarrow[\underline{or}\ SbF_5]{CsF} \{CH_2CF_2CF_2O\}_n \qquad (121)$$

(IV)

The polyether (IV) may then be fluorinated further or chlorinated, both using an ultra violet initiation process. *i.e.* fluorination

$$\{CH_2CF_2CF_2O\}_n \xrightarrow[\Delta]{\overset{F_2}{h\nu}} \{CH_2CF_2CF_2O\}_p\{CHFCF_2CF_2O\}_q\{CF_2CF_2CF_2O\}_r$$

or chlorination

$$\text{-}(CH_2CF_2CF_2O)\text{-}_n \xrightarrow[h\nu\ \Delta]{Cl_2} \text{-}(CH_2CF_2CF_2O)\text{-}_a\text{-}(CHClCF_2CF_2O)\text{-}_b\text{-}(CCl_2CF_2CF_2O)\text{-}_c$$

It is claimed that a perfluoropolyether of the general formula:

$$\text{-}(CF_2CF_2CF_2O)\text{-}_n$$

may be produced, but as the patent[121] concerns mainly polyhalogenated ethers it must be assumed that the perfluoroether is difficult to obtain in a pure form. As yet no details of the chemical and thermal properties of these polyhalogenated materials have appeared in the literature.

IIB2. Preparation of Polyethers by Direct Fluorination of Polymers

Lagow *et al*[122] have applied the LaMar[43] technique to a series of partially fluorinated and non-fluorinated polyethers, Table 15.

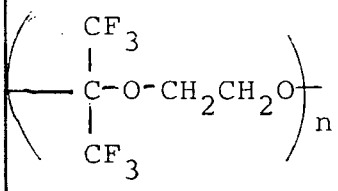
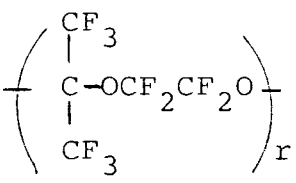
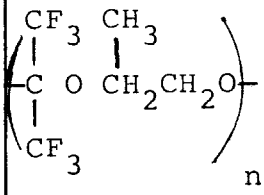
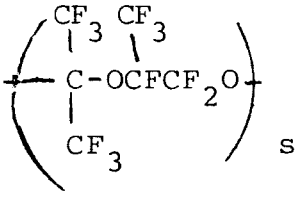
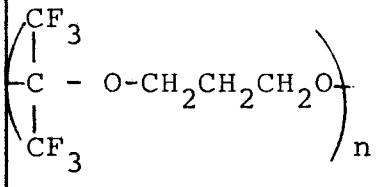
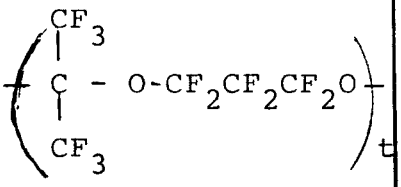
Using a slightly different approach Lagow *et al*[123] directly fluorinated a polyester using the LaMar[43] process and subsequently converted the carbonyl groups to difluoromethylene groups using sulphur tetrafluoride.

$$\text{-}\left(CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle CH_2}{C}}CH_2OCCH_2CH_2CO\right)\text{-}_n \xrightarrow[2.SF_4/HF]{1.F_2/He} \text{-}\left(CF_2\overset{\displaystyle CF_3}{\underset{\displaystyle CF_3}{C}}CF_2O(C_2F_4)_2O\right)\text{-}_n \qquad (123)$$

(no yield given)

poly (2,2-dimethyl-1,3-propylene succinate.

TABLE 15. LaMar fluorination of Polyethers

Substrate	Conditions	Product	Ref
$+CH_2CH_2O+_n$ polyethyleneoxide	He/F_2 1. Ambient 2. heat	$+CF_2CF_2O+_p$	81
$+CHCH_2O+_n$ (CH_3) polypropyleneoxide	He/F_2 1. Ambient 2. heat	$+CFCF_2O+_q$ (CF_3)	81
$+CH_2O+_n$ polyethyleneoxide	He/F_2 1. Ambient 2. heat	decomposition COF_2 + volatile ethers	81
 hexafluoroacetone ethylene oxide copolymer	He/F_2 1. Ambient 2. heat		122
 hexafluoroacetone polypropylene oxide copolymer	He/F_2 1. Ambient 2. heat		122
 hexafluoroacetone oxetane copolymer	He/F_3 1. Ambient 2. heat		122

$$\text{poly(1,4 butylene adipate)} \xrightarrow[2.SF_4/HF]{1.F_2/He} [(CF_2)_4O(CF_2)_6O]_n \quad \text{(no yield given)} \qquad (123)$$

However, although the LaMar process would seem to be a particularly adaptable technique resulting in a variety of interesting polymers, there are several distinct drawbacks which have already been discussed in Chapter One, Section B4.

C. The Durham Strategy

In our laboratory we have proposed a new synthetic route to P.F.P.Es. of known structure and molecular weight range.

As previously discussed in Chapter One it is known that the progressive fluorination of hydrocarbon compounds becomes easier to control after partial fluorination.

Previous studies in our laboratory[124,125] have investigated a free radical addition of F-alkenes to simple hydrocarbon ethers. The introduction of a polyfluoroalkyl group in this manner has a dramatic stabilising effect on the molecule during further fluorination using CoF_3 at elevated temperatures.[125]

Using a similar approach, for the synthesis of P.F.P.Es., we proposed to investigate the addition of F-alkenes to higher molecular-weight systems such as glymes and subsequently perfluorinate the addition products using elemental fluorine,

i.e.

$$CH_3O(CH_2CH_2)_nCH_3 + \text{F-alkene} \xrightarrow[(ii)]{(i)} RfCH_2O(CH_2\overset{Rf}{\overset{|}{C}}HO)_nCH_2Rf$$

(i) = peroxide, heat
(ii) = γ rays

(Rf = polyfluoroalkyl)

$$\xrightarrow[\Delta]{F_2} Rf'CF_2O(CF_2\overset{Rf'}{\overset{|}{C}}FO)_nCF_2Rf'$$

(Rf' = perfluoroalkyl)

As the process avoids a polymerisation step the molecular weight range of the product will be dependent on the original polyether. This limited molecular weight range is desirable in P.F.P.Es. as it enables them to be applied more specifically.

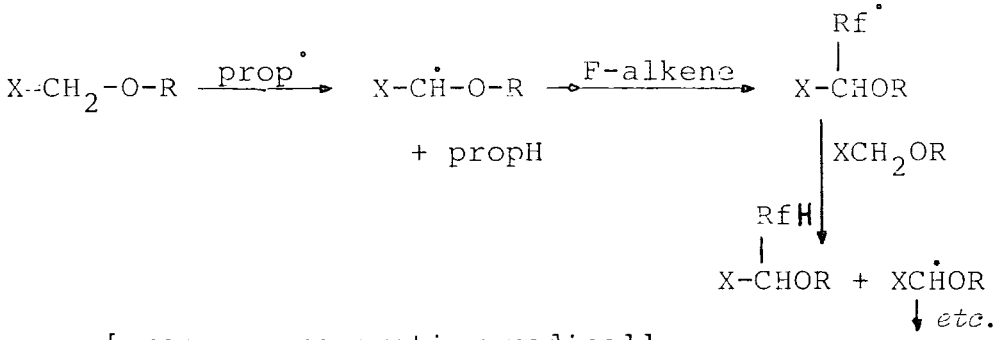
Before the attempt to prepare a P.F.P.E. by this proposed route, 2 main areas have been investigated: (1) the free radical addition of F-alkenes to acyclic ethers and (2) the development of a direct fluorination process.

CHAPTER THREE

THE FREE RADICAL ADDITION OF ETHERS TO FLUORINATED ALKENES

A. Introduction

In our laboratory there is an ongoing project[124,125] investigating the use of the carbon hydrogen bond as a functional group in free radical addition reactions to fluorinated alkenes.



[prop = propagating radical]

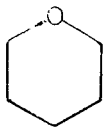
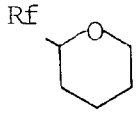
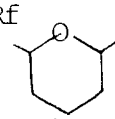
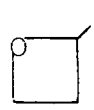
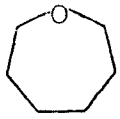
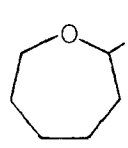
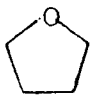
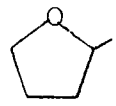
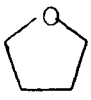
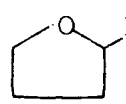
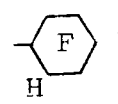
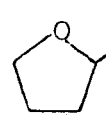
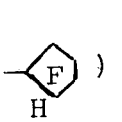
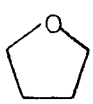
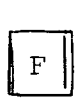
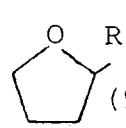
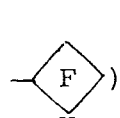
Various investigations have been carried out and, in particular, the effects of the substituents (-X) on these radical processes have been studied in detail.[124,126] The technique has proved to be a useful route to functionalised fluorocarbons and, more specifically fluorinated ethers. The ethers that have been prepared by other workers using this technique are listed in Table 16.

TABLE 16 Free Radical Addition of Ethers to F-olefins using excess Ether

Ether	F-alkene	Conditions	Products (%yield)
$CH_3CH_2OCH_2CH_3$	$CF_3CF{=}CF_2$	gamma rays, 20°C	$CH_3CHOCH_2CH_3$ (Rf) (38) + $CH_3CH(Rf)CH_2CH_3$ (Rf Rf) (43) (Rf=CF_2CFHCF_3)
$(CH_3CH_2CH_2)_2O$	$CF_3CF{=}CF_2$	gamma rays, 20°C	$CH_3CH_2CH_2OCHCH_2CH_3$ (Rf) (12) + $CH_3CH_2CHOCHCH_2CH_3$ (Rf Rf) (28) (Rf=CF_2CFHCF_3)

contd.....

TABLE 16 (contd.)

Ether	F-alkene	Conditions	Products (% yield)
$(CH_3CH_2CH_2CH_2)_2O$	$CF_3CF=CF_2$	gamma rays, 20°C	$CH_3CH_2CH_2\underset{\displaystyle Rf}{\underset{\vert}{C}}HOCH_2CH_2CH_2CH_3$ (16) + $CH_3CH_2CH_2\underset{\displaystyle Rf}{\underset{\vert}{C}}HO\underset{\displaystyle Rf}{\underset{\vert}{C}}HCH_2CH_2CH_3$ (28) + $CH_3CH_2CH_2\underset{\displaystyle Rf}{\underset{\vert}{C}}HO\underset{\displaystyle Rf}{\underset{\vert}{C}}HCH_2CH_2CH_3$ (26) ($Rf=CF_2CFHCF_3$)
	$CF_3CF=CF_2$	gamma rays, 20°C	 (61) +  (35) ($Rf=CF_2CFHCF_3$)
	$CF_3CF=CF_2$	gamma rays, 20°C	 (65) ($Rf=CF_2CFHCF_3$)
	$CF_3CF=CF_2$	gamma rays, 20°C	 (70) ($Rf=CF_2CFHCF_3$)
	$CF_3CF=CF_2$	gamma rays, 20°C	 (95) ($Rf=CF_2CFHCF_3$)
		gamma rays, 20°C	 (91) ($Rf'=$ )
		gamma rays, 20°C	 (83) ($Rf''=$ )
		gamma rays, 20°C	 (91) ($Rf'''=$ )

1. Free Radical Reaction Mechanisms

Free radical reactions between ethers and F-alkenes have been adequately reviewed by other workers in the laboratory[124,125] and so will only be dealt with briefly here.

Fluorinated ethers of the type illustrated in Table 16 are produced *via* a free radical chain mechanism. There are several steps involved in chain mechanisms which are outlined in Scheme 4.

	Reaction	Step
1.	$R - H \longrightarrow R^{\bullet} + H^{\bullet}$	Initiation
2.	$R^{\bullet} + \rangle\!=\!\langle \longrightarrow R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot$	Addition
3.	$R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot + \rangle\!=\!\langle \longrightarrow R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot$	Telomerisation
4.	$R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot + R\text{-}H \longrightarrow R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}H + R^{\bullet}$	Chain Transfer or Propagation
5.	$R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot + H^{\bullet} \longrightarrow R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}H$	} Combination
6.	$R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot + R^{\bullet} \longrightarrow R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\text{-}R$	
7.	$R\text{-}\overset{|}{\underset{|}{C}}\text{-}\overset{|}{\underset{|}{C}}\cdot \xrightarrow{\text{wall}}$	} Termination

Scheme 4

Several factors contribute to a successful free radical addition of an ether to a F-alkene.

a. Formation of α ether Radicals

In the case of hydrocarbon ethers the formation of the α ether radical is energetically favourable due to the stabilisation of the resulting radical by the adjacent oxygen atom. This stabilisation may be rationalised by the interactions shown in Figure 2.

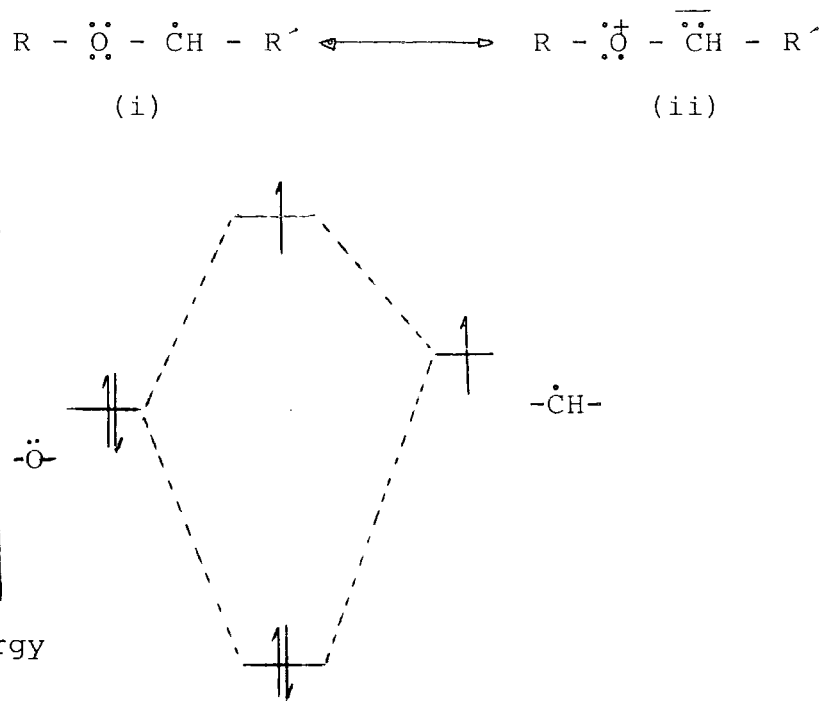


Figure 2

b. The Addition Step (step 2 scheme 4)

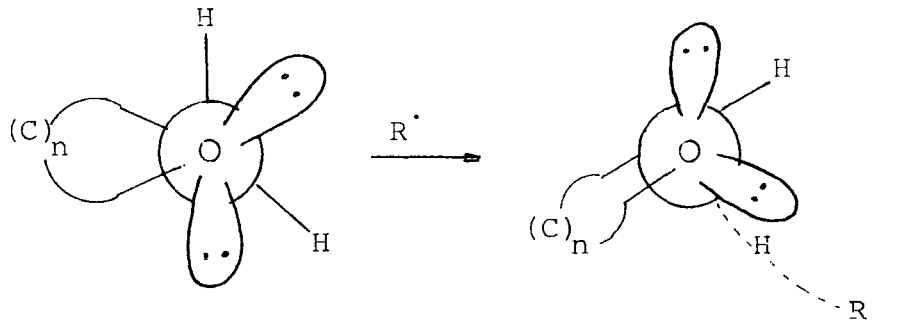
The addition of the α ether radical to the F-alkene is generally favourable. Considering Figure 2, it is clear from the structures (i) and (ii) that the α ether radical is nucleophilic in character. Consequently we find that the ether radicals in general react readily with fluorocarbon olefins which are themselves usually susceptible to nucleophilic attack.

c. The propagation or chain transfer step (step 4 scheme 4)

The propagation step relies on a favourable reaction between the propagating radical (R-C-C•) and the hydrocarbon ether. If this step is hindered then a 'short chain' mechanism will result with low conversion to product.

2. Stereoelectronic Effects

Considering Table 16 several features emerge, most important of which is the difference in reactivities of the cyclic ethers. The reactivity of the cyclic ether is governed by a stereoelectronic effect:[127]



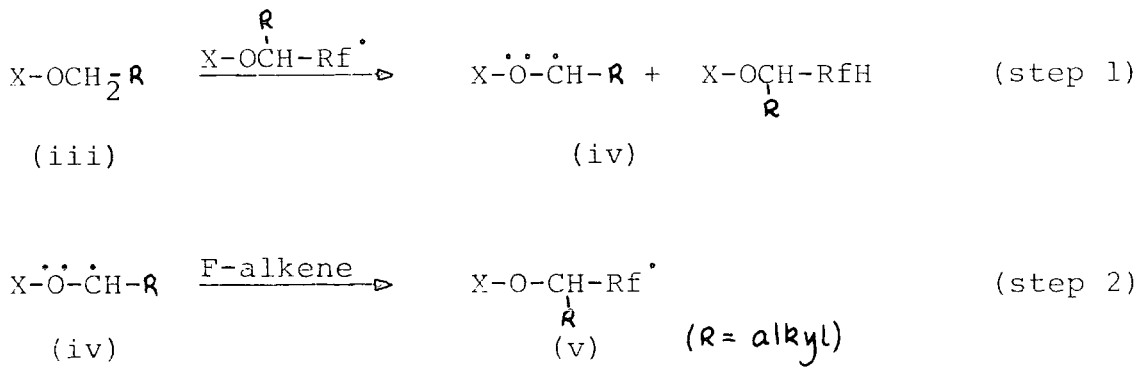
(cyclic ether) (transition state)

Figure 3

For the transition state (Figure 3), leading to the radical, a maximum interaction between the oxygen lone pair and the breaking carbon-hydrogen bond will lead to enhanced reactivity. Table 16 indicates that for values of n=5 or 7 a more favourable conformation may be obtained than for n=6.

3. Substituent Effects

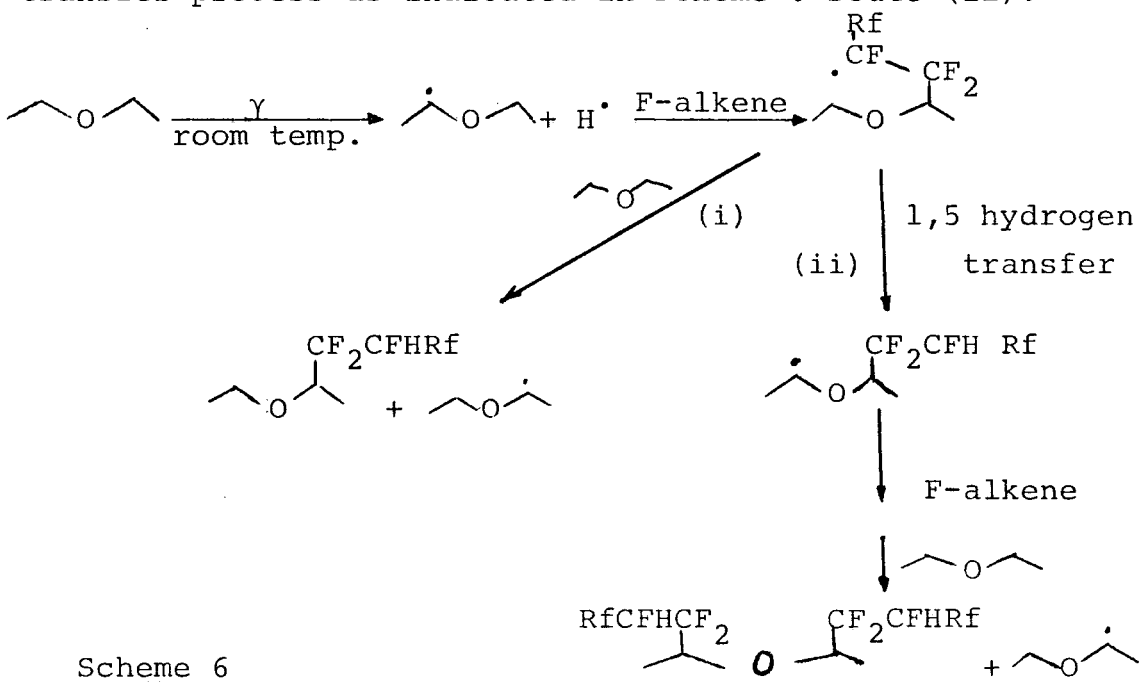
Studies[126] into the free radical additions of substituted ethers to F-alkenes indicate that when x- is electron withdrawing the reaction is inhibited (Scheme 5).



Scheme 5

The electron withdrawing substituent is thought to effect the propagation step (step 1 scheme 5) rather than the addition (step 2 scheme 5). The inhibition of step 1 is most probably due to reduced reactivity of the ether (iii) with the electrophilic propagating radical.

Therefore when X is a perfluoroalkyl group the ether is deactivated to further addition. Table 16 however, indicates that, even in the presence of excess ether, polyadducts are produced with acyclic ethers. The formation of the polyadducts may be explained[128] by an intramolecular hydrogen transfer process as indicated in Scheme 6 route (ii).



Scheme 6

B. Discussion

In this chapter the addition reactions of various simple ethers to several fluorinated alkenes have been used as models for the corresponding addition using polyether systems. Using these model compounds the factors controlling polysubstitution have been investigated. Two factors have been found to make major contributions in producing polyadducts: 1, the structure of the ether; and 2, a 1,5 hydrogen transfer process.

1. Effects of the hydrocarbon ether structure

Model compound studies with methoxy glymes revealed that attack does not occur readily at the methoxy site, and mono-adducts predominate in the products.

$$CH_3OCH_2CH_2OCH_3 + C_3F_6 \xrightarrow[20^{\circ}C]{\gamma \text{ rays}} RfCH_2OCH_2CH_2OCH_3 + CH_3O\underset{\displaystyle Rf}{\underset{|}{C}}HCH_2OCH_3$$

(1) 30% (2) 60%

(Rf = CF_2CFHCF_3)

$$CH_3OCH_2CH_2OCH_3 + C_2F_4 \xrightarrow{1.} CH_3O\underset{\displaystyle Rf'}{\underset{\diagdown}{C}}HCH_2OCH_3 + Rf'CH_2OCH_2CH_2OCH_3$$

(3) 53% (4) 18% ($Rf' = CF_2CF_2H$)

[1.= di-tertiarybutyl peroxide, 140°C]

+ telomeric adducts 31% (5)

Conversely using ethoxy ether systems attack occurred preferentially at the end groups.

$CH_3CH_2OCH_2CH_2OCH_2CH_3 + C_3F_6 \xrightarrow{\gamma\ rays}$

$CH_2CH_2OCHCH_2OCH_2CH_3$ (Rf on CHCH$_2$) (14) [5]

(6)

$+ CH_3CHOCH_2CH_2OCH_2CH_3$ (Rf on CHCH$_3$) (48) [16]

(7)

Ether: C_3F_6

- 3:1 (% yields):
  - $+ CH_3CHOCHCH_2OCH_2CH_3$ (Rf on both CH) (8)
  - $+ CH_3CHOCH_2CHOCH_2CH_3$ (Rf on both CH) (minor component) (9)
- 1:2 [% yields]:
  - $+ CH_3CHOCH_2CH_2OCHCH_3$ (Rf on both CH) (10)
  - $+ CH_3CHOCHCH_2OCHCH_3$ (Rf on all three CH) (11)

(27) [22]

(11) [16]

[14]

(Rf = CF_2CFHCF_3)

These results indicate the following order of reactivity.

$CH_3CH_2O - > - OCH_2CH_2O - > CH_3O$.

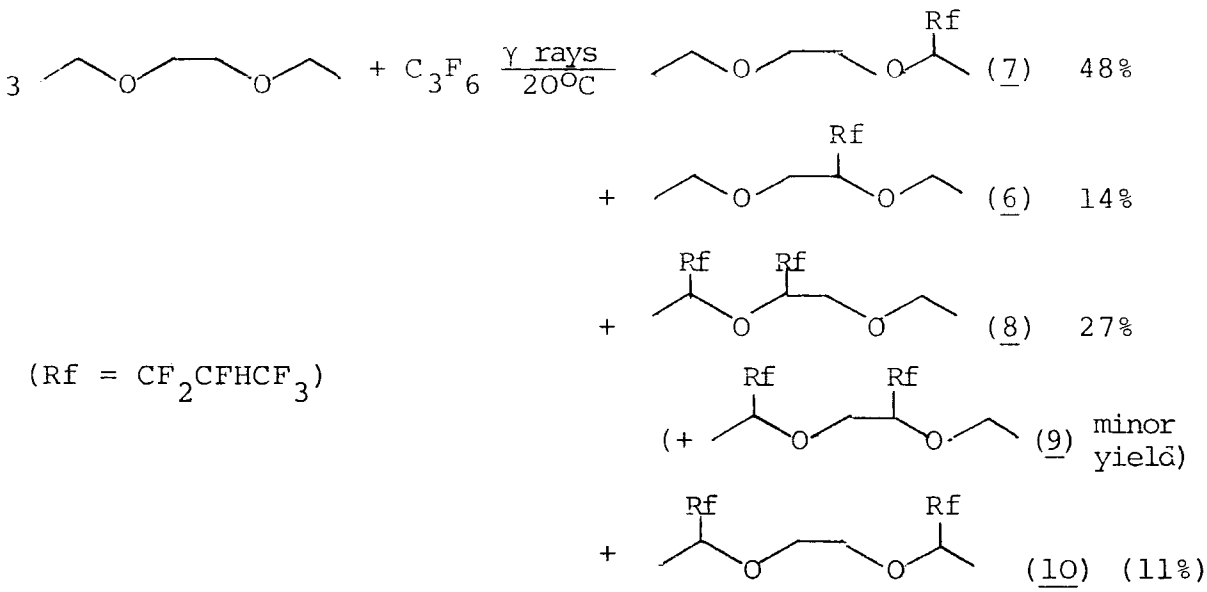
The difference in reactivity between the ethoxy and methoxy groups may be accounted for by the difference in stability of the secondary and primary radicals formed respectively. However, the order of reactivity of the OCH_2CH_2O group requires a different explanation as it is a secondary site yet less reactive than the ethoxy group. The explanation has previously been discussed in the introduction of this chapter in that electron withdrawing substituents lower the reactivity of the ether toward electrophilic propagating radicals. A further cause of the deactivation of

the - OCH_2CH_2O - group may be steric hindrance, if the ether molecule is bulky, as in the case of glymes, the approach of the propagating radical may be hindered.

2. The Hydrogen Transfer Mechanism

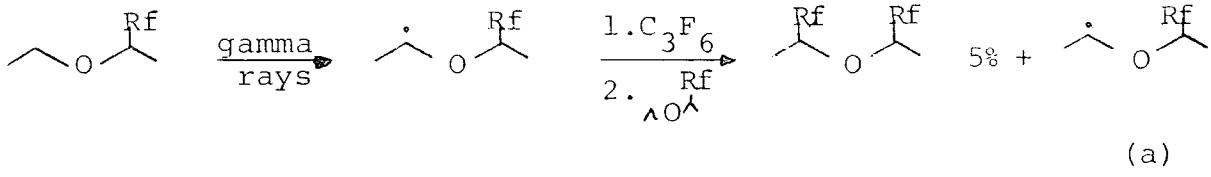
a. Evidence for intramolecular hydrogen transfer

An intramolecular 1,5 hydrogen transfer mechanism may be used to account for the product distribution in the addition of ethyl glyme to hexafluoropropene. Although attack occurs preferentially at the end groups (8) is produced in higher yield than (10).

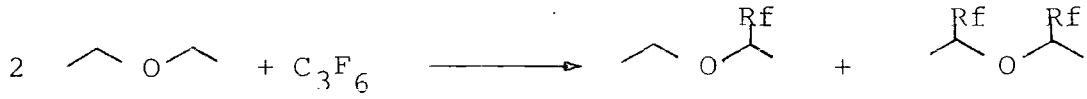


It is clear that the intramolecular hydrogen transfer plays a major role in producing poly adducts.

The attempted addition of (13) to hexafluoropropene gave poor conversion to the di-adduct (14) [reaction a]. However addition of excess diethyl ether to hexafluoropropene produced (14) in *ca.* 52% yield. [reaction b].



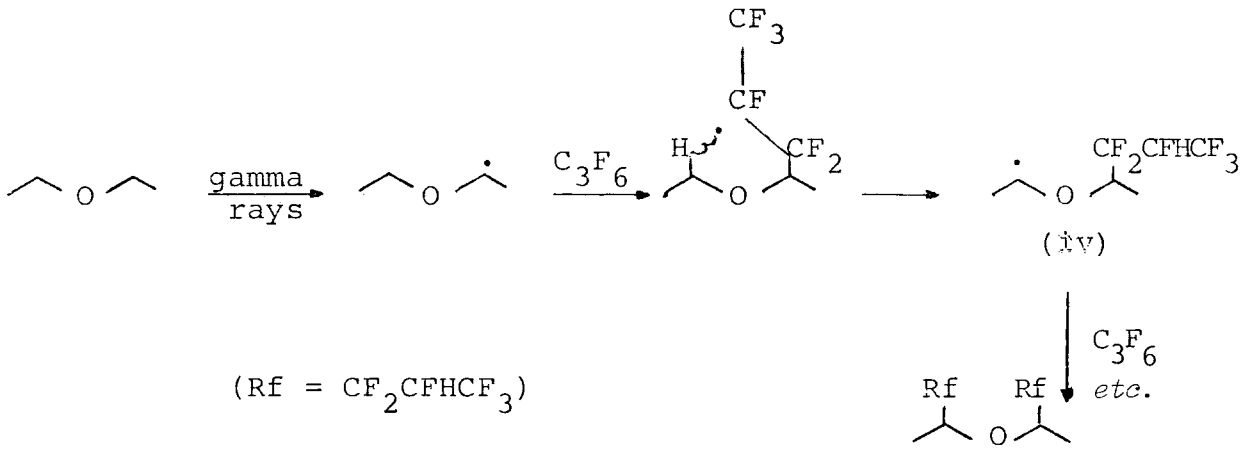
(a)



(b)

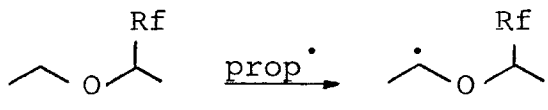
(13) 48% (14) 52%

It is probable that in reaction (b) the intramolecular hydrogen transfer process facilitates the production of the radical (iv)



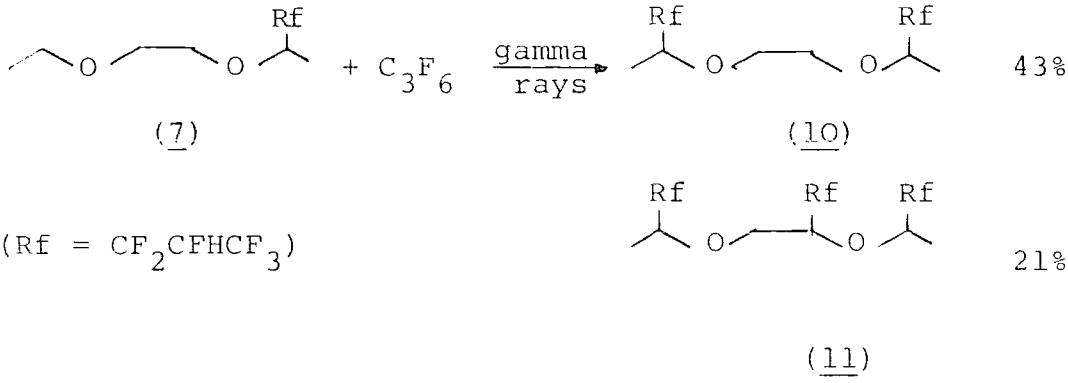
(Rf = CF_2CFHCF_3)

The low conversion to the di-adduct (14) from (13) (reaction (a)) may be accounted for by the limited reaction of (13) with the electrophilic propagating radical due to the inductive effects of the polyfluoroalkyl group.

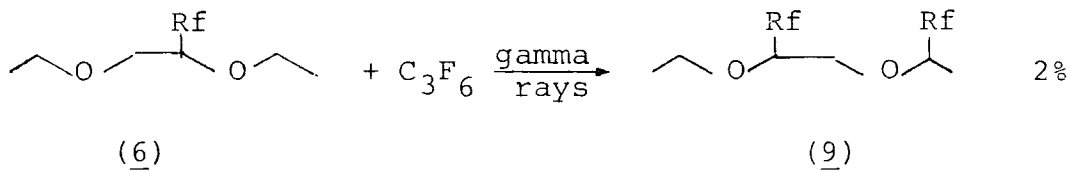


(13) (iv)

Further evidence of the intramolecular mechanism was given by the addition of adduct (7) to hexafluoropropene resulting in the production of (10) and (11) in good yield.



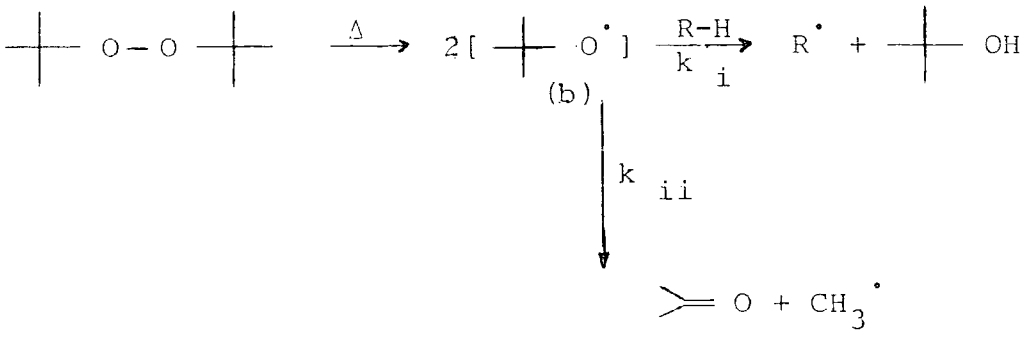
Adduct (6), however, gave little further reaction with hexafluoropropene.



The difference in reactivity between (6) and (7) was assessed by measuring the acetone/t-butyl alcohol ratio obtained by the decomposition of di-tertiarybutyl peroxide in each adduct system (see later). Other workers[124,126] have shown the acetone/t-butyl alcohol ratio may be related to ease of hydrogen abstraction from the adduct system. It was found, by measuring this ratio that (6) is much less reactive toward free radical addition than (7). The cause of this low reactivity is most probably due to the inductive influence of the polyfluoroalkyl group, over the whole molecule, being greater in (6) than in (7).

(1) Acetone/Butanol Ratios

Acetone/butanol ratios are based on the deposition sequence of di-tertiary butyl peroxide (DTBP) at a specified temperature:



If $R^{\cdot}$ is formed easily, then the tertiary butoxy radical (b) will react to give mainly tertiary butanol *via* route i. If $R^{\cdot}$ is not formed easily then the tertiary butoxy radical will decompose to give acetone and a methyl radical *via* route (ii). Therefore measuring the ratio of the acetone and butanol in the products will give an indication to the reactivity of the substrate R-H.

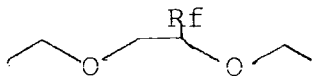
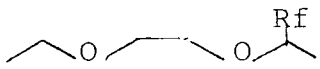
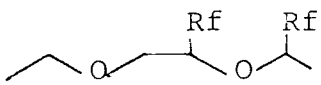
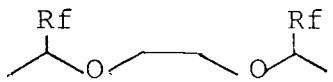
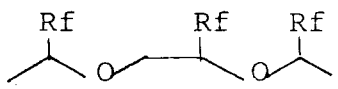
Acetone/butanol ratios have been measured for adducts (6), (7), (8), (10) and (11), the results are shown in Table 17.

Clearly these results indicate that sites adjacent to polyfluoroalkyl groups are deactivated to further free radical reaction with hexafluoropropene. It may be anticipated therefore that polysubstitution *via* a stepwise mechanism would be unfavourable. However as the reaction of (7) and (13) indicate, polysubstitution does occur by means of an intramolecular hydrogen transfer process.

(b) Effect of alkene structure on intramolecular hydrogen transfer

Further studies probing the effect of changing the structure of the alkene upon intramolecular hydrogen transfer have been carried out. The results of these additions are summarised in Table 18.

TABLE 17 Acetone/Butanol measurements at 140°C

Substrate	Ratio
	0.1
 (6)	1.9
 (7)	0.9
 (8)	2.5
 (10)	75.0
 (11)	∞ no t-butanol detected

---

Rf = CF_2CFHCF_3 .

TABLE 18 Free Radical Addition of F-alkenes and cycloalkenes to Ethers (γ ray. 20°C)

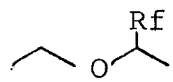
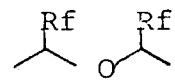
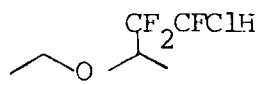
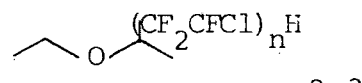
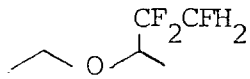
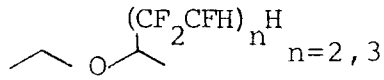
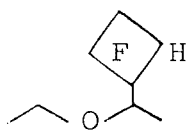
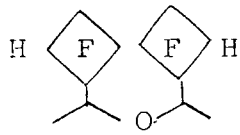
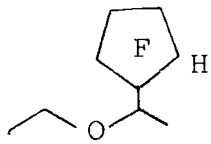
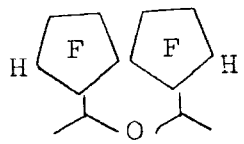
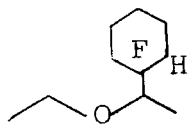
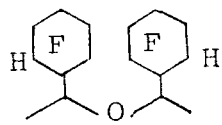
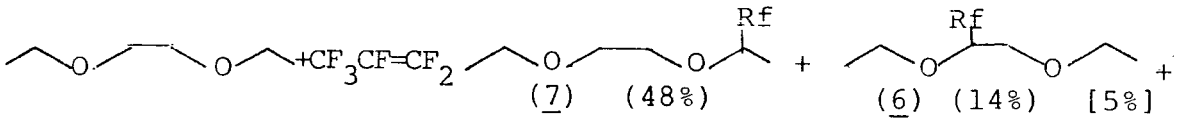
Reactants	Products (Yield)
Et_2O + $CF_3CF=CF_2$ 2 : 1	 (57%) (13)  (43%) (14)
Et_2O + $CF_2=CFCl$	 (90%) (15)  (10%) (16) n=2,3

TABLE 18 (contd.)

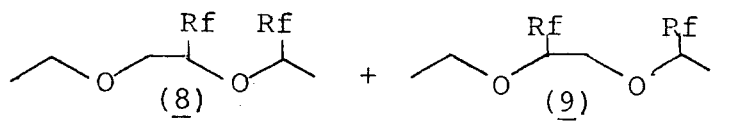
Reactants	Products (Yield)
Et_2O + CF_2CFH	 (17) (80%)  (18) (16%) n=2,3
Et_2O + 	 (19) (90%)  (20) (5%)
Et_2O + 	 (21) (60%)  (22) (27%)
Et_2O + 	 (23) (40%)  (24) (40%)



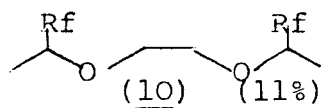
3 : 1 (Yield)

1 : 2 [Yield]

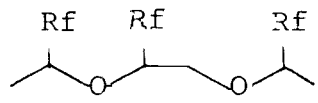
(Rf = CF_2CFHCF_3)



(27%) [22%]

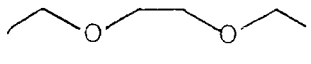
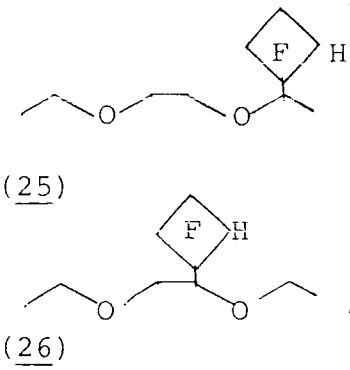
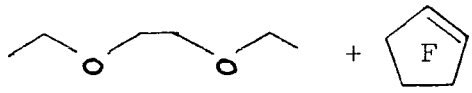
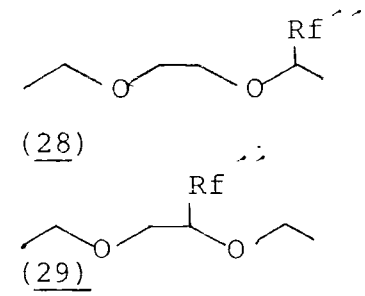
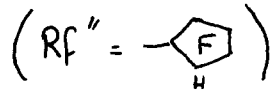
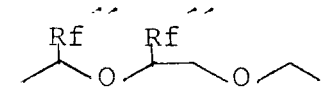
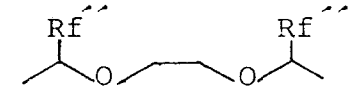
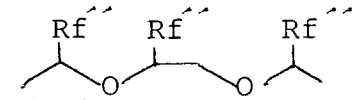
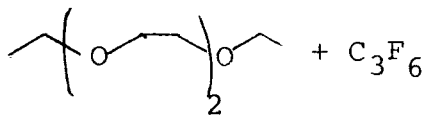


(10) (11%) [16%]



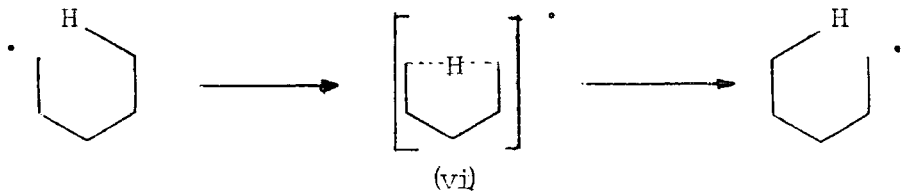
(11) [14%]

TABLE 18 (contd.)

Reactants	Products (Yield)
 1 : 3	 (25) (26) (50%)
	+ Diadducts (16%) (27)
 1 : 3	 (28) (29) (33%)
(Rf'' = )	+  (30%) (20%)
	 (31) (14%)
	 (32) (6%)
 1 : 4	monoadducts (24%) (33)
	diadducts (33%) (34)
	triadducts (34%) (35)
	tetradducts (8%) (36)

It is clear that, with the exception of F-cyclobutene, F-cycloolefins favourably undergo the 1,5-hydrogen transfer step. Hexafluoropropene also readily abstracts a hydrogen atom intramolecularly but chlorotrifluoroethene and trifluoroethene produce telomer adducts (18) and (16) rather than di-substituted compounds.

The hydrogen transfer process, both inter- and intramolecular mechanisms, is well documented [129] and is generally believed to occur through a linear transition state (Scheme 8).



(vi)

Scheme 8

If this is true, it would be expected that the conformation of the transition state (vi) would be a major factor in controlling the hydrogen transfer mechanism. Model building studies indicate that a bulky Rf group would, sterically, prefer to have the conformation of the molecule such that 1,5-hydrogen transfer is favoured. Diagrams 3a,b show the conformations that produce least steric interactions and that are favourable for 1,5-hydrogen transfer.

This is confirmed by the experimental evidence shown in Table 18. An exception to this observed trend is the addition to F-cyclobutene. It is obvious that with F-cyclobutene, the strained 4-membered ring is not flexible enough to allow a linear transition state to form easily and hence mainly mono-adducts (19), (25) and (26) are formed.

3a demonstrates the case for the F-cyclopentyl adduct.

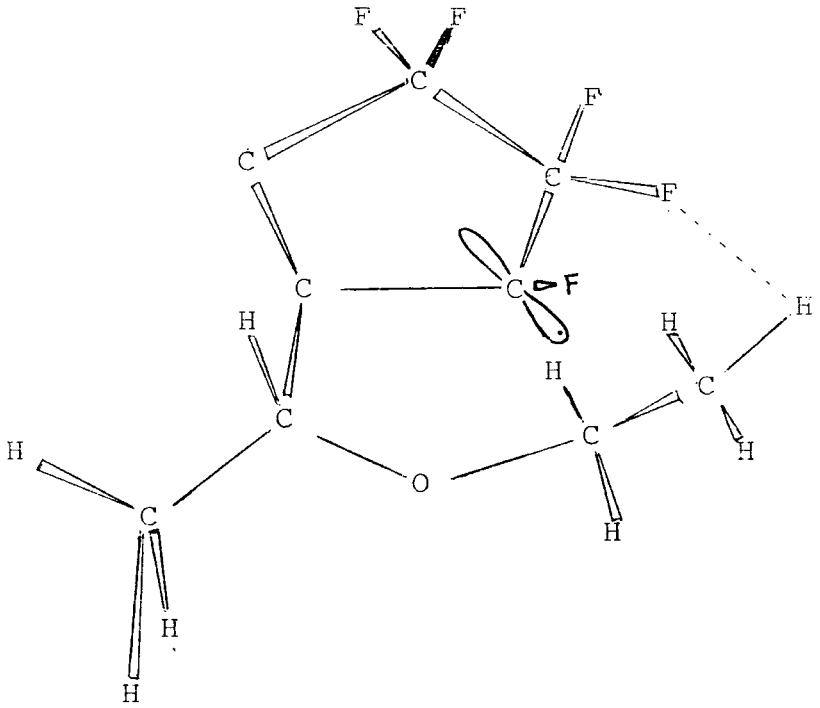


DIAGRAM 3a

3b demonstrates the general case

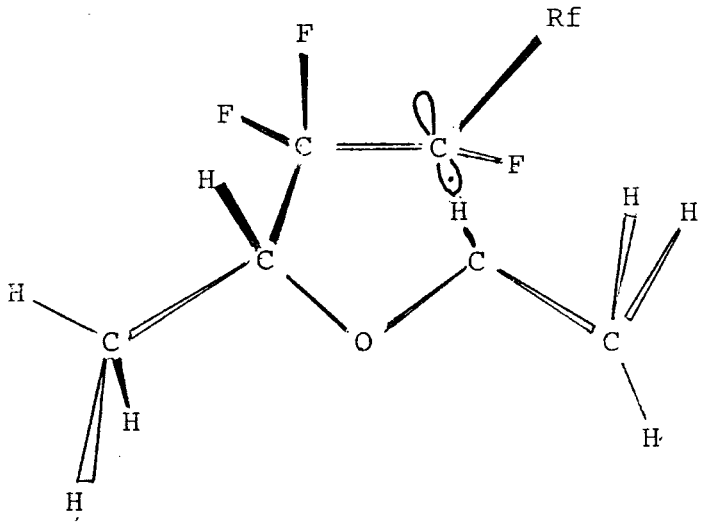


DIAGRAM 3b

Considering Figure 4 as n increases from 1 → 3 the 1,5-hydrogen transfer occurs more readily.

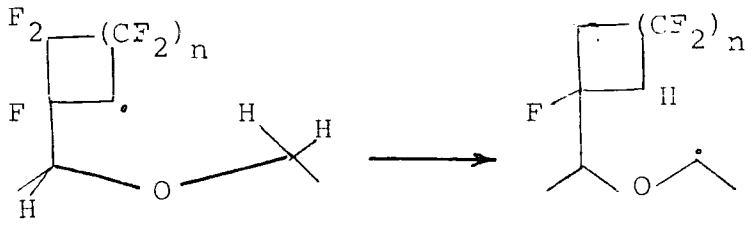
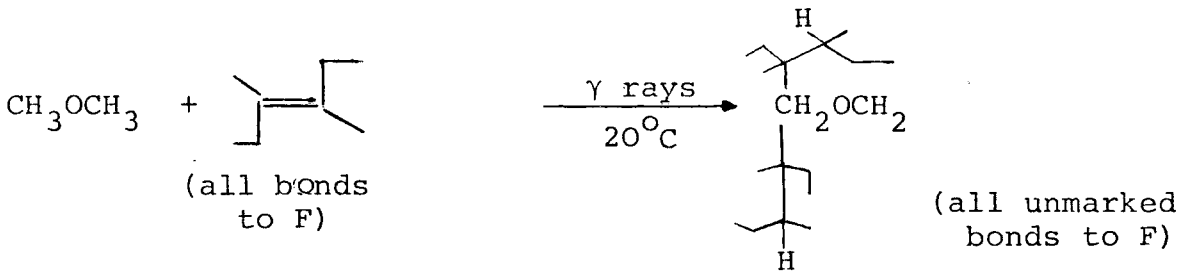


FIGURE 4

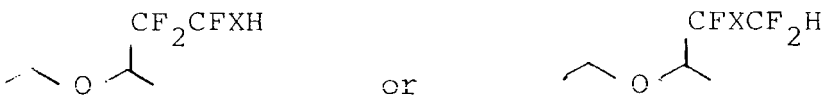
The presence of substantial intramolecular hydrogen-fluorine bonding (H.....F ——) in these adduct systems has been noted in direct fluorination reactions (Chapters Five and Six). It must not be overlooked that some H....F bonding may help form the desirable conformations required for hydrogen transfer.

Perfluoro-3,4-dimethylhex-3-ene (tetramer of TFE) does not react, under free radical conditions with diethyl ether due to steric shielding of the carbon-carbon double bond by the bulky perfluoroalkyl groups. It is interesting to note that with dimethyl ether only di-adducts are formed.[124]



From this observation it may be suggested that <u>inter</u>-molecular steric hindrance may have a role in reducing reactivity. It is known that chlorotrifluoroethene and trifluoroethene have a propensity to telomerise and this is observed with the results given in Table 18. The mono adducts

formed may, theoretically, have two possible structures



X = Cl, H

Two factors govern orientation: (1), stability of the radical intermediate and, (2), preferred site of attack on the ethene molecule.

It is known that reaction with chlorotrifluoroethene is regiospecific as factors (1) and (2) supplement each other,

i.e.

$$-CF_2-\dot{C}FCl \quad > \quad -CFCl-\dot{C}F_2$$

order of stability

Also, nucleophilic attack will occur preferentially at the $-CF_2-$ group of the olefin.

Trifluoroethylene, is a more complex case, as factors (1) and (2) are opposing

i.e.

$$-CF_2-CFH^{\bullet} \quad < \quad -CFH-CF_2^{\bullet}$$

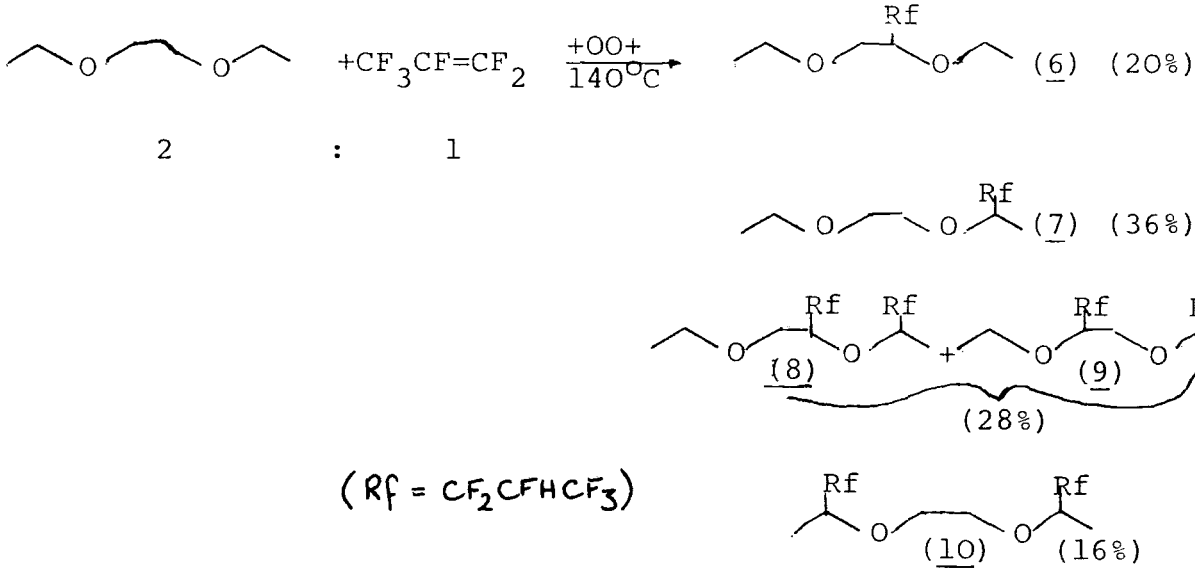
order of stability.

However, nucleophilic attack on the olefin will occur once again preferentially at the difluoromethylene group. Consequently it is not surprising that mixed products resulting from attack at either carbon of trifluoroethene are generally observed.

Using chlorotrifluoroethene and trifluoroethene as model olefins for 1,5-hydrogen transfer it was observed that telomer type adducts (16) and (18) were produced rather than disubstituted adducts. The mono-adducts produced were somewhat surprising . In the case of chlorotrifluoroethene the product (15) was produced as predicted. With trifluoroethene, however, the only mono-adduct produced was (17) derived solely from preferred site of nucleophilic attack and not a mixture of isomers as anticipated.

(c) Effect of Temperature

Some addition reactions carried out using gamma ray initiation at 20°C were repeated at higher temperatures using DTBP as the initiator.



mono-adducts (32%)
(33)

di-adducts (42%)
(34)

tri-adducts (24%)
(35)

$$CH_3OCH_2CH_2OCH_3 + C_2F_4 \xrightarrow[140^{\circ}C]{+OO+} \underset{(3)}{CH_3OCHCH_2OCH_3}\ (Rf' = CF_2CF_2H) \quad (53\%) \quad \text{(Product ratio)}$$

$$CH_3OCH_2CH_2OCH_2CF_2CF_2H \quad (4) \quad (15\%)$$

$$+ \text{ telomers.} \quad (31\%)$$

The results of these peroxide reactions show clearly an increase in temperature has two effects: (a) the initial attack on the ether is less selective but still favours the end groups and the order of reactivity shown below is still valid,

$$CH_3CH_2O > OCH_2CH_2O > CH_3O$$

(b) the 1,5 hydrogen transfer process, although still important, participates to a lesser degree as more products from a stepwise process are produced.

C. Conclusion

The model compound studies completed in this chapter have encouraging results. Initially it has been established that the position of attack on the ether may be directed by choice of ether structure. Further, the models demonstrated that polysubstitution is possible in relatively small ethers and consequently this finding was applied to polyethers.

CHAPTER FOUR

OXIDATIVE FLUORINATION USING COBALT TRIFLUORIDE

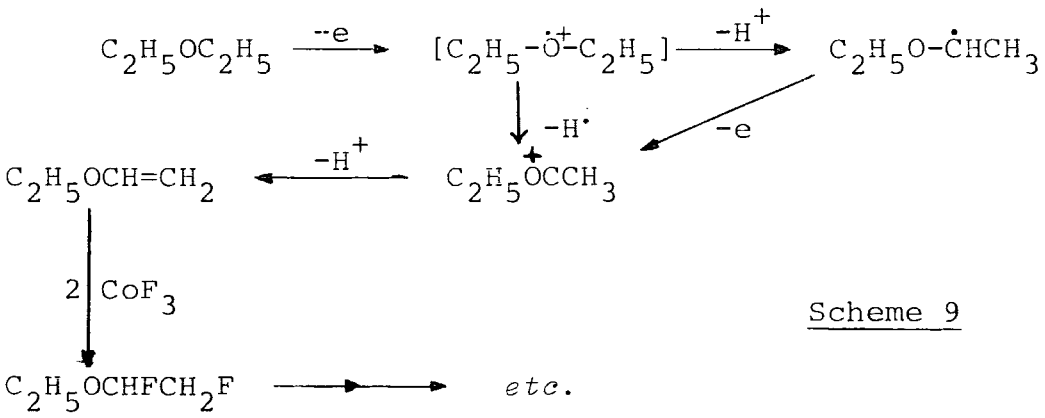
IVA Introduction

The use of cobalt trifluoride as a fluorinating agent has been known for some time and the advantage of using cobalt trifluoride over, for example, direct fluorination is due to the endothermic nature of the following step

$$2CoF_3 \longrightarrow 2CoF_2 + F_2 \qquad \Delta H^{o}_{473} = +52 \text{kcal mol}^{-1}$$

Consequently the overall exotherm of the cobalt trifluoride fluorination process is less than that for direct fluorination.

The mechanism of the reaction most probably involves an initial oxidation step (Scheme 9).



Scheme 9

The technique was introduced by R.D. Fowler,[129] but has been extensively developed by Tatlow and co-workers.[130]

Using this process hydrocarbons may be partially fluorinated by passing through a reactor filled with cobalt trifluoride, heated to around 20°C above the boiling point of the substrate. Typically, diethyl ether may be fluorinated over cobalt trifluoride at 60-80°C to yield a mixture of the penta-, hexa- and septa-fluoro derivatives.[131]

$$C_2H_5OC_2H_5 \xrightarrow[CoF_3]{60\text{-}80^{o}C} (CHF_2CHF)_2O + CFH_2CFHOCFHCF_2H + CF_2HCF_2OCFHCF_2H$$

The process was limited in application as often only partially fluorinated products resulted which were difficult to separate. Recycling the products from the above process and fluorinating at a higher temperature resulted in fragmentation and lower overall yields.

Recently another worker in the laboratory has developed the CoF_3 fluorination process further.[125,132]

It was shown that ethers with α-substituted polyfluoroalkyl groups may be successfully fluorinated over cobalt trifluoride at around 440°C, to produce the corresponding perfluorinated ethers in high yield. It is important to stress that unlike earlier reports on CoF_3 fluorination of ethers, the product mixture usually contained only two components, the perfluoro-ether (50-70% yield) and a perfluorocarbon fragment (5-10% yield) arising from α cleavage of the ether. Development of the Durham process produced a convenient, high yield route to volatile perfluorinated ethers. The process is now a general laboratory technique which produces better yields than the rather less convenient electrochemical process. Some of the perfluorinated ether products produced from cyclic and acyclic ether systems are shown in Table 19.

TABLE 19. Oxidative Fluorination over CoF_3[132,125]

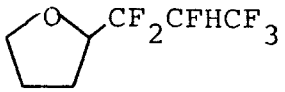
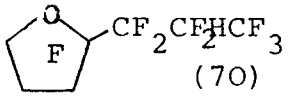
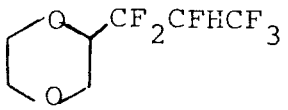
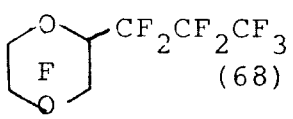
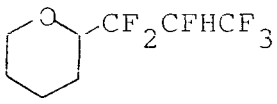
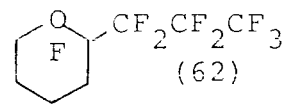
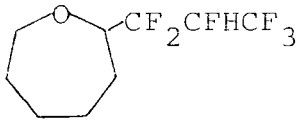
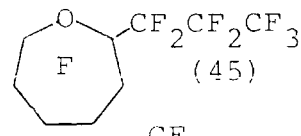
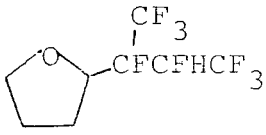
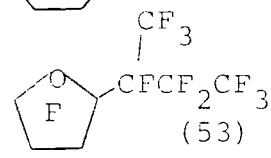
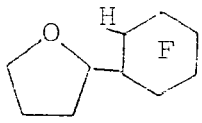
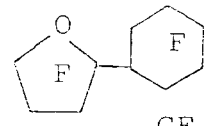
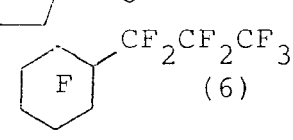
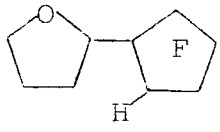
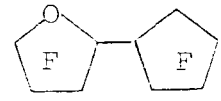
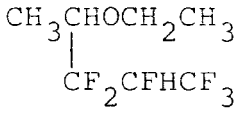
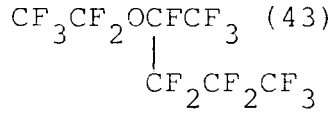
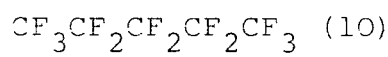
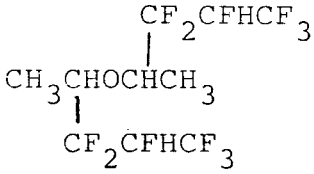
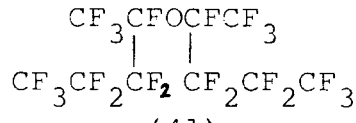
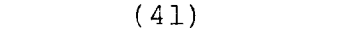
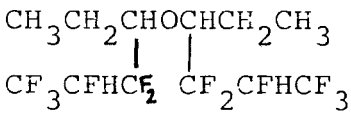
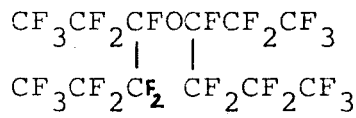
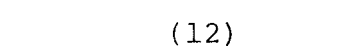
Substrate	Temperature	Products (Yield %)
	440°C	 (70)
		$CF_3(CF_2)_4CF_3$ (3)
	440°C	 (68)

TABLE 19 (contd.)

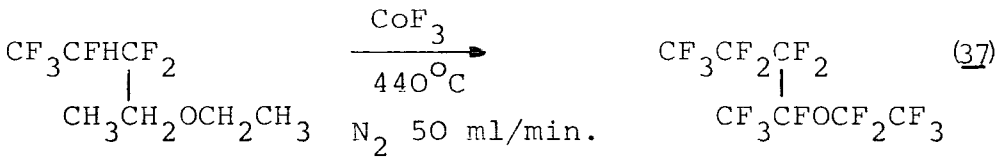
Substrate	Temperature	Product(s) (Yield%)
	420	 (62)
	440	 (45)
	440	 (53)
	440	 (51)  (6)
	440	 (65)
	440	 (43)  (10)
	440	 (41)  (9)
	440	 (12)  (30)

IVB Discussion

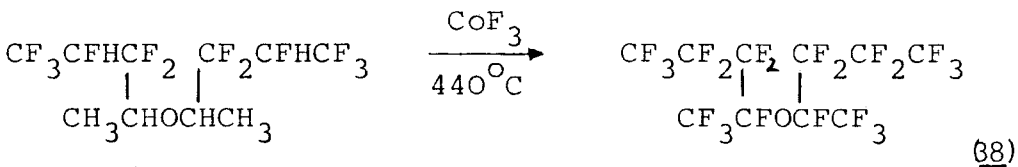
The work described in this chapter was carried out to determine (1) the limits to which the Durham process may be applied to produce medium molecular weight range perfluorinated polyethers, and (2) the effect of structural changes of the polyfluoroalkyl group in acyclic systems.

1. Acyclic polyether adducts

Grieveson and Chambers[132] have already reported the successful fluorination of adducts (13) and (14) in good yield. These reactions were repeated in order to standardise the conditions to be used for the fluorination of higher molecular weight ethers.



(37)



(38)

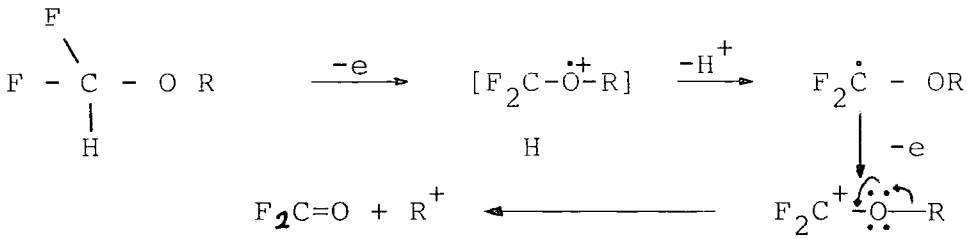
To extend the above process it was necessary to prepare adducts of various polyethers to fluorinated olefins. The most readily available source of polyethers are methyl glymes which are capped with methoxy groups, for example:

$CH_3OCH_2CH_2OCH_3$ — monoglyme (dimethoxyethane)

$CH_3O(CH_2CH_2O)_2CH_3$ — diglyme

Several adducts derived from monoglyme have now been fluorinated over cobalt trifluoride at 440°C but considerable

fragmentation occurred in each case. The most probable cause of this extensive decomposition is due to α carbon oxygen cleavage, resulting in the formation of the stable molecule carbonyl fluoride (Scheme 10).



Scheme 10

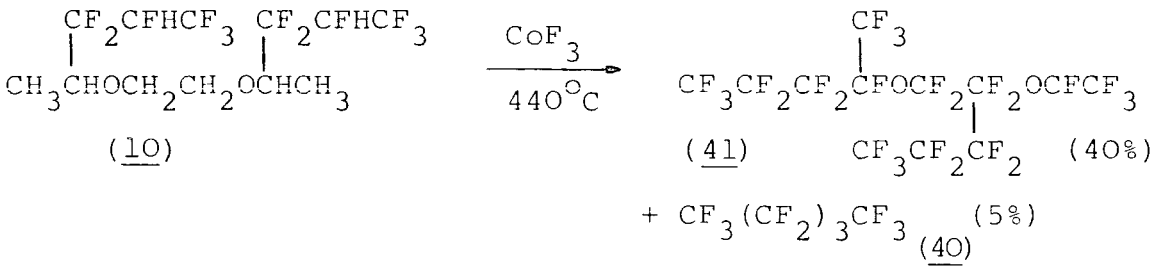
The following adducts all gave fragmented products in this fashion $CH_3OCH_2CH(Rf)OCH_3$ (2)(3), $RfCH_2OCH_2CH_2OCH_3$(1) (4), [where for (1) (2) Rf = CF_3CFHCF_3 and for (3), (4) Rf = CF_2CF_2H] and $CH_3OCH_2CH(Rf)OCH_3$ (5) [where Rf = $(CF_2CF_2)_nH$, n=2 or 3]. Lowering the reaction temperature had little effect on the stability of these compounds; the fluorination of adduct (5) at 206°C still resulted in products derived mainly from decomposition of the substrate molecule.

The instability to CoF_3 of methyl glyme adducts is, however, in sharp contrast with the great stability exhibited by the ethyl glyme adducts. This is clearly demonstrated by the successful fluorination of (7). The fluorination of (7) also indicates the dramatic stabilisation, of a relatively large molecule, that it is possible to obtain, by incorporation of a single polyfluoroalkyl group into an ether skeleton.

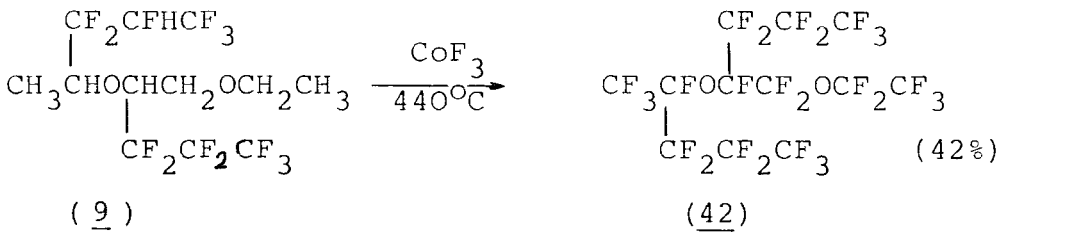
$$CF_3CFHCF_2\underset{|}{\overset{CH_3}{C}}HOCH_2CH_2OCH_2CH_3 \xrightarrow{440^\circ C} CF_3CF_2CF_2\underset{|}{\overset{CF_3}{C}}FOCF_2CF_2OCF_2CF_3 + CF_3(CF_2)_3CF_3$$

(7) (39) (16%) + (40) (7%)

With 2:1 adducts of hexafluoropropene ethyl glyme (10), (8) fluorination over CoF_3 at 440°C yielded the corresponding perfluoroethers (41) and (42) in *ca.* 40% yield

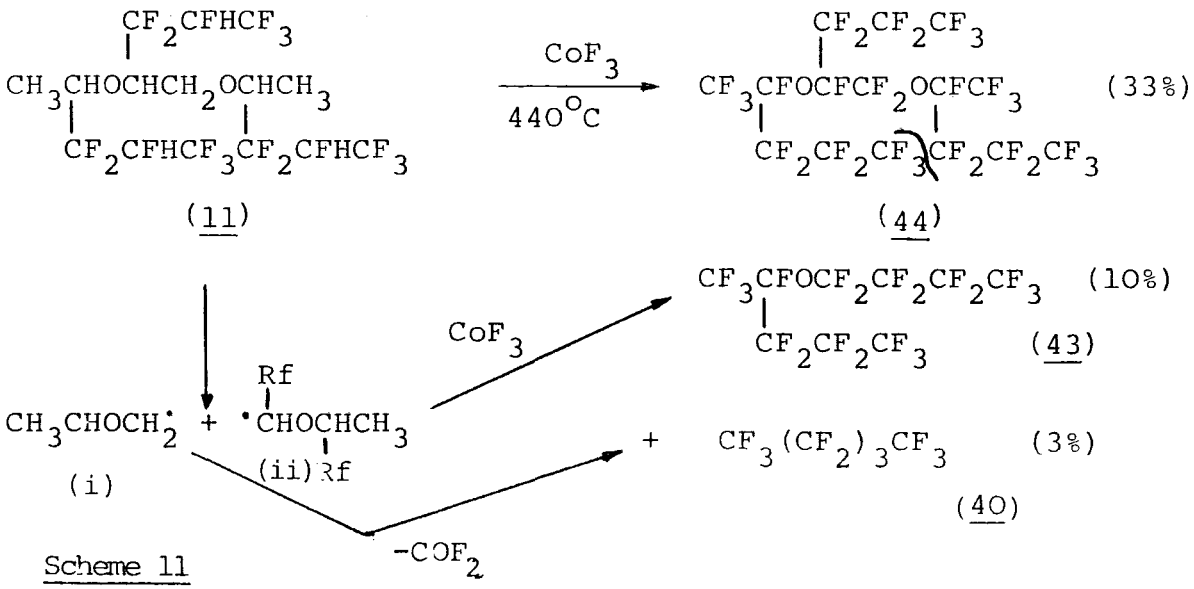


(10) → (41) $CF_3CF_2CF_2CF(CF_3)OCF_2CF_2OCF(CF_3)CF_2CF_2CF_3$ (40%) + $CF_3(CF_2)_3CF_3$ (40) (5%)



(9) → (42) $CF_3CF(CF_2CF_2CF_3)OCF(CF_2CF_2CF_3)CF_2OCF_2CF_3$ (42%) + $CF_3CF(CF_2CF_2CF_3)OCF_2CF_2CF_2CF_3$ (43) (10%) + $CF_3(CF_2)_3CF_3$ (40) (6%)

Similarly the tri-adduct of hexafluoropropene (11) yielded the perfluoroether (44) although in lower yield than (41) or (42).



(11) → (44) $CF_3CF(CF_2CF_2CF_3)OCF(CF_2CF_2CF_3)CF_2OCF(CF_3)CF_2CF_2CF_3$ (33%)

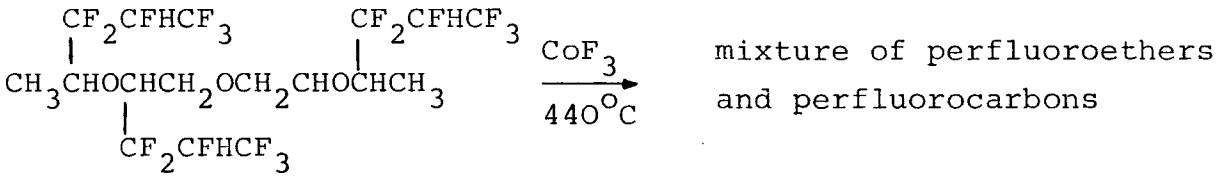
$CH_3CHOCH_2^{\bullet}$ (i) + $^{\bullet}CH(Rf)OCHCH_3$ (ii) —CoF_3→ (43) $CF_3CF(CF_2CF_2CF_3)OCF_2CF_2CF_2CF_3$ (10%) + (40) $CF_3(CF_2)_3CF_3$ (3%)

(ii) —$-COF_2$→ (40)

Scheme 11

The most likely cause of the diminished yield of (44) is indicated by Scheme 11: the molecule fragmenting to form 2 stable α-ether radicals. Subsequent fluorination of radical (ii) leads to formation of (43). Radical (i), however, contains a radical which, as previously discussed, tends to eliminate carbonyl fluoride and produce the F-pentane. A similar type of fragmentation is expected to occur for the bis-adduct (10), however, both resulting radicals will rapidly decompose forming F-pentane.

In an attempt to extend the process to produce ethers of increased molecular weight a mixture of the tris adducts of hexafluoropropene (HFP) and ethyl diglyme (35) was passed over CoF_3 at 440°C. However a complex mixture of products resulted. It was determined using mass spectrum glc techniques and nmr that the product mixture consisted largely of volatile perfluorocarbon ethers and perfluorocarbons which have arisen from fission of the carbon skeleton of the substrate.



(35)

In conclusion the CoF_3 process gives moderate yields of perfluorinated ethers of intermediate molecular weight (up to 820), however, yields noticeably decrease on (a) extensive branching in the carbon skeleton, and (b) on increasing the length of the polyether backbone.

2. Effect of the Structure of the polyfluoroalkyl group

Several F-alkenes have been added to diethyl ether and subsequently fluorinated over cobalt trifluoride at 440°C. The investigation has been used to determine the stabilising effect of various polyfluoroalkyl groups upon the ethers during oxidative fluorination. The results will be used, assuming similar parameters govern stability, to give insight into which polyfluoroalkyl groups will give greatest stability in direct fluorination processes.

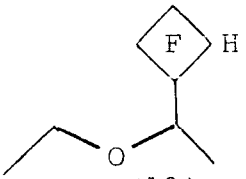
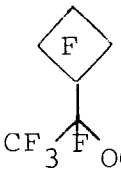
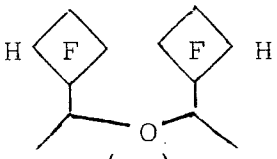
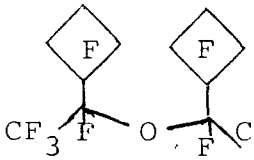
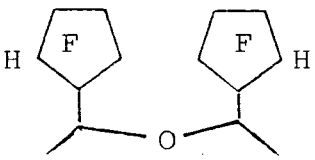
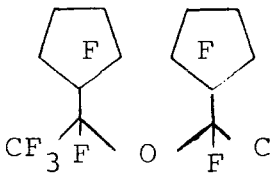
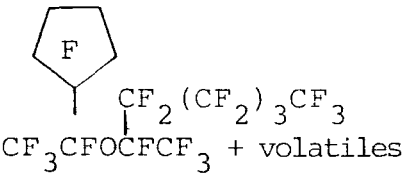
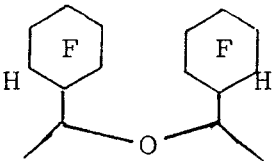
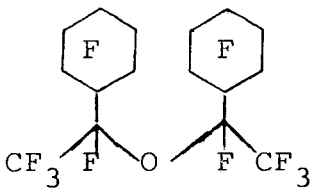
The fluorination of the hexafluoropropene adducts (13) and (14) have been dealt with earlier in this chapter.

Several adducts containing polyfluorocycloalkyl groups, derived from addition of diethyl ether to the relevent F-cycloalkene, have been successfully fluorinated. The results are given in Table 20.

Fluorination of the F-cyclobutyl mono-adduct (19) gave the corresponding perfluoroether and F-n-hexane which arises from α cleavage of the ether together with ring opening of the cyclobutyl ring. Similar results were obtained for the di-adduct (20) and the F-cyclohexyl di-adduct (24). In the case of the F-cyclopentene diadduct (22) the volatile components were not isolated but as well as the perfluoroether (48), a product resulting from the ring opening of one cyclopentyl group was isolated (49).

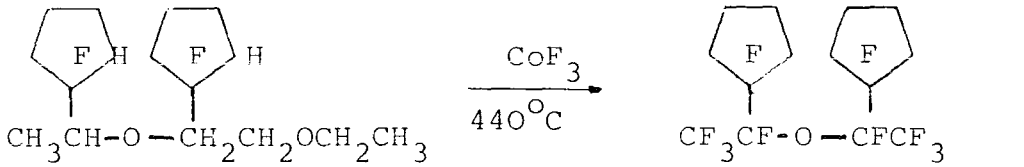
In summary the polyfluorocycloalkyl groups do not have a greater stabilising effect toward further fluorination compared to the hexafluoropropyl group. It would seem

TABLE 20 Fluorination of F-cycloalkene adducts over CoF_3 at 440°C

Adduct	Product(s) (% Yield)
 (19)	 (45) (20%) + perfluoro-n-hexane (46) (20%)
 (20)	 (47) (37%) + $CF_3(CF_2)_4CF_3$ (46) (12%)
 (22)	 (48) (40%) +  (6%) (49) (6%)
 (24)	 (50) (42%) + $CF_3(CF_2)_6CF_3$ (51) (15%)

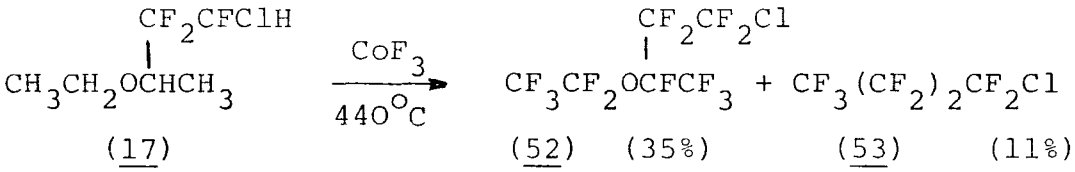
that the tertiary site in the cycloalkyl group is a source of instability and may well be responsible for the fragmentation products observed in several cases.

Preliminary investigations using ethyl glyme F-cyclopentene di-adducts also suggest that polyfluorocycloalkyl groups do not stabilise the molecule to fluorination as well as hexafluoropropyl groups.



(30) (48) + other fragmentation products

Fluorination of the adduct (17) yielded perfluoro-3-chloro-1-methyl-propyl ethyl ether (52).



(17) (52) (35%) (53) (11%)

It is interesting that the chlorine atom is retained in (52) as this will allow the molecule to be functionalised further.

C. Conclusions

The reason for the stabilisation imparted by the polyfluoroalkyl group is not well understood. Initially, the polyfluoroalkyl group, due to inductive effects, may raise the oxidation potential of the ether hence lowering the reactivity toward oxidative fluorinating agents.

Another plausible explanation, given by Lagow, when discussing stability in direct fluorination processes, is the ability of the molecule to dissipate energy through vibrational and rotational relaxation processes without fragmentation, which is an essential feature in high energy fluorination processes.

Finally, it may be argued that the presence of the perfluoroalkyl group prevents fluorination to occur on adjacent

carbon atoms by sterically protecting the ether skeletons. This has the effect of preventing enough energy to be liberated, in order to allow carbon carbon bond fission, from the exothermic fluorination process, at any one point on the molecule.

CHAPTER FIVE

DEVELOPMENT OF DIRECT FLUORINATION TECHNIQUES

VA INTRODUCTION

Recently there has been considerable interest in direct fluorination processes and it was envisaged that such a technique may be appropriate for producing high molecular weight perfluoroethers from adducts of fluorinated olefins and polyethers. The adducts of simple ethers and hexafluoropropene have been used to probe the feasibility of direct fluorination in higher molecular weight systems.

The background to direct fluorination has already been discussed adequately in Chapter One and will not be dealt with further here.

VB Discussion

1. Preliminary Reactions

Preliminary experiments with adduct (10) highlighted the remarkable stability of adducts to direct fluorination. The product mixture from the reaction was shown to contain a substantial proportion of OCF_2 groups by examination with n.m.r. spectroscopy. The products illustrated are only a representation and not a defined structure

$$CH_3\underset{\displaystyle Rf}{\underset{|}{C}}HOCH_2CH_2O\underset{\displaystyle Rf}{\underset{|}{C}}HCH_3 \xrightarrow{F_2/N_2} Ca.\ Rf\text{-}\underset{\displaystyle Rf'}{\underset{|}{C}}FOCF_2CH_2O\underset{\displaystyle Rf'}{\underset{|}{C}}H\text{-}Rf$$

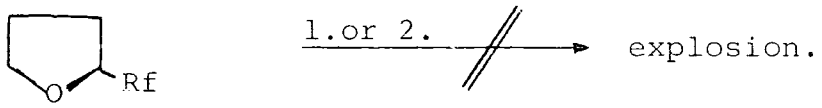
(10)

$Rf = CF_2CFHCF_3$

$\left[\begin{array}{l} Rf = CF_2CFHCF_3 \\ Rf' = CH_3, CHF, CH_2F \end{array}\right]$

The experiment with adduct (10) was relatively primitive, the ether simply being stirred vigorously in an atmosphere of nitrogen and fluorine in glass apparatus.

Similar experiments with the cyclic ether adduct (80) were less successful. Due to the volatile nature of the adduct, vapour phase reaction tended to occur leading to violent explosions. The use of inert solvents to dilute the adduct did not improve control of the reaction substantially



(80) 1. $0^{o}C$ F_2/N_2.

2. $0^{o}C$, F_2/N_2, Arcton 113

2. Copper tube reactions

The success of the preliminary reactions lead to the design of a more sophisticated technique. It was realised that several features would be important, namely: (a) an efficient heat dissipation medium to avoid vapour phase fluorination and to control the exothermic reaction; (b) dilution of fluorine in nitrogen and control of flow rates of this mixture; and (c) dispersion of the substrate over a large surface area to avoid side reactions of polymerisation as observed by other workers.[21,36] The eventual design of reactor used for model compound studies is illustrated in diagram 4.

Several model compound adducts were directly fluorinated with the copper "U" tube reactor resulting in a mixture of partially fluorinated ethers. The results of these experiments are given in Table 21.

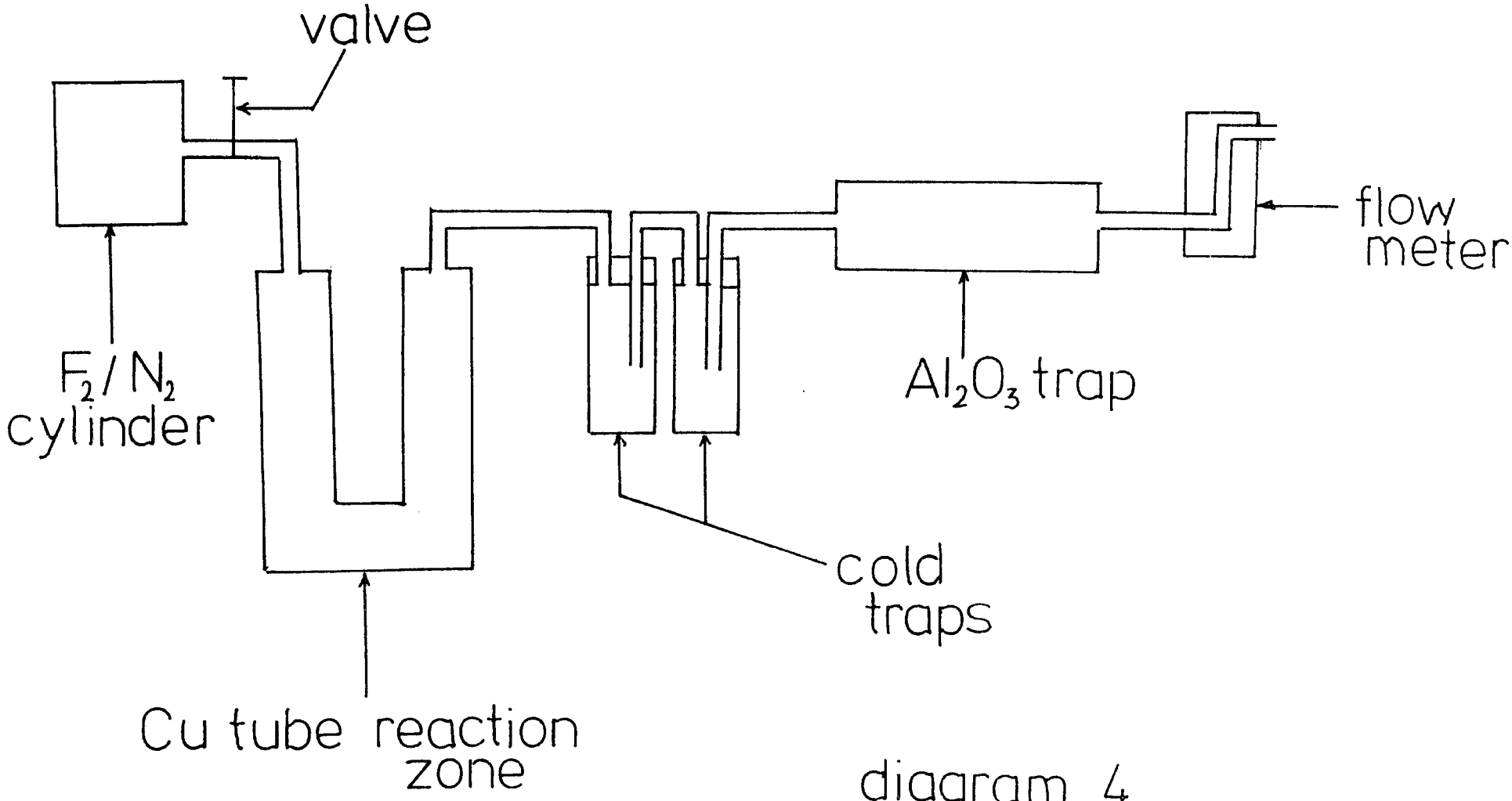

valve
F_2/N_2 cylinder
Al_2O_3 trap
flow meter
cold traps
Cu tube reaction zone

diagram 4

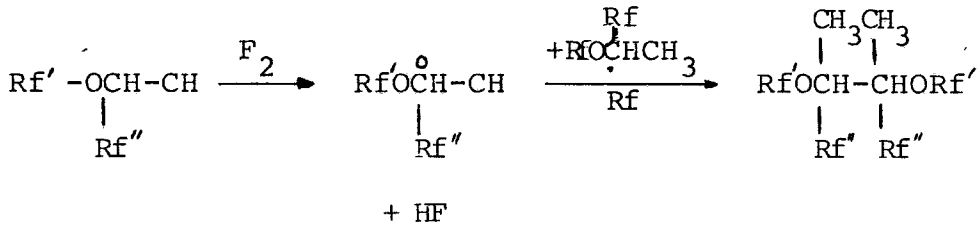
TABLE 21.

Substrate	Conditions	Product Empirical Formulae	% Yield
$CH_3CH(Rf)OCH_2CH_2OCH_2CH_3$ (7)	0°C, 5hrs. ~10% F_2 in N_2	$C_9H_{11.2}F_{8.8}O_2$ (54)	82
$CH_3CH(Rf)OCH_2CH_2OCH_2CH_3$ (7)	20°C, 5 hrs ~10% F_2 in N_2	$C_9H_8F_{14}O_2$ (55)	25
$CH_3CH(Rf)OCH_2CH_2OCH_2CH_3$ (7) (Rf = CF_2CFHCF_3)	0°C, 2.5 hrs 20°C, 2.5 hrs 10% F_2 in N_2	$C_9H_{9.5}F_{12.5}O_2$ (56)	40
$CH_3CH(Rf)OCH_2CH_2OCH(Rf)CH_3$ (10)	0°C, 5 hrs 10% F_2 in N_2	$C_{12}H_{11.5}F_{15.5}O_2$ (57)	95
$CH_3CH(Rf)OCH_2CH_2OCH(Rf)CH_3$ (10)	0°C, 2½ hrs. 20°C, 2½ hrs. 10% F_2 in N_2	$C_{12}H_{7.5}F_{18.5}O_2$ (58)	70
$CH_3CH(Rf)OCH_2CH_2OCH(Rf)CH_3$ (10)	0°C→20°C 5 hrs. 52°C 5 hrs.	$C_{12}H_5F_{21}O_2$ (59)	25

Examination of the product in Table 21, by gas liquid chromatography, showed them to be highly complex mixtures that were inseparable by normal techniques such as preparative glc. The degree of fluorination was measured by comparing the relative ^{19}F and ^{1}H NMR integrals of an internal standard (trifluoromethylbenzene) with those of the crude product. The NMR data also revealed that, in general, the ether linkages of the adducts remained intact throughout the reaction.

The results indicate that the greater substitution of polyfluoroalkyl groups into the ether molecule the greater the stability to direct fluorination. The stability of the adducts was found to be quite remarkable, the systems being able to withstand elemental fluorine up to 20°C without substantial fragmentation occurring.

Although the success of the "U" tube technique was extremely encouraging, several drawbacks emerged. It was not possible to achieve perfluorination in high yield since, when forcing conditions were used (Run 5, Table 21), there was considerable mass loss. The mass loss may be attributable to volatile products not being efficiently trapped. Although several attempts were made the product recovery could not be improved for the stages employing elevated temperatures. Also the product mixtures, except those arising from reaction at elevated temperatures, were rather unusual in that they were <u>extremely viscous liquids</u>. Normally it would be expected that the system would become increasingly mobile as more C-H sites were replaced by C-F sites. Consequently we at first derived the erroneous conclusion that the high viscosity was due to side reactions that involved fluorine induced coupling, *i.e.*



However, this conclusion was later disproved by fluorination of the viscous material over cobalt trifluoride. (These experiments are discussed in greater depth later in this chapter).

A modification of the "U" tube technique, consisting of a coiled copper tube packed with copper (mesh 20) powder, was used to avoid the supposed polymerisation process. The attempts, however, were unsuccessful. The reaction of (10) was extremely vigorous as a result of either the large surface area of the substrate exposed to the fluorine or, perhaps, to promotion of the reaction by catalytic activity of the copper mesh.

3. The Capillary Reactor

This novel approach was developed to achieve improved temperature control of the fluorinations. The apparatus used is illustrated in diagram 5. The stainless steel capillary allows fine control of the fluorine nitrogen mixture *via* micro-bubbles, thus preventing vigorous reaction. The geometry of the glass reactor vessel maximises the fluorine/substrate contact and allows intimate mixing of the substrate molecules.

(a) Fluorination Reactions

Initial fluorinations were carried out to probe the causes of the viscous intermediate stages of the reaction. The adducts (9) and (10) were reacted with a 10% fluorine in nitrogen mixture to produce the viscous materials (59) and (60). The products (59) and (60) were found to be an inseparable

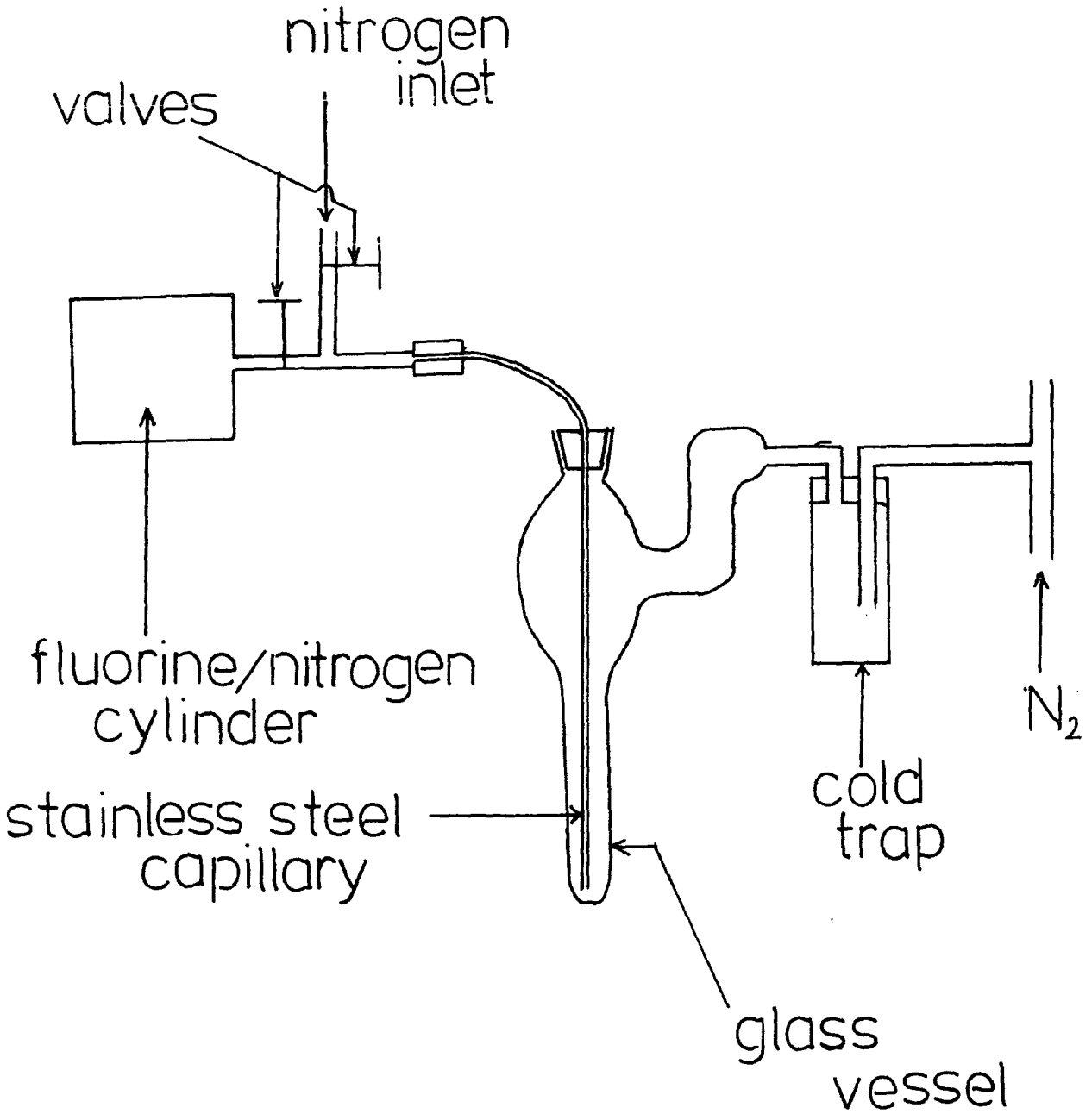
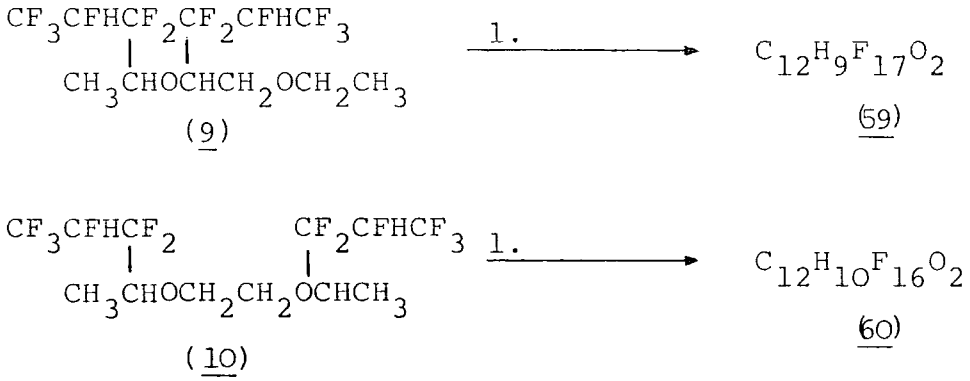

nitrogen
inlet
valves
fluorine/nitrogen
cylinder
stainless steel
capillary
cold
trap
N_2
glass
vessel

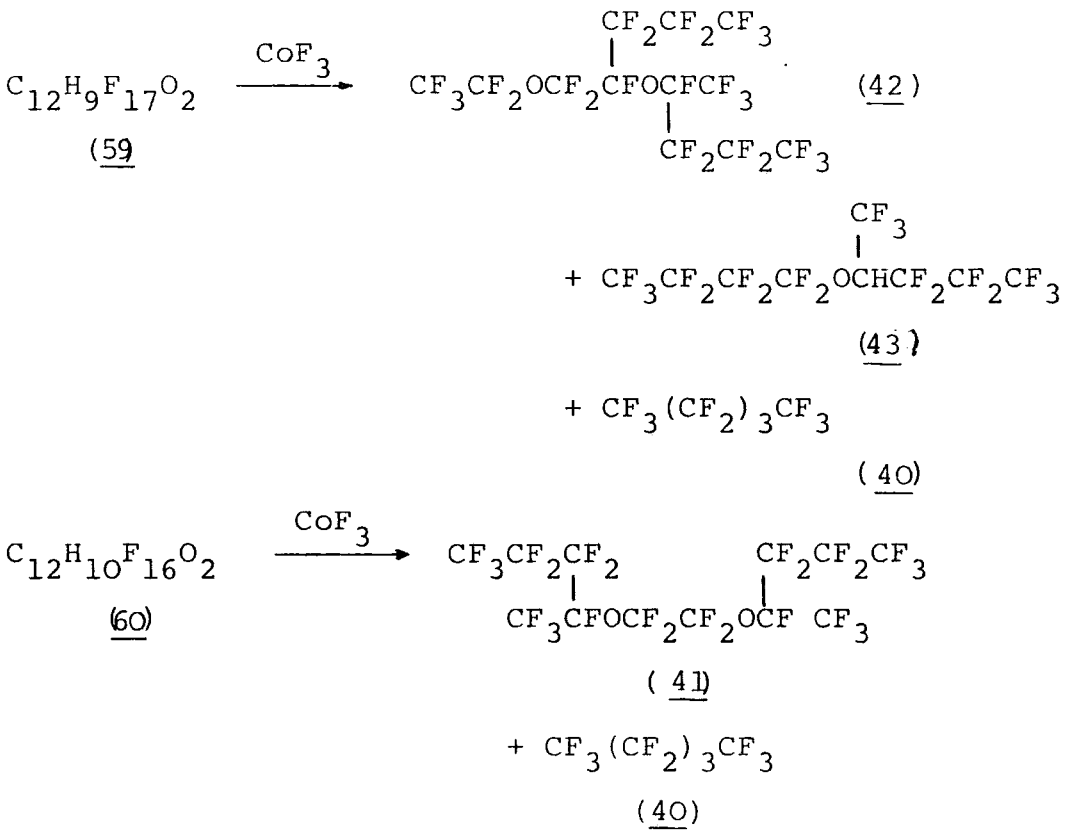
DIAGRAM 5

mixture of partially fluorinated ethers. The degree of fluorination was estimated by relative integrations of the relative n.m.r. signals of an internal standard trifluoromethylbenzene



[1. = 10% F_2 in nitrogen up to 50°C]

The product mixtures (59) and (60) were taken in turn and passed over cobalt trifluoride at 440°C to produce the perfluoroethers (42) and (41).



From this evidence it may be deduced that the adducts (9) and (10) did not undergo coupling reactions in the capillary system, as originally thought, nor is the viscosity due to polymeric type products. If coupling had occurred then the products from the CoF_3 reaction would have been more complex due to random cleavage of the substrate. It is concluded that the intermediate viscous stage is due to extensive hydrogen-fluorine bonding.

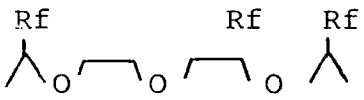
Further fluorination of adduct (10) using more forcing conditions to obtain more highly fluorinated products was only partially successful.

$$CH_3CH(Rf)OCH_2CH_2OCH(Rf)CH_3 \xrightarrow[2.]{1.} C_{12}F_{23}H_3O_2 \text{ containing some } CF_3CF_2CF_2CF(CF_3)OCF_2CF_2OCF(CF_2CF_2CF_3)CF_3$$

(Rf=CF_2CFHCF_3) (10) (0.25g) (41)

[1. = 10% F_2 0→70°C 10 hrs.
2. = 25% F_2 up to 110°C 6 hrs]

Although some of the perfluoroether (41) was detected by glc. there was significant mass loss in the reaction. Similar reactions using higher molecular weight adducts (35) were again affected by poor mass recovery.



(3.3g) (35)

$$\xrightarrow[2.]{1.} C_{17}F_{29}H_7O_3 \quad (61)$$

(0.18g)

(mixture of tri-adducts)

1. = 10% F_2 0 → 70°C 10 hrs.

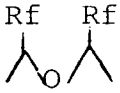
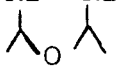
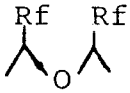
2. = 25% F_2 0 → 100°C 10 hrs.

4. Fluorination of Di(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether

(a) Capillary Fluorination

The comparitive mild conditions of the capillary reactor enabled studies to be carried out on an even simpler model compound the di-adduct of hexafluoropropene and diethyl ether (14). The adduct proved to be more stable than either (9) or (10). Although perfluorination could not be obtained without poor mass recovery a significant degree of fluorination could be achieved as can be seen in Table 22.

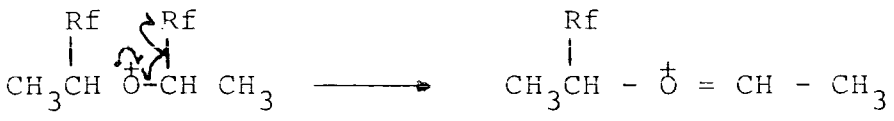
TABLE 22

Adduct	Conditions	Av.Empirical Formulae of Products	% Yield
Rf Rf  (14)	25% F_2 20°C, 2 hrs 50°C, 3 hrs.	$C_{10}F_{14}H_8O$ (62)	85
Rf Rf  (14)	25% F_2 20°C→50°C 5 hrs. 50% F_2 20°C→50°C 5 hrs.	$C_{10}F_{16}H_6O$ (63)	75
Rf Rf  (14)	25% F_2 20→50°C 5 hrs. 50% F_2 24→50°C 5 hrs. 100% F_2 20→110°C 10 hrs.	$C_{10}H_{2.5}F_{19.5}O$ (64)	10

The product mixtures were, understandably, inseparable. However, using mass spectral/glc techniques it was possible by investigating fragmentation patterns to identify isomeric components.

Generally the major fragment of a partially fluorinated ether (parent ions are not observed in electron impact spectra) arises from a β cleavage resulting in the loss of a polyfluoro-

alkyl group, Scheme 12.



(a) (b)

Scheme 12

Depending on the degree of fluorination the number of hydrogens remaining in (b) may be calculated from the mass of the fragment, see Table 23.

TABLE 23

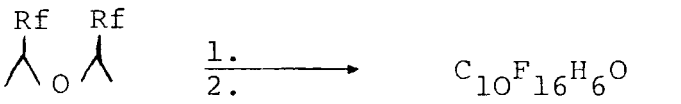
Isomer	MWt.	Side Chain lost	Mass of Expected Fragment
$C_{10}F_{18}H_4O$	482	CF_3CFHCF_2	331
$C_{10}F_{17}H_5O$	464	CF_3CFHCF_2	313
$C_{10}F_{16}H_6O$	446	CF_3CFHCF_2	295
$C_{10}F_{15}H_7O$	428	CF_3CFHCF_2	277
$C_{10}F_{14}H_8O$	410	CF_3CFHCF_2	259
$C_{10}F_{13}H_9O$	392	CF_3CFHCF_2	241
$C_{10}F_{12}H_{10}O$	374	CF_3CFHCF_2	223

The mass spectral/glc investigation illustrated that the fluorination was a relatively random process. The products (62) and (63) (Table 22) both contained a large range of isomers, typically $C_{10}F_{15}H_7O$ to $C_{10}F_{17}H_5O$. However, as the reaction proceeded, fluorination became increasingly difficult and as in product (64) the isomer range decreased [$C_{10}F_{18}H_3O$ to $C_{10}F_{19}H_2O$].

(b) Sealed System Reactor

Previously techniques such as u.v. initiation[59] have been used by other workers to produce perfluoro-compounds. We have developed a more convenient technique using enclosed vessels containing the substrate and fluorine/nitrogen mixes or neat fluorine under pressure.

The first attempt at sealed system reactions was carried out using a 70ml nickel tube fitted with a monel valve. The di-adduct (14) was initially fluorinated in the capillary reactor using up to 50% fluorine in nitrogen



(14) (63)

1. 25% F_2 20°C → 50°C 5 hrs.
2. 50% F_2 20°C → 50°C 5 hrs.

Then product (63) from this reaction was pressurised with 50% fluorine in nitrogen in the nickel tube. Remarkably, analysis of the products by glc. indicated little reaction had occurred.

The degree of fluorination was calculated by the glc/mass spec. method.

Therefore a similar reaction using neat fluorine for the sealed tube stage was carried out. Products from the capillary reactor (63) were sealed in the nickel tube and fluorine, sufficient to generate seven atmospheres of pressure, was condensed into the tube. The products on examination by glc. were a series of highly fluorinated ethers with no sign of volatile compounds arising from fragmentation.

$$C_{10}F_{16}H_6O \xrightarrow{1.} C_{10}F_{19}H_3O \qquad 75\%$$

(63) (65)

[1 = 7 ats, 20°C, neat Fluorine]

Further reaction of $C_{10}F_{16}H_6O$ (63) using neat fluorine at a slightly elevated temperature in the sealed tube successfully produced the perfluoroether (38) together with the perfluoroethers (43) and (66).

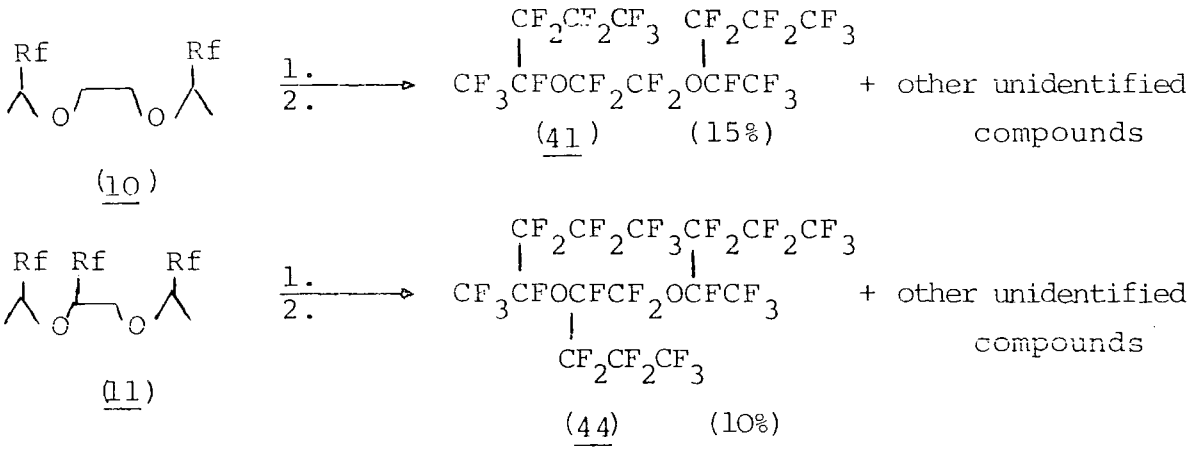
$$C_{10}F_{16}H_6O \xrightarrow{1.} \underset{(38)}{CF_3CF(CF_2CF_2CF_3)OCF(CF_2CF_2CF_3)CF_3} \qquad (37\%)$$

[1.=7at; neat fluorine; 20°C, 10hrs; 40°C, 24 hrs.:]

$$+ \underset{(43)}{CF_3CF_2CF_2CF_2OCF(CF_2CF_2CF_3)CF_3} \qquad (14\%)$$

$$+ \underset{(66)}{CF_3CF_2CF_2CF(CF_3)OCF(CF_3)CF_3} \qquad (11\%)$$

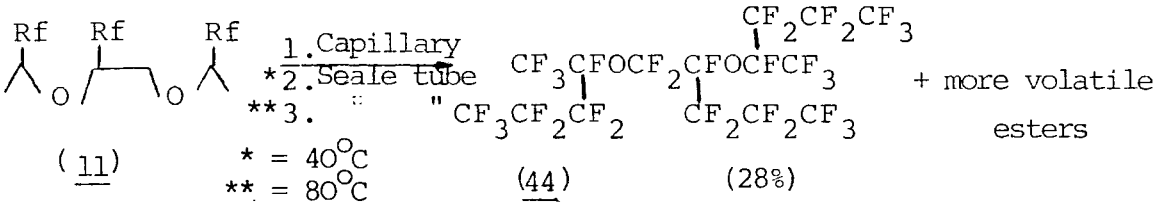
A preliminary survey was conducted investigating fluorination of other model compounds. Adducts (10) and (11) were directly fluorinated in this manner to yield the perfluoro ethers (41) and (44) respectively but in low conversion. The remainder of the product mixtures consisted of partially fluorinated compounds as indicated by n.m.r., and in addition, some compounds arising from fragmentation. Fragmentation may result due to incomplete fluorination at the capillary stage leaving the products less stable to the sealed tube step.



1.= Capillary reactor up to 50°C using 25% then 50% F_2 in N_2

2.= Sealed tube reactor 7at, 100% F_2 40°C

Fluorination of (11) using slightly elevated temperatures at the sealed tube step gave a higher yield of (44)



It is apparent that with better temperature control at both the capillary and sealed tube steps fragmentation will be minimised and consequently conversion improved.

5. Miscellaneous sealed tube reactions

The possibility of developing a process using only a sealed tube technique was investigated. The reactions used the di-adduct (14) as this had been found to be the most useful fluorination to monitor. Several sets of conditions were used including attempts to initiate the reaction with γ rays. The results of the reactions are listed in Table 24.

TABLE 24.

Substrate	Conditions	Empirical Formula of Product	% Yield
Rf Rf O (14)	100% F_2, 20°C 7ats	Carbon deposited + volatile (fragmented) products	-
Rf Rf O (14)	30% F_2, 3ats -78°C, 4 hrs. 20°C, 4 hrs. 80°C, 4 hrs.	$C_{10}F_{13}H_9O$ (67)	95
Rf Rf O (14)	30% F_2 3ats -78°C, 4 hrs. 20°C 4 hrs. γ rays 24 hrs.	$C_{10}F_{13.5}H_{8.5}O$ (68)	93
Rf Rf O (14)	1.Capillary 25% F_2 20°C→50°C; 50% F_2 20°C→50°C 2.Sealed tube 20°C, 10 hrs. γ 24 hrs.	$C_{10}H_3F_{17}O$ (69)	30
Rf Rf O (14)	1.Capillary 25% F_2 20°C→50°C 50% F_2 20°C→50°C 2.Sealed tube 20°C 10 hrs. γ 120 hrs.	Carbon deposited + gaseous products	-

The Table 24 illustrates that some fluorination may be affected using lower concentration of fluorine in nitrogen (< 50%). However, the reaction, at the pressure used, does not proceed as far as the capillary flow system. The limited reaction

may be due to the slow diffusion of the fluorine to the substrate and the build up of hydrogen fluoride in the vicinity of the substrate, preventing efficient diffusion.

Without a prefluorination step, the adduct (14) is not sufficiently stable to withstand neat fluorine. However, the initial results using 30% fluorine in nitrogen indicate that future work investigating perfluorination *via* a sealed tube technique, using the adduct (14) as the substrate, may well prove promising.

Initial investigations into the use of γ rays to initiate fluorination suggest that some promotion of the reaction may occur. However, further studies to assess optimum reaction conditions will be necessary.

C. Conclusions

It is evident that partial fluorination of the adducts is essential before exposure to neat fluorine. The most successful technique used to achieve this was the capillary system. A more efficient process however, would be to effect the partial fluorination in the sealed tube, hence allowing the whole process to be carried out in one vessel.

There is no evidence from the model compounds studied to suggest that, given the optimum conditions, the process cannot be extended to polyether adducts. Some fragmentation of the side chains may occur with polyethers, however, this would not affect the properties of the resulting perfluoroether dramatically and therefore will be of little consequence.

CHAPTER SIX

PREPARATION OF A PERFLUOROPOLYETHER

A. INTRODUCTION

This chapter deals with the attempted synthesis of a perfluoropolyether using direct fluorination techniques. The importance and commercial syntheses of such materials has already been discussed in the introduction chapters.

B. DISCUSSION

A new perfluoropolyether has been prepared using the direct fluorination technique developed, successfully, for simple model compound ethers (Chapter Five). The process is dependent on two steps: (1), the free radical addition of a polyether to hexafluoropropene, and, (2), the direct fluorination of the partially fluorinated adducts resulting from step 1.

1. $CH_3CH_2O(CH_2CH_2O)_nCH_2CH_3 \xrightarrow{(i)}$ *Ca.* $CH_3CHO(CHCH_2O)_y(CH_2CH_2O)_{n-y}CHCH_3$ (Rf = CF_2CFHCF_3)

(70) (n=8-9) (71) (y=4-5)

[(i) = Excess C_3F_6, di-tertiarybutyl peroxide 140°C, autoclave]

2. $\xrightarrow[(iii)]{(ii)}$ *Ca.* $C_{40}F_{45}H_{37}O_{10}$ (72)

(ii) 25% Fluorine in Nitrogen 20°C → 50°C 5 hrs

(iii) 50% Fluorine in Nitrogen 40°C → 50°C 5 hrs.

(72) $\xrightarrow[(v)]{(iv)}$ *Ca.* $C_{40}F_{82}O_{10}$ (73) (20%)

[(iv) = F_2/autoclave, -195°C → 20°C, 10 hrs
(v) = F_2/autoclave, 60°C 20 hrs]

Yield calculated from adduct (71)

1. Free Radical Addition

(a) Modification of Polyethylene glycol (400) (PEG 400)

In Chapter Three it was stressed how important, ethoxy rather than methoxy end groups are, in directing addition toward the ends of the ether molecule. It was necessary to prepare the polyethylene glycol diethyl ether in the labor-

atory. This was achieved by diethylation of PEG(400) using a Williamson type synthesis (Scheme 13)

$$HO(CH_2CH_2O)_nH \xrightarrow[Toluene]{NaH} Na^+ {}^-O(CH_2CH_2O)_nCH_2CH_2O^-Na^+$$

(74)

$$(74) \xrightarrow[2.]{1.} EtO(CH_2CH_2O)_nEt \quad (70)$$

1. Et-I, 90°C 2. Purification over alumina

Scheme 13

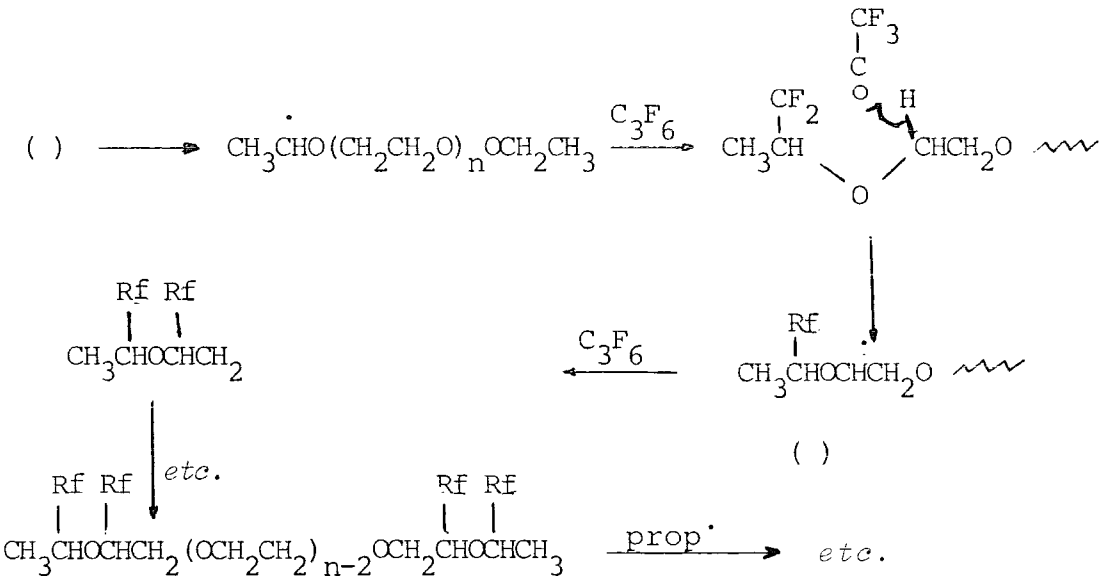
The high purity of the ether (70) was found to be essential for the free radical addition step. Purification was achieved by passing over alumina in a solvent, resulting in a product free of polyethylene glycol and peroxides.

(b) Addition Process

Reaction of (70) with hexafluoropropene, under free radical conditions, resulted in an extensive incorporation of hexafluoropropene units into the polyether backbone.

The adduct (71) is a representation of the products easily obtained by this route. It is known from model compound studies that, when ethyl derivatives are used, the addition is directed initially to the end groups, followed by a series of intramolecular hydrogen transfer processes (Scheme 14).

After the formation of the tetra-adduct (79) the following addition steps will proceed in a less ordered manner:



(75) Scheme 14

The average molecular formula of the polyadduct (71) was deduced using n.m.r. integratians of the relevant signals relative to an internal standard (trifluoromethyl benzene). The adduct (71), itself, shows some interesting properties, initial tests indicate it to be thermally stable in glass apparatus up to temperatures of 200°C but rather less stable when heated in the presence of metals.

2. Direct Fluorination Process

Following the successful preparation of simple perfluoroethers the polyadduct (71) was directly fluorinated in two stages: (a) using a flow system introducing the fluorine/nitrogen mixtures through capillary tubes; and (b) an autoclave reaction using neat fluorine under pressure.

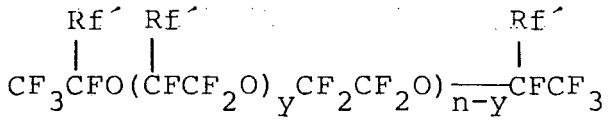
(a) Capillary Fluorination

Purification of the polyadduct (71) by passing over alumina was essential to the success of the fluorination. The capillary fluorination of (71) began at room temperature

using 25% fluorine in nitrogen. The polyadduct (71) quickly became viscous after about one hour due to the added effects of hydrogen bonding. From this point it was generally necessary to heat the reactor to enable a smooth flow of fluorine bubbles. The product is a clean colourless material of average molecular formula $C_{40}F_{45}H_{37}O_{10}$ (72) as estimated by relative n.m.r. integrals.

(b) Sealed Tube Fluorination

The sealed tube reaction of the partially fluorinated material $C_{40}F_{45}H_{37}O_{10}$ (72) carried out at 60°C yields a clear colourless liquid, which by n.m.r. and elemental analysis contains no residual protons. The n.m.r. spectrum is consistent with the structure (73)



(73)

n = 7-8 y = 4-5 Rf´ = $CF_2CF_2CF_3$

The infra-red spectrum of (73) shows the presence of carbonyl groups. The cause is most likely due to ingression of oxygen into the system at the capillary stage. However, later developments of the process,[133] replacing the capillary stage with a sealed tube step has avoided oxygen incorporation.

C Conclusions

The fluorination process that has been developed is a simple yet effective technique. The initial mild conditions are possible due to the remarkable stability of

the ethers which is achieved by the prior incorporation of polyfluoroalkyl groups. The process is capable of scale up or conversion to continuous process.

The preparation of the perfluoropolyether is, to the best of knowledge, the first example of a synthesis where the molecular weight and structure of the polyether is predetermined. Therefore, this approach will enable the synthesis of high performance fluids tailored for a specific use.

CHAPTER SEVEN

MISCELLANEOUS REACTIONS

A. Introduction

Several reactions of the adducts have been attempted with the general aim of increasing molecular weight, *via* some form of coupling mechanism. The reactions are, perhaps, not particularly relevant to any of the preceding chapters and so are described here.

B. Discussion

1. Attempted Dehydrodimerisation of adducts (3) and (4)

Attempts to dehydrodimerise (3) and (4), under free radical conditions, were unsuccessful.

$CH_3O\underset{\displaystyle Rf}{\underset{|}{C}}HCH_2OCH_3$ —DTBP, 140°C, autoclave→ ✗

(3)

(Rf = CF_2CF_2H)

$RfCH_2OCH_2CH_2OCH_3$ —DTBP, 140°C, autoclave→ ✗

(4)

(Rf = CF_2CF_2H)

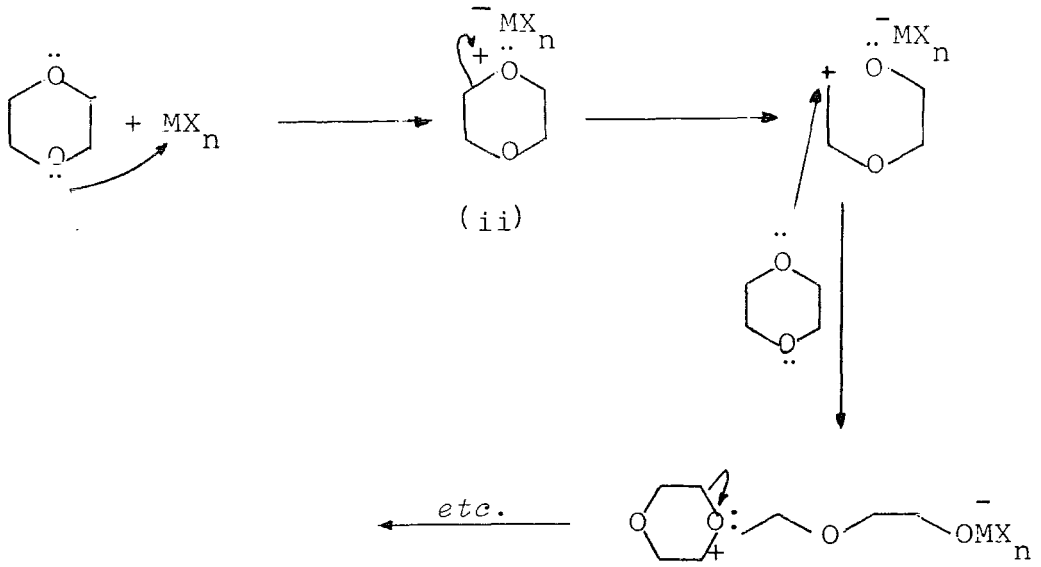
This confirms the findings of previous workers [126] that the intermediate radical (i) (Scheme 15) is not stabilised by capto-dative type interactions.

$CH_3O\underset{\displaystyle Rf}{\underset{|}{C}}HCH_2OCH_3$ (3) —DTBP, 140°C→ $CH_3O\overset{\displaystyle Rf}{\overset{|}{\dot{C}}}-CH_2OCH_3$ (i) —Combination→ ✗ $CH_3O\overset{\displaystyle Rf}{\overset{|}{C}}-CH_2OCH_3$ / $CH_3O\underset{\displaystyle Rf}{\underset{|}{C}}-CH_2OCH_3$

Scheme 15

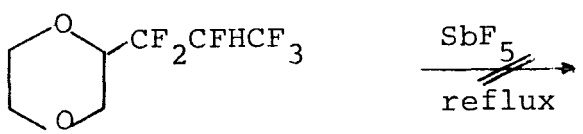
2. Attempted Ring Opening Polymerisation of Cyclic Adduct  (where Rf = CF_2CFHCF_3) (76)

The polymerisation of cyclic ethers using Lewis acid catalysts are known reactions[134] (Scheme 16).



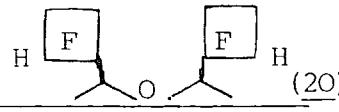
Scheme 16

However, it was not possible to achieve the same effect by reacting the cyclic adduct (76) and antimony pentafluoride. Only the original adduct (76) was recovered from the reaction.

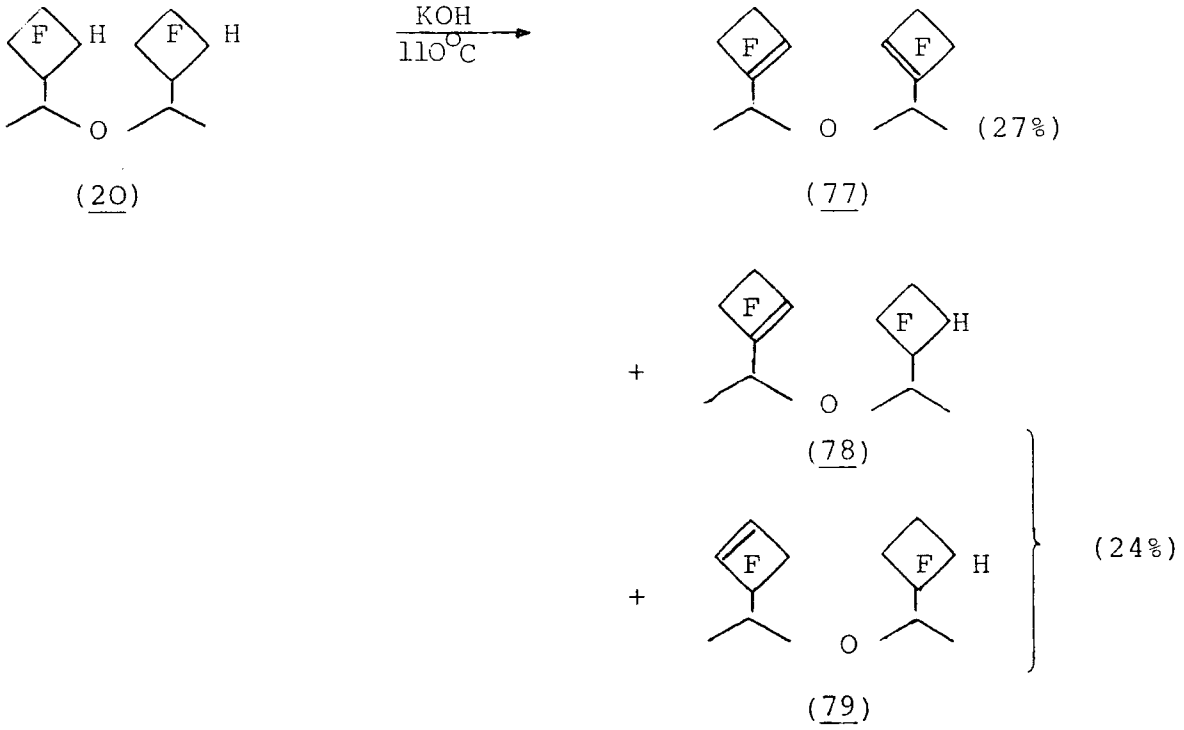


(76)

Presumably, the polyfluoroalkyl group draws electron density from the oxygen preventing formation of the intermediate adduct corresponding to (ii).

3. Dehydrofluorination of  (20)

Dehydrofluorination of the adduct (20) over KOH afforded the diene (77) and a mixture of alkenes presumably (78) and (79) although a separation of the latter was not possible.



(20) (77) (78) (79) (27%) (24%)

Compound (77) was identified by a combination of NMR and IR spectra. The ^{19}F NMR spectrum of (77) consisted of three multiplet resonances assigned as: 115.3 ppm. (-CF=); 118.2 ppm. ($-CF_2-$); and 120.9 ppm. ($-CF_2-$). The ^{1}H n.m.r. spectrum consisted of a doublet of multiplets, 1.06 ppm. $J_{13}=4.8H_3(C\underline{H}_3-CH)$ and a multiplet at 3.8 ppm assigned as the tertiary proton ($[CH_3CH[Rf]]_2O$). The I.R. spectrum gave a characteristic resonance at 1715 cm^{-1} arising from the C=C stretch.

The compounds (78) and (79) were assigned as the IR of the mixture gave two olefinic resonances 1785 cm^{-1} and 1720 cm^{-1}. The ^{1}H n.m.r. spectrum consisted of a broad resonance at 1.2 ppm ($C\underline{H}_3$), a resonance at 4.1 ppm (-$\underline{C}H$-) and a multiplet at 4.5 ppm (-CFH-). The ^{19}F n.m.r. spectrum was complex with resonances at 114.9 ppm (vinylic F); 118.2, 118.8, 121.3 ppm assigned as $-CF_2-$; 133.5 ppm (tertiary F); 172.2 (a doublet J_{12}=78H_3) assigned as -CFH-.

CHAPTER EIGHT

IDENTIFICATION OF COMPOUNDS

A. General Introduction

Structural identification of the partially fluorinated adducts and the perfluoroethers was achieved using a combination of several mass spectral techniques and N.M.R. spectroscopy. Unfortunately, many of the compounds did not give good analytical results, presumably due to incomplete combustion as re-purification did not improve the correspondence of calculated and found figures.

Before proceeding, the mass spectral techniques used will be discussed more generally, as these techniques are relatively new to our laboratories.

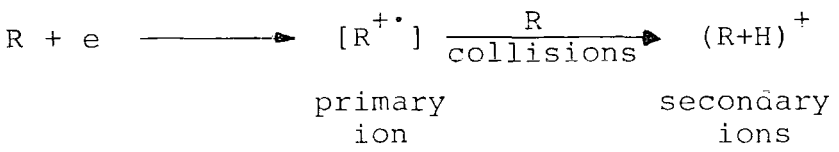
B. Mass Spectrometric Techniques

1. Chemical Ionisation (CI) mass spectrometry

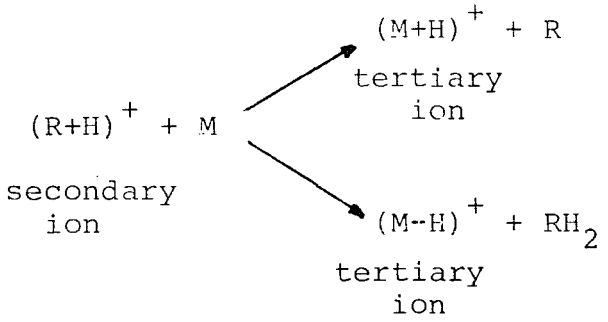
(a) Positive CI

CI is termed a soft ionisation technique as low energy charged particles are used to ionise sample molecules. CI differs from the more conventional electron impact (EI) technique in that the ion source is operated at a relatively high pressure of 0.2 to 2 torr (*cf.* 10^{-6} torr for EI). The pressure is maintained by allowing a reagent gas (R) to leak into the evacuated ion source. As a result the reagent gas is more abundant and hence more likely to be ionised than the sample compound. Ionisation of the reagent gas produces primary ions $R^{\cdot +}$ (Scheme 17). Through collisions with other unionised reagent gas molecules, the more stable secondary ions $(R+H)^{+}$ are formed. The secondary ions then proceed to

react further with sample molecules (M) forming other stable ions (Scheme 18).



Scheme 17



Scheme 18

The quasi-molecular ions $(M+H)^+$ or $(M-H)^+$, obtained by CI, are produced with little internal energy hence formation of fragment ions is unlikely. However any fragmentation that does occur is usually particularly significant as to the structure of the sample molecule. In comparison EI techniques may afford complex fragmentation patterns, as the high energy conditions used for EI can promote unusual cleavage reactions. As a consequence CI is a powerful technique used to observe $(M+1)^+$ or $(M-1)^+$ ions, especially when parent ions are absent from the EI spectrum. However CI may give little structural elucidation due to the limited fragmentation.

Reagent Gases

Several reagent gases are commonly used for CI mass spectrometry, some examples include: methane, CH_4; isobutane,

C_4H_8; ethane, C_2H_6; hydrogen, H_2; and ammonia, NH_3. Reagent gases may vary as different ones may produce different fragmentation patterns in the same sample molecule. The varying fragmentation patterns observed are due to different net energy release in the formation of the quasi molecular ion $(M+H)^+$ or $(M-H)^+$. The net energy release is dependent on the relative proton affinities of the conjugate base of the secondary ion $(R+H)^+$ and the sample molecule (M). Hence, the more acidic $(R+H)^+$ the greater the fragmentation of the sample molecule.

Reactions other than proton transfer may occur depending on the acidity of the sample molecule and the nature of the reagent gas. For example, adduct ions may be formed with several reagent gases,

i.e. $M + NH_4^+ \longrightarrow (M + NH_4)^+$

$M + C_2H_5^+ \longrightarrow (M + C_2H_5)^+$

$M + C_3H_7^+ \longrightarrow (M + C_3H_7)^+$

Even cluster ions may be formed:

$2M + H^+ \longrightarrow (2M + H)^+$

The formation of adduct species may be controlled by choice of reagent gas in relation to a particular sample molecule.

(b) Negative ion chemical ionisation. CI-ve

Chemical ionisation may also be operated in the negative mode, generating negative rather than positive sample ions. There are two methods used to generate the negative ions for this technique, (1) electron capture and (2) reactant ion chemical ionisation.

(1) Electron capture

For this technique to be successful the sample molecule (M) must be able to accommodate the low energy electron, generated in the ion source, into a vacant low energy orbital. Typical compounds capable of this contain one of the following: sulphur, phosphorus, halogen or C=C. As a result alkanes are generally inert to electron capture techniques and are frequently used as buffer gases (B) in the ion source. The function of the buffer gas is two-fold (a) to slow the impacting electrons, hence making them less energetic, and (b) to remove excess energy from the negative ion as it forms.

$$B + e^- + M \longrightarrow M^- + B$$

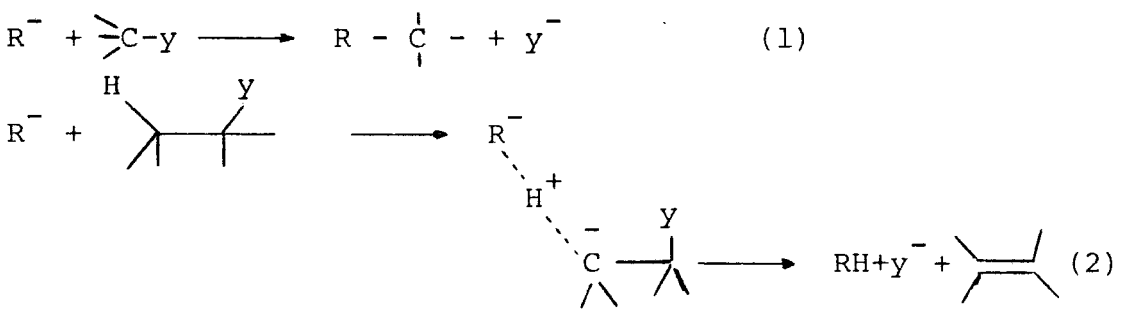
(2) Reactant ion chemical ionisation

Negative reactant ion CI is similar to CI+ve as already discussed. The negative ions are formed by reaction of the sample molecule (M-H) with the reactant ion $R^{\cdot -}$ or R^-. The most common process is proton abstraction:

$$M - H + R^- \longrightarrow M^- + RH$$

Most of the energy release in the proton abstraction process is absorbed as vibrational energy in the new R-H bond, leaving the M^- species relatively stable.

Other typical reactions which occur are nucleophilic displacement (1) and base induced eliminations (2)



Adduct type ions may also be produced.

$$R^- + M \longrightarrow [R+M]^-$$

As in positive chemical ionisation the choice of reagent gas (*e.g.* ammonia, argon) determines the type of reaction that occurs between R^- and M and also any subsequent fragmentation of the sample ion.

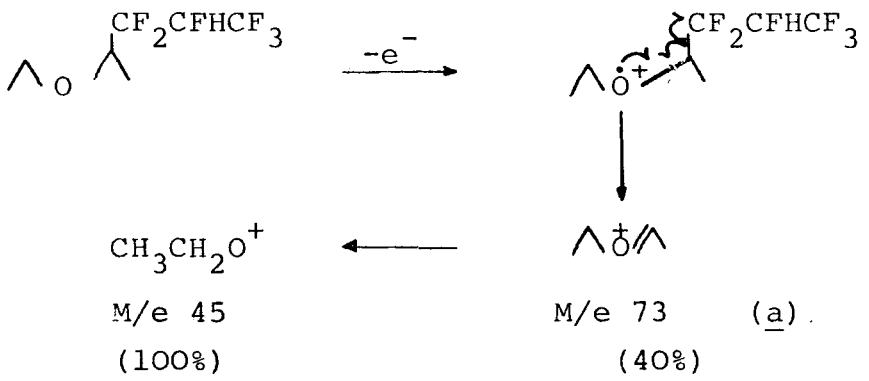
C. Identification of ether/F-alkene adducts

The most useful techniques for identification of ether/F-alkene adducts were mass spectrometry and NMR spectroscopy.

1. Mass Spectrometry

(a) Electron impact mass spectrometry

The molecular ion peak was usually absent or appeared with weak intensity in the EI spectrum of the adducts. The highest mass number observed generally arises from β cleavage of the parent adduct molecule resulting in the loss of the perfluoroalkyl group:



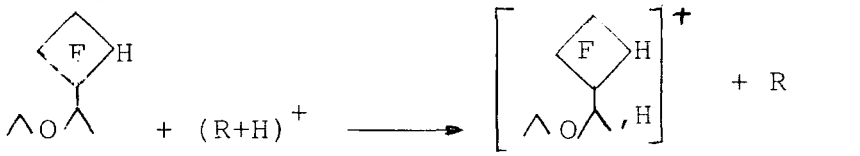
The resulting fragment (a) then readily undergoes cleavage at the carbon-oxygen bond to give the base peak.

(b) Positive Chemical Ionisation Mass Spectrometry

Isobutane was used as the reagent gas in all CI+ve spectra.

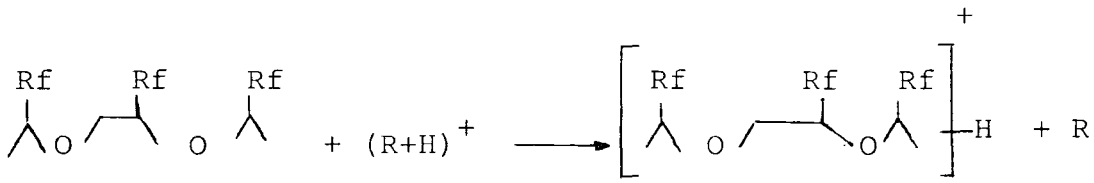
The CI spectrum of the adducts generally exhibits a $(M+1)^+$ peak which is also usually the highest intensity peak. Few fragment ions are observed in the CI mode.

For example:



(19) M/e 237 (41%) (M+1)

$(R=C_4H_8)$



(11) M/e 573 (2%) (M+1)

(Rf = CF_2CFHCF_3

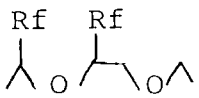
R = C_4H_8)

2. NMR Spectroscopy

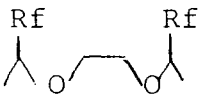
(a) ^1H NMR Spectra

The proton spectra usually exhibits a distinct doublet of multiplets arising from a -CFH-group (δ=4.7 ppm; TMS external reference) with a coupling constant *ca.* 42 to 45Hz. The $-OCH_2-$ protons give a broad resonance at approximately δ=3.5 ppm. and cannot be distinguished from the tertiary proton of the group -CH(Rf)-O-. The resonances assigned to the methyl hydrogens of the ethoxy end groups may be used to distinguish between an unsubstituted end group CH_3CH_2O ($\delta_H \sim 0.9$ ppm.T, J_{13}=4.2Hz) and a substituted end group $CH_3CH(Rf)O$ ($\delta_H \sim 1.1$ ppm.D, J_{13}=4.7Hz). This was particularly

useful in the identification of the adduct types (i) and (ii)



(i)



(ii)

(b) ^{19}F NMR spectra

The ^{19}F spectra of the hexafluoropropene/ether adducts were all similar irrespective of the structure of the ether. As the adducts usually contained two (or more) assymetric centres the ^{19}F n.m.r. spectra contained separate resonances for the diastereomers corresponding to RS+SR and RR+SS configurations. The separate diastereomer resonances were distinguishable for simple mono-adducts but as the molecule became more complex the resonances broadened and were ill-defined. In general the trifluoromethyl group produced a resonance between 73 ppm and 77 ppm (external $CFCl_3$ reference); the difluoromethylene group appeared as an AB type formation at *ca.* 125 ppm ($J_{12} \sim 240$Hz); the tertiary fluorine of the -CFH- group gave a doublet at *ca.* 220 ppm ($J_{12} = 40$Hz).

The diastereomers were not separated nor were the spectra assigned to a specific diastereomer.

Adducts derived from perfluorocycloalkenes were obtained as a mixture of *cis* and *trans* isomers. The ^{19}F spectra of such mixtures are relatively complex. However, assignment of the resonances due to the tertiary fluorines $HC\underline{F}\text{---}C\underline{F}\text{-}R$ for each isomer is possible.[124]

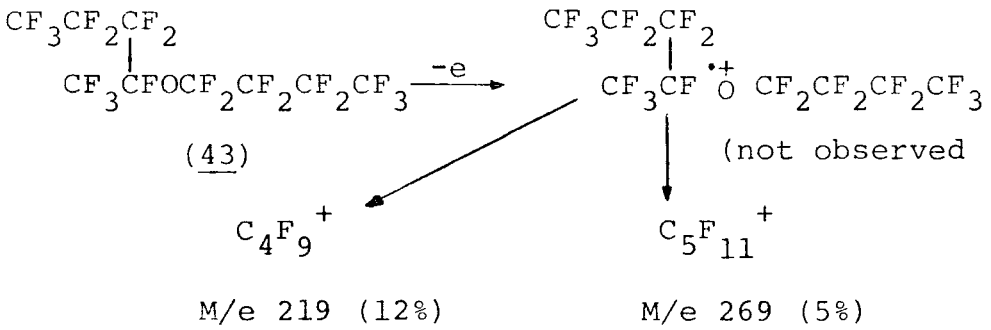
D. Identification of Perfluoroethers

The most useful techniques for identification of perfluoroethers were mass spectrometry and N.M.R. spectroscopy.

1. Mass Spectrometry

(a) Electron Impact mass spectrometry

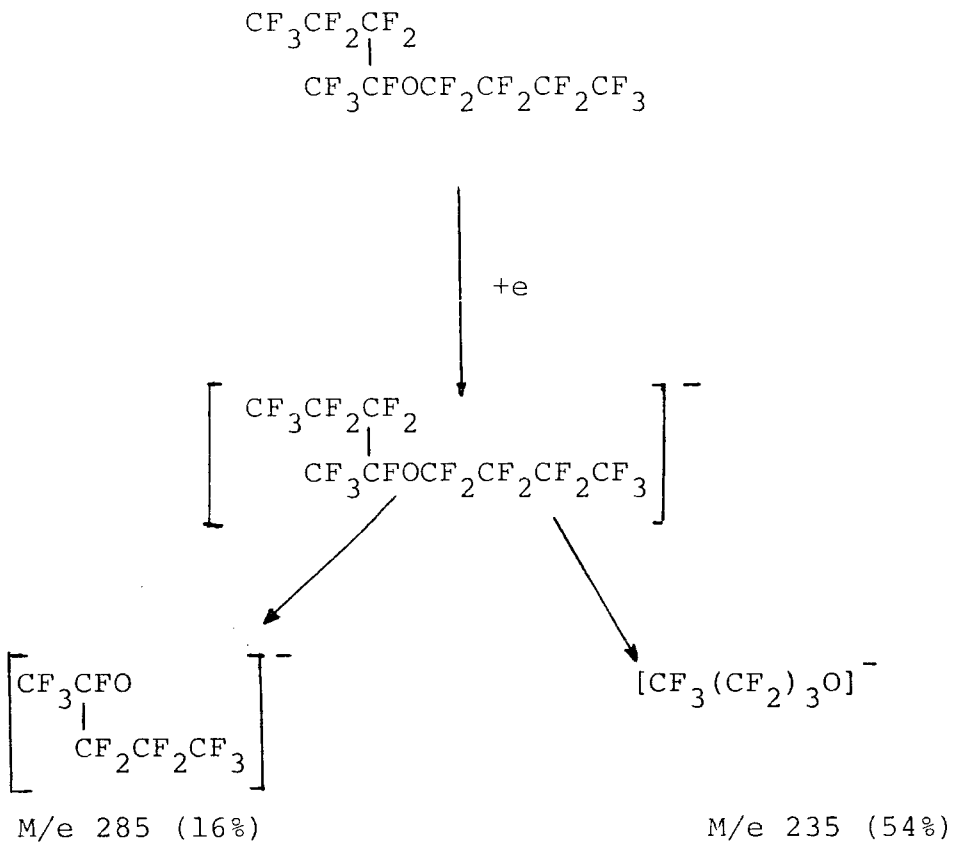
Parent ions were not present in the EI spectra of perfluoroethers. The highest mass number peaks usually arise from α cleavage of the ether linkage producing a perfluorocarbon fragment, Scheme 19.



Scheme 19

(b) Electron capture negative ionisation spectroscopy

The parent ion of the perfluoroether was usually absent from the CI-ve spectrum. The highest mass was derived from the α cleavage of the ether linkage (Scheme 20).



Scheme 20.

2. N.M.R. Spectroscopy

The ^{19}F NMR spectra of the perfluoroethers were relatively simple. Typical chemical shifts of characteristic groups are as follows: $RfC\underline{F}_2O$, 85 ppm; $C\underline{F}_3$-RF, 83 ppm; Rf-$C\underline{F}_2$-Rf, 120 ppm; $(Rf)_2C\underline{F}O$, 135 ppm.

EXPERIMENTAL

INSTRUMENTATION

Infra-red spectra were recorded on a Perkin-Elmer 457 Grating Spectrophotometer using kBr plates or gas cells.

Fluorine (^{19}F) and proton (^{1}H) nuclear magnetic resonance (NMR) spectra were recorded on a varian A56/60D spectrometer operating at 56.4 and 60MHz respectively or on a Brucker HX90E spectrometer operating at 84.6 and 90MHz respectively. Chemical shifts are quoted relative to $CFCl_3$ (upfield shifts being quoted positive) and TMS (downfield shifts quoted positive).

CI, Negative and electron impact mass spectra were recorded on a VG2020 spectrometer or on a VG micromass 12B spectrometer fitted with a Pye 104 gas chromatograph.

Carbon and hydrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analyses for halogens were performed as described in the literature.[135]

Fractional distillations of products were carried out using Fischer-Spaltrohr MS200 and HMS500 systems.

Analytical and preparative scale gas liquid chromatography (g.l.c.) were carried out on a Varian Aerograph Model 920. Columns used were packed with: 20% Krytox (perfluoropolypropyleneoxide) on chromosorb P (column K); 20% di-isodecyl phthalate on chromosorb P (column A); and 30%, 10%, and 5% silicone elastomer on celite (column O).

Boiling points were determined at atmospheric pressure, unless otherwise stated, and are uncorrected. Boiling points were measured using the Siwoloboff method or recorded during distillation.

CHAPTER NINE

EXPERIMENTAL TO CHAPTER THREE

A. Introduction

1. Purification of Reagents

Hydrocarbon ethers were tested for peroxides which, if present, were destroyed by stirring over KOH. The ethers were then dried over anhydrous K_2CO_3 and distilled from sodium onto activated type 4A molecular sieve.

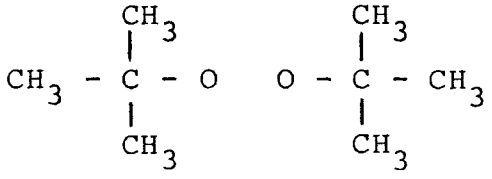
2. Gamma Ray Initiated Free Radical Additions

All free radical reactions using γ initiation were carried out using the Durham University Co^{60} source, (Figure 5). The Co^{60} pellet is contained in a steel container attached to a steel hawser. The pellet is moved into a bunker surrounded by birytes bricks ($BaSO_4$) when not in use.

The samples to be irradiated are placed in a stainless steel holder which has two possible positions at 5cm and 8cm from the source. The dose rate received by a sample positioned at 5cm from the source has been calculated, using Fricke Dosimetry by other workers in the laboratory, to be 200 krads.hr.$^{-1}$.

3. Chemical Initiation

Ditertiary butyl peroxide has been used to initiate some reactions



$$RH + {}^{t}BuO\cdot \longrightarrow R\cdot + {}^{t}BuOH.$$

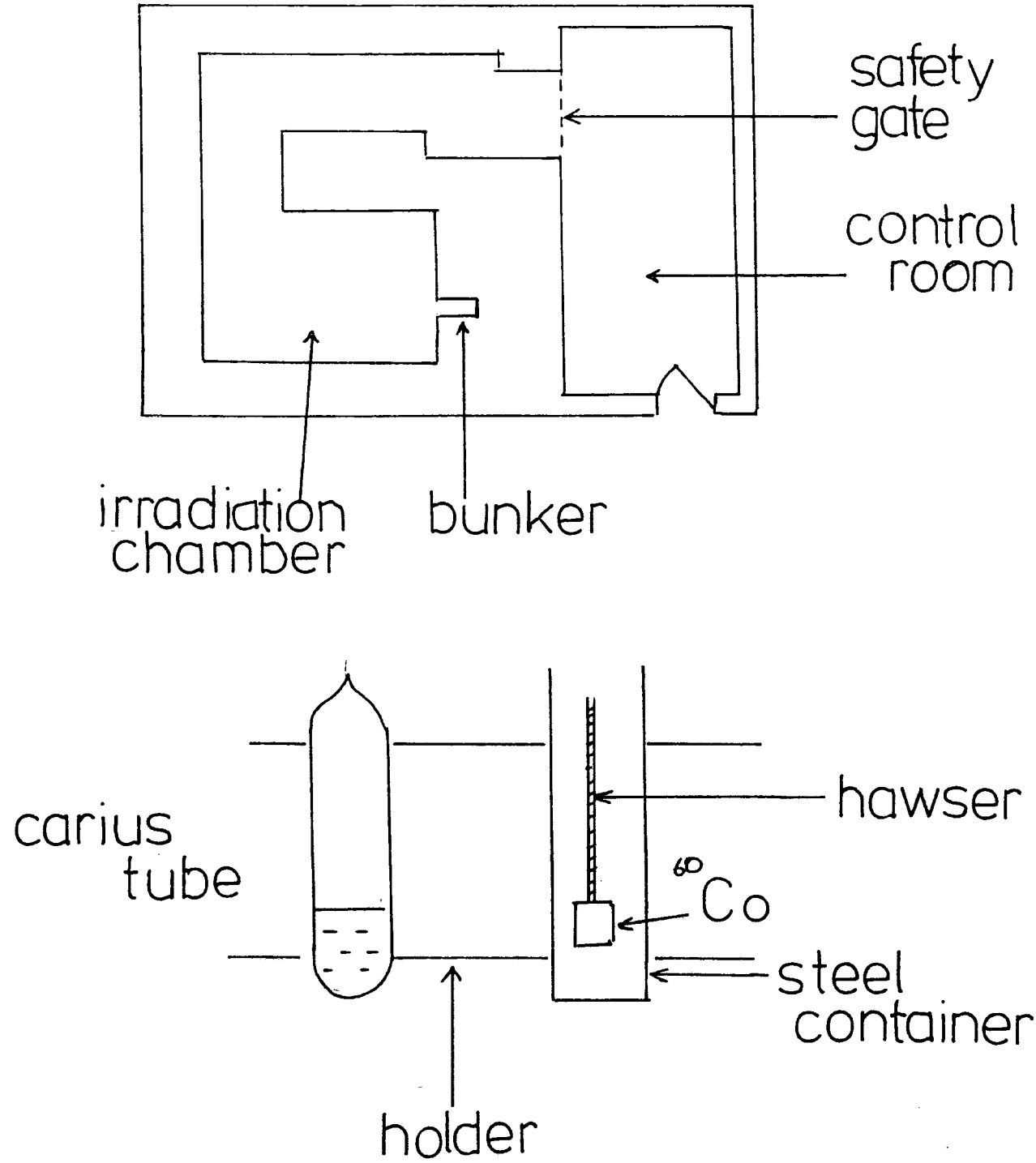

safety
gate
control
room
irradiation
chamber
bunker
carius
tube
hawser
60
Co
steel
container
holder

FIGURE 5

The peroxide is added to the reactants in approximately 1% concentration (wt:wt) and the reaction vessel heated, in a thermostatically controlled furnace, to the required temperature, in the University's high pressure facility.

B. General Procedure

1. Gamma Ray Initiated Reactions

The ether contained in a nickel tube (70ml), fitted with a valve, was degassed using freeze thaw cycles under vacuum. The F-alkene was transferred, under vacuum, into the cooled (liquid air) tube, the valve sealed and the mixture irradiated at 18°C on the Co^{60} source for 72 hours (200 krads.$hr.^{-1}$). The tube was then cooled (-196°C), opened to a vacuum and volatile components transferred to a cold trap by allowing the tube to warm to *ca.* 10°C. The liquid products were then recovered and distilled using conventional apparatus.

2. Chemical Initiated Free Radical Reactions

The hydrocarbon ether and di-tertiarybutyl peroxide contained in an autoclave fitted with a valve were degassed using freeze thaw cycles under vacuum. The F-alkene was transferred, under vacuum to the cooled (-196°C) autoclave, the valve sealed and the vessel heated, while rocking, to the required temperature in a thermostatically controlled furnace. The autoclave was then cooled (-196°C) opened to a vacuum and gaseous material transferred to a cold trap by allowing the autoclave to warm slowly to *ca.* 10°C. The liquid products were then recovered and distilled using conventional apparatus.

C. Additions with Diethyl Ether

1. Addition to hexafluoropropene

Diethyl ether (12.4g, 0.17mol) and hexafluoropropene (7.7g, 0.05mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled to give 2,2,3,4,4,4-hexafluoro-1-methylbutyl ethyl ether (13), (57%); b.p. 116°C (lit.125 116-118°C). Identified by comparison of NMR, IR and mass spectra with those of authentic material. IR, NMR and mass spectra 1. The residue was distilled *in vacuo* to give di(2,2,3,4,4,4-hexafluoro-1-methylbutyl)ether (14), (35%); $b.p._{12}$, 66.5°C (lit.125 67-68°C). (Found: C, 32.2; H, 3.0; F, 60.5. Calc. for $C_{10}F_{12}H_{10}O$: C, 32.0; H, 2.6; F, 60.9%). IR, NMR and mass spectra 2.

2. Addition to perfluorocyclobutene

Diethyl ether (11.1g, 0.15mol) and perfluorocyclobutene (9.2g, 0.056mol) were irradiated in a sealed tube with gamma gays. The liquid products were distilled *in vacuo* to give: 1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ethyl ether (19), (90%); b.p. 130°C (Siwolaboff); (CI, m/e 237 [M+1]). Found: C, 40.7; H, 4.6; F, 48.7. $C_8F_6H_{10}O$ requires: C, 40.6; H, 4.2; F, 48.3%). IR, NMR and mass spectra 3; and di (1-[1,2,3,3,4,4-hexafluorocyclobutyl]ethyl)ether (20), (5%); b.p. 204-206°C (Siwolaboff); (CI, m/e 399 [M+1]); (Found: C, 36.4; H, 2.2; F,56.7. $C_{12}F_{12}H_{10}O$ requires: C, 36.1; H.2.5; F, 57.2%); IR, NMR and mass spectra 4.

3. Addition to perfluorocyclopentene

Diethyl ether (10.15g, 0.14mol) and perfluorocyclopentene (10.4g, 4.9mmol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled *in vacuo* to give: 1-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)ethyl ethyl ether (21), (60%); b.p. 148°C (Siwolaboff); (CI, m/e 287, [M+1]); (Found: C, 37.6; H, 3.3; $C_9H_{10}F_6O$ requires: C, 37.8; H, 3.5%); IR, NMR and mass spectra 5; and di (1-[1,2,3,3,4,4,5,5-octafluorocyclopentyl]ethyl)ether (22), (30%); b.p. 225°C (Siwolaboff); (CI, m/e 499, [M+1]); (Found: C,34.0; H, 1.2. $C_{14}H_{10}F_{16}O$ requires: C, 33.7; H, 2.0%); IR, NMR and mass spectra 6.

4. Addition to perfluorocyclohexene

Diethyl ether (11.0g, 0.15mol) and perfluorocyclohexene (14.4g, 0.055mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled to give: 1-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)ethyl ethyl ether (23), (40%); b.p. 169°C; (CI, m/e 337, [M+1], (Found: C, 35.8; H, 3.1; F, 56.9. $C_{12}F_{10}H_{10}O$ requires: C, 35.7; H, 2.9; F, 56.5%), IR, NMR and mass spectra 7; and di-(1-[1,2,2,3,4,4,5,5,6,6-decafluorocyclohexyl]ethyl) ether (24), (40%); $b.p._5$ 165°C; (CI, m/e 599, [M+1]); (Found: C, 32.3; H, 1.6; F, 63.8. $C_{16}F_{20}H_{10}O$ requires: C, 32.1; H, 1.6; F, 63.5%), IR, NMR and mass spectra 8.

4. Addition to perfluorocyclohexene

Diethyl ether (11.0g, 0.15mol) and perfluorocyclohexene (14.4g, 0.055mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled to give: 1-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)ethyl ethyl ether (23), (40%); b.p. 169°C; (CI, m/e 337, [M+1], (Found: C, 35.8; H, 3.1; F, 56.9. $C_{12}F_{10}H_{10}O$ requires: C, 35.7; H, 2.9; F, 56.5%); IR, NMR and mass spectra 7; and di-(1-[1,2,2,3,4,4,5,5,6,6-decafluorocyclohexyl]ethyl) ether (24), (40%); $b.p._{5}$ 165°C; !CI, m/e 599, [M+1]; (Found: C, 32.3; H, 1.6; F, 63.8. $C_{16}F_{20}H_{10}O$ requires: C, 32.1; H, 1.6; F, 63.5%); IR, NMR and mass spectra 8.

5. Addition to Chlorotrifluoroethene

Diethyl ether (11.1g, 0.15mol) and chlorotrifluoroethene (6.2g, 0.05mol) were irradiated in a sealed tube with gamma rays. The products were distilled *in vacuo* to give: 3-chloro-2,2,3-trifluoro-1-methylpropyl ethyl ether (15), (90%); $b.p._{65}$, 61°C; identified by a combination of NMR and mass spectra. (CI, m/e 191, [M+1]); IR, NMR and mass spectra 9; and a residue containing a mixture of telomers $CH_3CH_2OCH[(CF_2CFCl)_nH]CH_3$, [n=2 or 3]; (16), (10%); IR, NMR and mass spectra 10.

6. Addition to Trifluoroethene

Diethyl ether (15.54g, 0.21mol) and trifluoroethene (5.7g, 0.069mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled to give: 2,2,3-trifluoro-1-methylpropyl ethyl ether (17), (80%); b.p. 106.6°C; identified by a combination of NMR and mass spectra (CI, m/e 157, [M+1]); IR, NMR and mass spectra 11; and a residue containing a mixture of telomers $C_2H_5O\ CH(CH_3)$-$[CF_2CFH]_nH$, (n=2,3). (18), (16%); IR, NMR and mass spectra 12.

7. Attempted Addition to perfluoro-3,4-dimethyl-hex-3-ene

Diethyl ether (7.6g, 0.1mol) and perfluoro-3,4-dimethyl-hex-3-ene (21.0g, 0.53mol) were irradiated in a sealed tube with gamma rays. The starting materials were recovered (glc, column K, 75°C).

D. Additions with 1,2-diethoxyethane

1. Addition to Hexafluoropropene

(a) Using excess ether

1,2-diethoxyethane (23.7g, 20mmol) and hexafluoropropene (15g, 10mmol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled *in vacuo* to give: 4-[1,1,2,3,3,3-hexafluoropropyl]-3,6-dioxaoctane (6), (15%); $b.p._{40}$ 78°C; (CI, m/e 269 [M+1]; (Found: C, 40.4; H, 5.5; F, 42.7. $C_9F_6H_{14}O_2$ requires: C, 40.3; H, 5.5; F, 42.5%); NMR, IR and mass spectra 13; 1,1,1,2,3,3-hexafluoro-4-methyl-5,8-dioxadecane (7), (48%); $b.p._4$ 90°C;

(CI, m/e 269 [M+1]); (Found: C, 40.3; H, 5.5; F, 42.3. $C_9F_6H_{14}O_2$ requires: C, 40.3; H, 5.2; F, 42.5%); IR, NMR and mass spectra 14; 1,1,1,2,3,3-hexafluoro-4-methyl-6-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadecane (9), (27%) b.p.$_{10}$ 94°C; (CI, m/e 419, [M+1]); (Found: C, 34.7; H, 3.6; F, 54.9. $C_{12}F_{12}H_{14}O_2$ requires: C, 34.5; H, 3.35; F, 54.5%). IR, NMR and mass spectra 15; 1,1,1,2,3,3-hexafluoro-4-methyl-7-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxodecane (9) (minor yield) obtained as a mixture with (9); and 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-5,8-dioxadodecane (10), (12%); b.p.$_6$ 106°C; (CI, m/e 419, [M+1]; (Found C, 34.2; H,3.6; F, 54.0. $C_{12}F_{12}H_{14}O_2$ requires: C, 34.5; H, 3.35; F, 54.5%); IR, NMR and mass spectra 16.

(b) Using excess olefin

1,2-Diethoxyethane (5.9g, 0.05mol) and hexafluoropropene (17.1g, 0.114mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled *in vacuo* to give: adduct (6), (5%); adduct (7), (16%), adducts (8 and 9), (22%); adduct (10), (16%); and 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-6-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadodecane (11), (14%), b.p.$_{0.1}$ 64°C; (CI, m/e 569, [M+1]; (Found: C, 31.9; H, 2.4; F, 60.6. $C_{15}F_{18}H_{14}O_2$ requires: 31.7; H, 2.5; F, 60.2%); IR, NMR and mass spectra 17.

(c) Using excess ether and chemical initiation

1,2-diethoxyethane (23.6g, 0.2mol), hexafluoropropene (15.0g, 0.1mol) and di-tertiarybutyl peroxide (0.4g, 2.7mol) were heated to 140°C in an autoclave, while rocking

for 24 hrs. The liquid products were distilled *in vacuo* to give: adduct (6) (20%); adduct (7) (36%); adducts (8) and (9) (28%); and adduct (10) (16%).

2. Additions to Perfluorocyclopentene

1,2-Diethoxyethane (3.8g, 0.03mol) and perfluorocyclopentene (23.1g, 0.11mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled *in vacuo* to give: a mixture of mono-adducts $C_{11}F_8H_{14}O_2$ (28) and (29), (33%); $b.p._{90}$ 140 to 160°C; identified by a combination of NMR and mass spectra; (CI, m/e 331, [M+1]); IR, NMR and mass spectra 18; 2,4-di [1, 2,3,3,4,4,5,5-octafluorocyclopentyl]-3,6-dioxaoctane (30), (20%); $b.p._5$ 148°C; (CI, m/e 543, [M+1]; (Found: C, 35.3; H, 2.2. $C_{16}F_{16}H_{14}O_2$ requires C, 35.4; H, 2.5%); IR, NMR and mass spectra 19; 2,7-di [1, 2,3,3,4,4,5,5-octafluorocyclopentyl]-3,6-dioxaoctane (31), (14%); $b.p._5$ 162°C; (CI, m/e 543, [M+1]); (Found: C, 35.3; H, 2.2. $C_{16}F_{16}H_{14}O_2$ requires: C, 35.4; H, 2.5%); IR, NMR and mass spectra 20; and a residue purified by molecular distillation 2,4,7-tri-[1, 2,3,3,4,4,5,5-octafluorocyclopentyl]-3,6-dioxaoctane (32), (6%); identified by a combination of NMR and mass spectra; (CI, m/e 755, [M+1]); IR, NMR and mass spectra 21.

3. Addition to perfluorocyclobutene

1,2-Diethoxyethane (9.49g, 0.08mol) and perfluorocyclobutene (51.9g, 0.32mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled *in vacuo* to give: a mixture of mono-adducts, $C_{10}F_6H_{14}O_2$ (25), (50%); $b.p._3$ 70°C; identified by a combination of NMR and mass spectra;

(CI, m/e 287 [M+1]); IR, NMR and mass spectra 22; and a residue presumed to be a mixture of di-adducts $C_{14}F_{12}H_{14}O_2$ (27), (16%); b.p.$_3$ 90-95°C; IR, NMR and mass spectra 23.

E. Addition with 2,2´-Diethoxydiethyl ether

1. Addition to hexafluoropropene

(a) Gamma Ray Initiation

2,2´-Diethoxydiethyl ether (4.5g, 0.025mol) and hexafluoropropene (14.6g, 0.098mol) were irradiated in a sealed tube with gamma rays. The liquid products were distilled *in vacuo* to give: a mixture of mono-adducts, $C_{11}F_6H_{18}O_3$, (33), (24%); b.p.$_5$ 85 to 90°C identified by a combination of NMR and mass spectra; (CI, m/e 313, [M+1]); IR, NMR and mass spectra 24; a mixture of di-adducts, $C_{14}F_{12}H_{18}O_3$, (34), (33%); b.p.$_5$ 100 to 105°C; identified by a combination of NMR and mass spectra; (CI, m/e 463, [M+1]); IR, NMR and mass spectra 25; a mixture of tri-adducts, $C_{17}F_{18}H_{18}O_3$ (35), (34%); b.p.$_{0.01}$ 68°C; identified by a combination of NMR and mass spectra: (CI, m/e 613, [M+1]); IR, NMR and mass spectra 26; and a mixture of tetra-adducts, $C_{20}F_{24}H_{18}O_3$, (36), (8%); b.p.$_{0.01}$ 110 to 120°C; identified by a combination of NMR and mass spectra; (CI, m/e 763, [M+1]); IR, NMR and mass spectra 27.

F. Addition with dimethoxyethane

1. Addition to hexafluoropropene

Dimethoxyethane (9.3g, 0.103mol) and hexafluoropropene (5.5g, 37mmol) were irradiated in a sealed tube with

gamma rays. The liquid products were distilled *in vacuo* to give: 1,1,1,2,3,3-hexafluoro-5,8-dioxanonane (1) (30%) b.p. 138°C (lit.124, 138°C).(Found: C, 34.7; H, 4.4; F,47.9. Calc. for $C_9H_{10}F_6O_2$; C, 35.0; H, 4.1, F, 47.5%), IR, NMR and mass spectra 28 and 3-[1,1,2,3,3,3-hexafluoropropyl]-2,4-dioxahexane (2) (60%), b.p.150°C, (lit.124, 150°C). Identified by comparison of NMR and mass spectra; with those of authentic materials, IR, NMR and mass spectra 29.

2. Addition to Tetrafluoroethene

Dimethoxyethane (214g, 2.4mol), ditertiarybutyl peroxide (4.0g, 0.027mol) and tetrafluoroethene (as required) were heated to 140°C in an autoclave. On completion of the reaction, after *ca.* 6 hours, the autoclave was vented and the liquid products distilled to give: 3-(1,1,2,2-tetrafluoroethyl]-2,5-dioxahexane (3), (53%); b.p. 130°C (lit. 136 130°C); identified by a combination of NMR and mass spectra; (CI, m/e 191, [M+1]); IR, NMR and mass spectra 30; 1,1,2,2-tetrafluoro-4,7-dioxaoctane (4), (18%); $b.p._{68}$ 84°C; identified by a combination of NMR and mass spectra; (CI, m/e 191, [M+L]); IR, NMR and mass spectra 31; and a mixture of telomeric adducts (5), (31%) $b.p._{23}$ 73°C to 85°C; IR, NMR and mass spectra 32.

G. Acetone/t-Butanol Ratios

Di-tertiarybutyl peroxide (0.1g, 0.7mmol) and the substrate ether (approx. 7mmol) were charged to a 7ml Carius tube. The tube was then sealed under vacuum and the mixture heated at 120°C for 10 hours. The product was analysed by

gas liquid chromatography (column K, 60°C) using a gas density balance detector and the acetone/t-butyl alcohol ratio determined from comparison of the areas of the relative peaks (adjusting for molecular weight).

H. Miscellaneous Additions

1. Addition of $CH_3CH(Rf)OCH_2CH_2OCH_2CH_3$ (7) to Hexafluoropropene

The adduct (7) (2.69g, 10mmol) and hexafluoropropene (1.4g, 9mmol) were irradiated in a sealed tube with gamma rays. The liquid products were purified by preparative scale glc (Column K, 150°C) to yield: 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-5,8-dioxadodecane (10), (43%); IR, NMR and mass spectra 16; and 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-6-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadodecane (11), (21%); IR, NMR and mass spectra 17.

2. Addition of $CH_3CH_2OCH(Rf)CH_2OCH_2CH_3$ (6) to Hexafluoropropene

The adduct (6) (1.69g, 6.3mmol) and hexafluoropropene (1.2g, 8mmol) were irradiated in a sealed tube with gamma rays. The liquid products, by examination with glc (Column K, 130°C, gas density balance detector), were shown to contain (6), (98%), and 1,1,1,2,3,3-hexafluoro-4-methyl-7-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadecane (9), (2%).

CHAPTER TEN

EXPERIMENTAL TO CHAPTER FOUR

A. Fluorination of Organic Compounds using Cobalt Trifluoride

A1. General Description of the Cobalt Trifluoride Reactor

The cobalt trifluoride reactor is illustrated in diagram 6. The reactor containing a mixture of calcium difluoride (150g) and cobalt trifluoride (150g) was constantly stirred by the paddles P and heated to the desired temperature, up to 460°C. The baffle tower prevents any of the fluorinating agent from being swept out of the reactor by the constant stream of nitrogen used in the reactions.

2. General Procedure

The reactor bed and baffle tower were heated to the desired temperature and the system purged with dry, oxygen free nitrogen (50ml/minute) for twenty minutes before use. The cold trap was cooled in liquid air (-196°C).

The substrate was allowed to drip into the reactor (3ml/minute) while constantly purging with nitrogen (50ml/minute). After all the substrate had been consumed, the reactor was purged for 20 minutes to ensure that all the products were collected. The cold trap was then allowed to warm to room temperature and the liquid products recovered. Hydrogen fluoride was removed from the products, using sodium bicarbonate, before purification using preparative scale gas liquid chromatography.

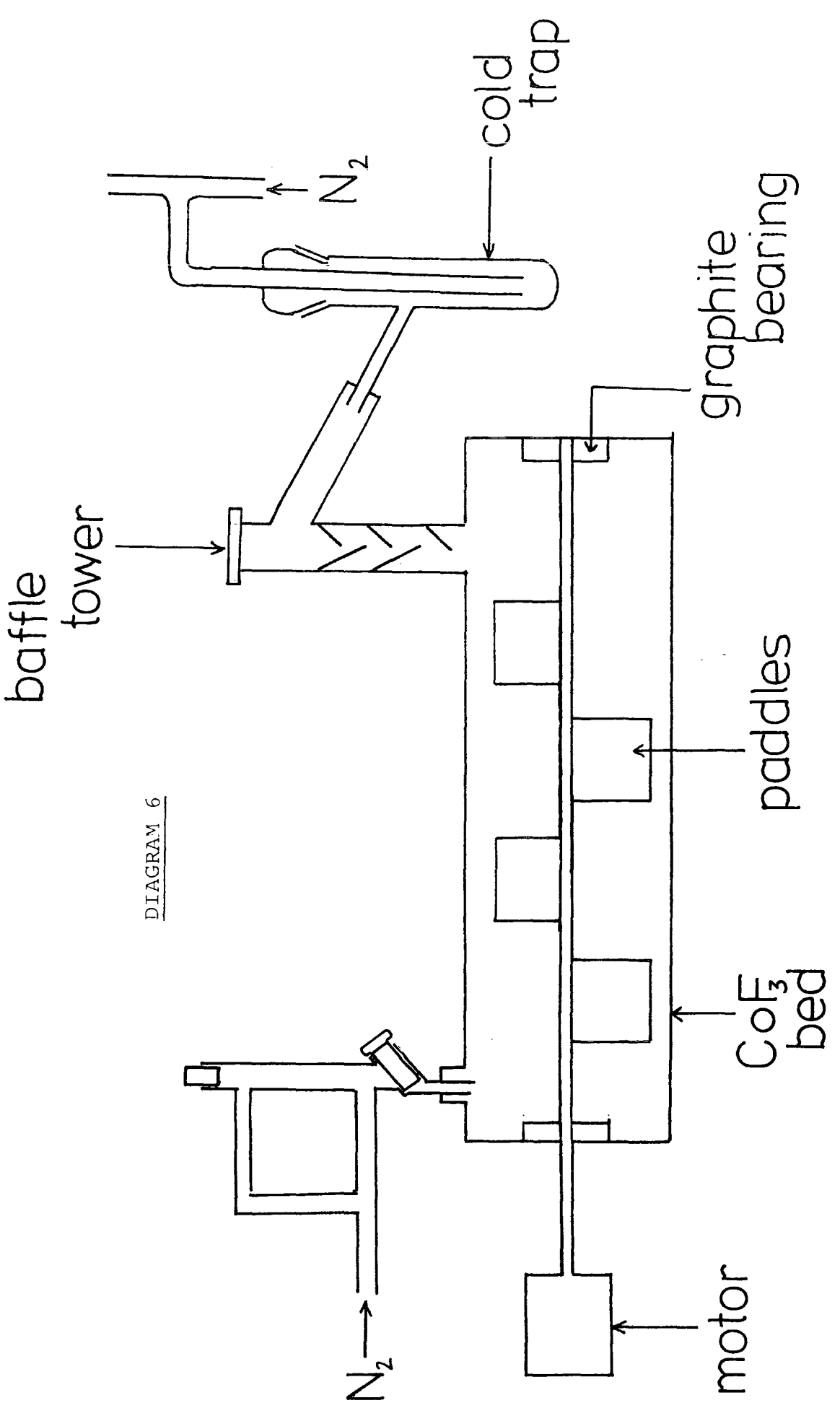

baffle tower
N_2
cold trap
graphite bearing
paddles
CoF_3 bed
N_2
motor

DIAGRAM 6

B1. Fluorination of 2,2,3,4,4,4-hexafluoro-1-methylbutyl ethyl ether (13)

Compound (13) (1.3g, 5.8 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc of the product (1.0g) gave perfluoro-1-methylbutyl ethyl ether (37) (47%); b.p. 78°C (Siwoloboff) (lit.125, 78°C). Identified by comparison of n.m.r. and I.R. spectra with those of an authentic sample. I.R., N.M.R., mass spectra 33 and perfluoropentane (2%) identified by comparison of mass spectra with that of an authentic sample.

2. Fluorination of di-(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether (14)

Compound (14) 2.58g, 6.9 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A.45°C) of the product (1.84g) gave perfluoro-di[1-methylbutyl]ether (38) (48%); b.p. 136°C (Siwoloboff) (lit 125, 136°C). (Found: C, 21.4; F, 75.8; Calc. for $C_{10}F_{22}O$: C, 21.6; F, 75.4%); I.R., N.M.R. Mass spectra 34.

3. Fluorination of 1,1,1,2,3,3-hexafluoro-4-methyl-5,8-dioxadecane (7)

Compound (7) (0.9g, 3.3 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A 70°C) of the product (0.4g) gave perfluoro-4-methyl-5,8-dioxadecane (39) (16%); b.p. 127°C; (Found: C, 20.5; F, 72.9. $C_9F_{20}O_2$ requires C, 20.7; F, 73.0%); I.R., N.M.R. mass spectra 35 and perfluoropentane (10%) identified by comparison of mass spectra with those of an authentic sample.

4. Fluorination of 1,1,2,3,3-hexafluoro-4-methyl-6[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadecane (9)

Compound (9) (1.79g, 4.3 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A,70°C) of the product (1.13g) gave: perfluoro-4-methyl-6-propyl-5,8-dioxadecane (42) (42%); b.p. 163°C; (Found: C, 21.2, $C_{12}F_{26}O_2$ requires: C, 21.5%). I.R., N.M.R., mass spectra 37; and perfluoro-1-methylbutyl butyl ether (43) (10%); b.p. 118°C; (Found C, 21.6; F, 74.8. $C_9F_{20}O$ requires, C, 21.4; F,75.4%) I.R., N.M.R. Mass spectra 36, and perfluoropentane (40) (5%) identified by comparison of the mass spectrum with that of an authentic sample.

5. Fluorination of 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-5,8-dioxadodecane (10)

Compound (10) (2.66g, 7.1 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A,75°C) of the product (1.96g) gave the major product as perfluoro-4,9-dimethyl-5,8-dioxadodecane (41) (40%);. b.p. 160-161°C; (Found: C, 21.2; F, 74.0. $C_{12}F_{26}O_2$ requires C, 21.5; F, 73.7%); I.R., N.M.R. mass spectra 38, and perfluoropentane (40) (11%) identified by comparison with the mass spectrum of an authentic sample.

6. Fluorination of 1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-6-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadodecane (11)

Compound (11) (1.58g, 2.8 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A, 72°C) of the products (1.2g) gave perfluoro-[4,9-dimethyl-6-propyl-5,8-dioxadodecane (44) (32%); b.p. 196°C (Siwoloboff)

(Found: C, 21.7; F, 74.3. $C_{15}F_{32}O_2$ requires C, 21.9; F, 74.1%). I.R., N.M.R. mass spectra 39, perfluoro-1-methylbutyl butyl ether (43) (15%), b.p. 118°C, (Found: C, 21.6; F, 74.8. $C_9F_{20}O$ requires, C, 21.4; F, 75.4%). I.R., N.M.R. mass spectrum 36 and perfluoropentane (40) (6%) identified by comparison of mass spectrum with that of an authentic sample.

7. Fluorination of 1-[1,2,3,3,4,4-hexafluorocyclobutyl]-ethyl ethyl ether (19)

Compound (19) (3.86g, 16.3 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A, 25°C) of the products (2.92g) gave perfluoro-n-hexane (46) (20%) identified by comparison of n.m.r. spectra 53 with that of an authentic sample and perfluoro-1-cyclobutylethyl ethyl ether (45) (20%), b.p. 89°C, (Found: C, 23.0; F, 72.6. $C_8F_{16}O$ requires: C, 23.1; F, 73.1%). I.R., N.M.R. mass spectra 40.

8. Fluorination of di-1-(1,2,3,3,4,4-hexafluorocyclobutyl)-ethyl ether (20)

Compound (20) (3.03g, 7.6 mmol) was passed over cobalt trifluoride. Preparative scale glc (Column A, 70°C) of the products (2.48g) gave: perfluoro-n-hexane (46) (12%), identified by comparison with an n.m.r. spectrum of authentic material (Spectrum No.53) perfluoro-di(1-cyclobutylethyl) ether (47) (Found: C, 24.7; F, 72.3; $C_{12}F_{22}O$ requires: C, 24.9; F, 72.3%); I.R., N.M.R. mass spectrum 41.

9. Fluorination of di-1-(1,2,3,3,4,4,5,5-octafluoro-cyclopentyl) ether (22)

Compound (22) (3.85g, 7.7 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A, 75°C) of the products (3.35g) gave a volatile unidentified compound (4%), perfluoro-di(1-cyclopentylethyl) ether (48) (40%); b.p. 157°C; (Found: F, 73.3, $C_{14}F_{26}O$ requires: F, 72.9:), I.R., N.M.R. mass spectra 42, and perfluoro-1-cyclopentylethyl-1-methylhexyl ether (41) (6%), identified by a combination of n.m.r. and mass spectrometry, spectra No.43.

10. Fluorination of di-1-[1,2,3,3,4,4,5,5,6,6-decafluoro-cyclohexyl]ethyl ether (24)

Compound (24) (1.51g, 2.5 mmol) was passed over cobalt trifluoride at 440°C. Prepatative scale glc (Column A, 70°C) of the products (0.96g) gave perfluoro-n-octane (35%) (51) NMR 54, and perfluoro-di[1-cyclohexylethyl] ether (50) (25%); b.p. 181°C; (Found: F, 73.0. $C_{16}F_{30}O$ requires: F, 73.2%). I.R., N.M.R., mass spectra 44.

11. Fluorination of 3-chloro-2,2,3-trifluoro-1-methyl-propyl ethyl ether (17)

Compound (17) (1.23g, 6.4 mmol) was passed over cobalt trifluoride at 440°C. Preparative scale glc (Column A, 30°C) gave perfluoro-1-chloro-n-butane (53) (17%), IR and NMR 45 and perfluoro 1-chloro-3-methylpropyl ethyl ether (52) (32%) b.p. 83°C, (Found: C, 19.2, Cl, 9.9, $C_6ClF_{13}O$ requires C, 19.4; Cl, 9.6%). I.R., N.M.R. mass spectra 46.

12. Fluorination of 2,4-[1,2,2,3,3,4,4,5-octafluorocyclopentyl]-3,6-dioxaoctane (30)

Compound (30) (2.1g, 3.8 mmol) was passed over cobalt trifluoride at 440°C. The products consisted of a complex mixture of fluorocarbon ethers, preparative scale glc (Column A, 60°C) gave a pure sample of the major component perfluoro-di [1-cyclopentylethyl]ether (48) (15 %) b.p. 157°C identified by comparison of N.M.R. spectrum with that of an authentic sample Spectrum No.42.

13. Attempted fluorination of a mixture of ethyl di-glyme: hexafluoropropene 1:3 adduct. $C_{17}F_{18}H_{18}O_2$ (35)

Compounds (35) (2.34g, 3.8 mmol) were passed over cobalt trifluoride at 440°C. The products (1.51g) consisted of a complex mixture of volatile fluorocarbon ethers. Separation using preparative scale glc techniques was not possible due to the complexity of the mixture.

14. Attempted fluorination of 1,1,1,2,3,3-trifluoro-4-methoxy-6-oxaheptane (2)

The adduct (2) (4.58g, 19 mmol) was passed over cobalt trifluoride at 440°C. The products consisted of a mixture of gaseous compounds. No examination of the mixture was attempted.

CHAPTER ELEVEN

EXPERIMENTAL TO CHAPTER FIVE

DIRECT FLUORINATIONS

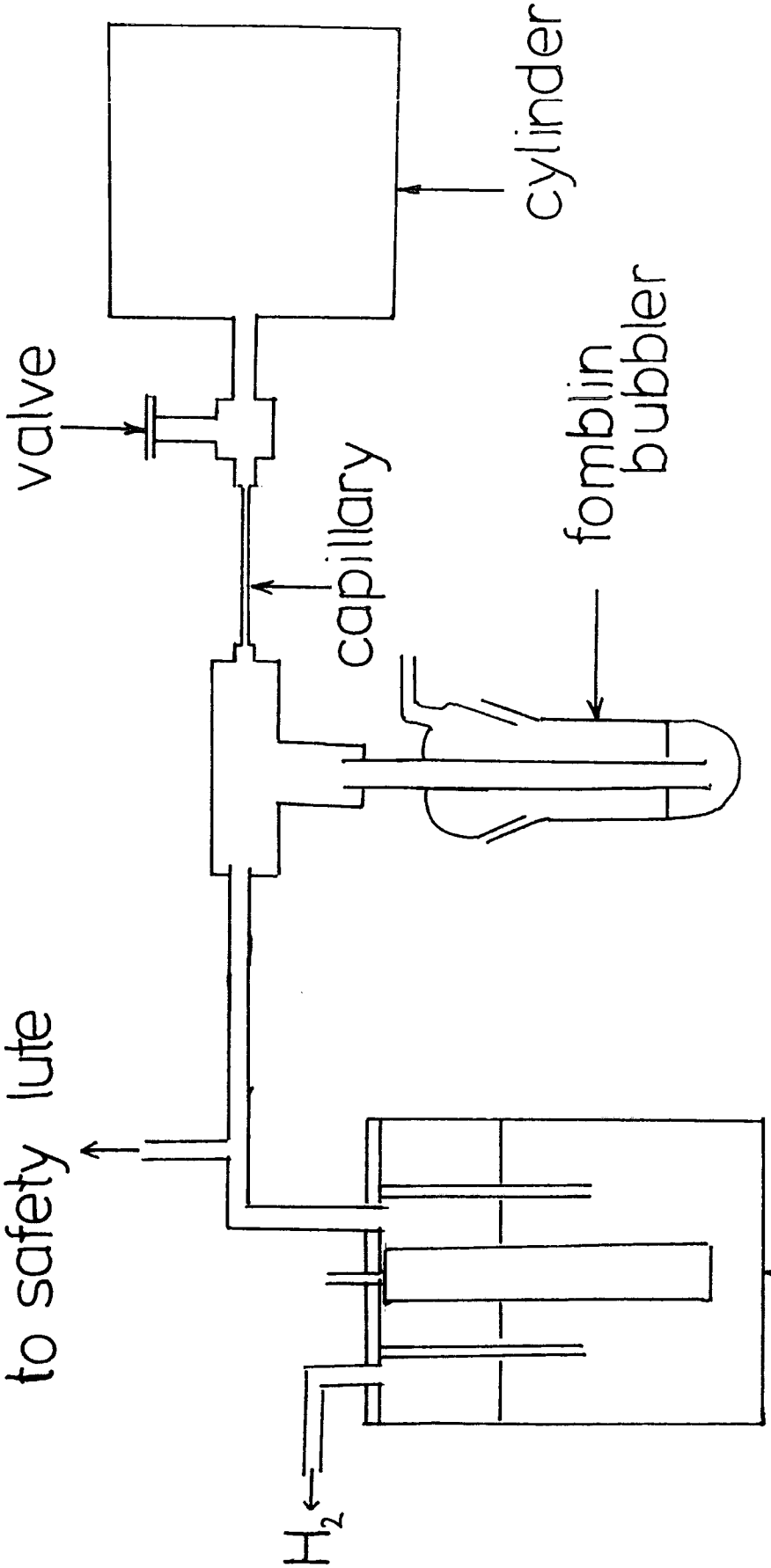

cylinder
valve
capillary
fomblin
bubbler
to safety lute
F_2 cell
H_2

DIAGRAM 7

A. General Techniques

The following general techniques were consistently used throughout the fluorination reactions.

1. Preparation of a cylinder filled with Fluorine, or with a fluorine/nitrogen mixture under pressure

The stainless steel cylinder, fitted with a monel valve, was evacuated to high vacuum and the valve sealed. The cylinder was connected to a "T" junction, *via* a stainless steel capillary tube, one end of which was connected to a Fomblin bubbler and the other to a 10 amp fluorine cell (Diagram 7). Fluorine, generated by the cell, was initially allowed to escape through the bubbler; the valve on the cylinder was then opened sufficiently to prevent fluorine from escaping from the bubbler yet not to allow a partial vacuum to occur in the cell. When the cylinder was completely full, as indicated by fluorine being forced through the bubbler, the valve was closed.

If necessary the cylinder was pressurised with nitrogen to obtain the desired concentration of fluorine.

2. Analysis of Products

The experiments in this chapter, in many cases, produced mixtures of partially fluorinated ethers which were not separable using conventional techniques. Two methods were employed to determine average emperical formulae of the partially fluorinated product; (a) by comparison of the ^{1}H and ^{19}F n.m.r. resonance integrations and (b) a mass spectrometry/g.l.c. technique developed for the fluorination of the di-adduct (14).

(a) The N.M.R. spectroscopy technique

Two drops of trifluoromethyl benzene were added to the product, the ^{19}F and ^{1}H n.m.r. spectra measured and the resonances integrated.

Example 1

A direct fluorination of $CH_3CH(Rf)OCH_2CH_2OCH(Rf)CH_3$ (10)

[Rf = CF_2CFHCF_3]

(i) Trifluoromethyl benzene resonances.

Trifluoromethyl benzene gives the following resonances δ_F 63.0 p.p.m. and δ_H 7.1 p.p.m. The fluorine and hydrogen atoms are present in the molecule in a ratio of 3:5 (F:H). Considering spectra (i) it is necessary to adjust the integral of either resonance to give this ratio.

From the spectra:

the ^{19}F integral for CF_3-  = 2.25mm.

the ^{1}H integral for CF_3-  = 13.2mm.

However, as $F_{atoms}:H_{atoms}$ = 3:5 the integrals are adjusted by introducing the factor x where:

$$13.2 : 2.25x = 5:3$$

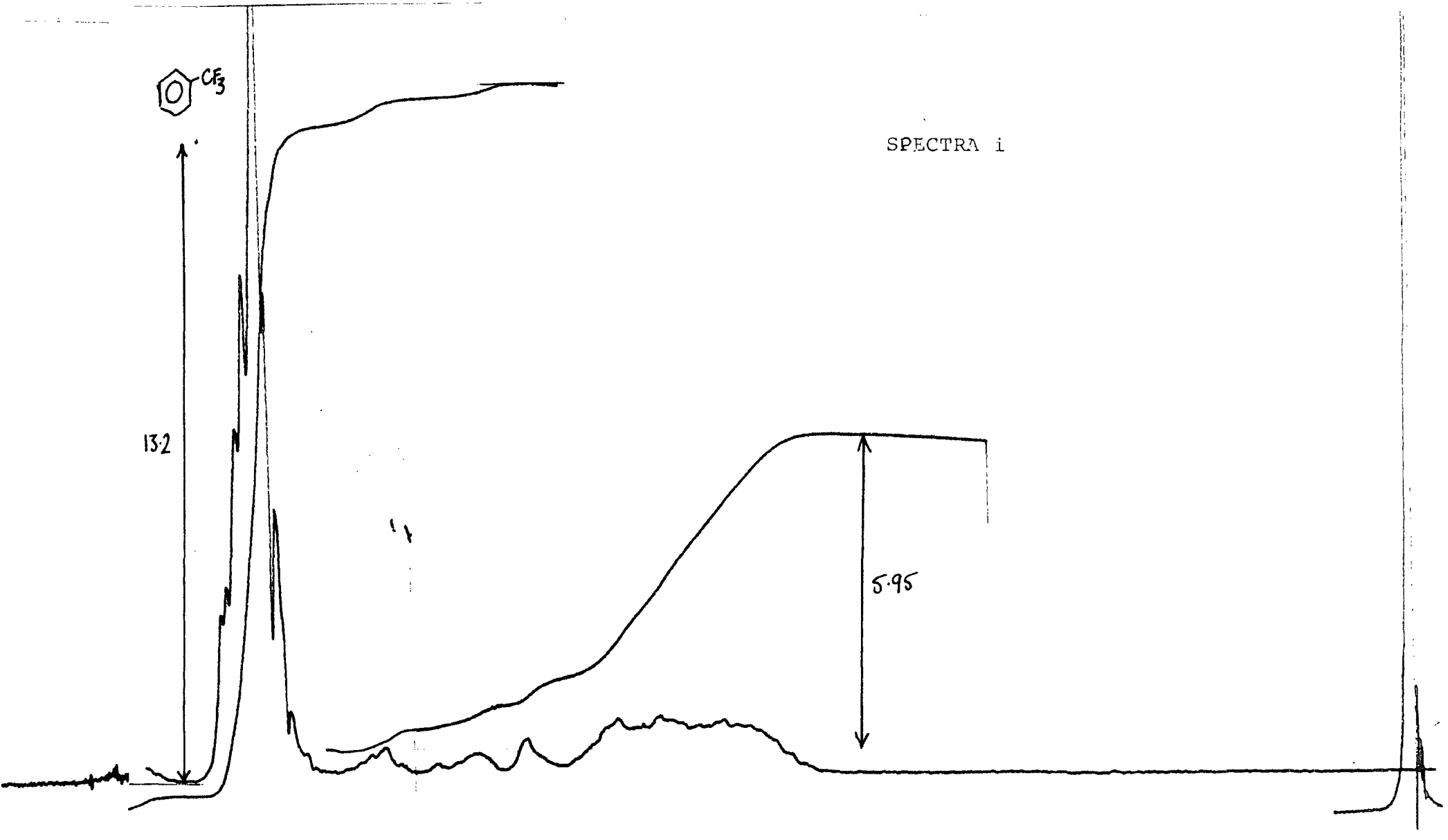
or

$$\frac{2.25x}{13.2} = \frac{3}{5}$$

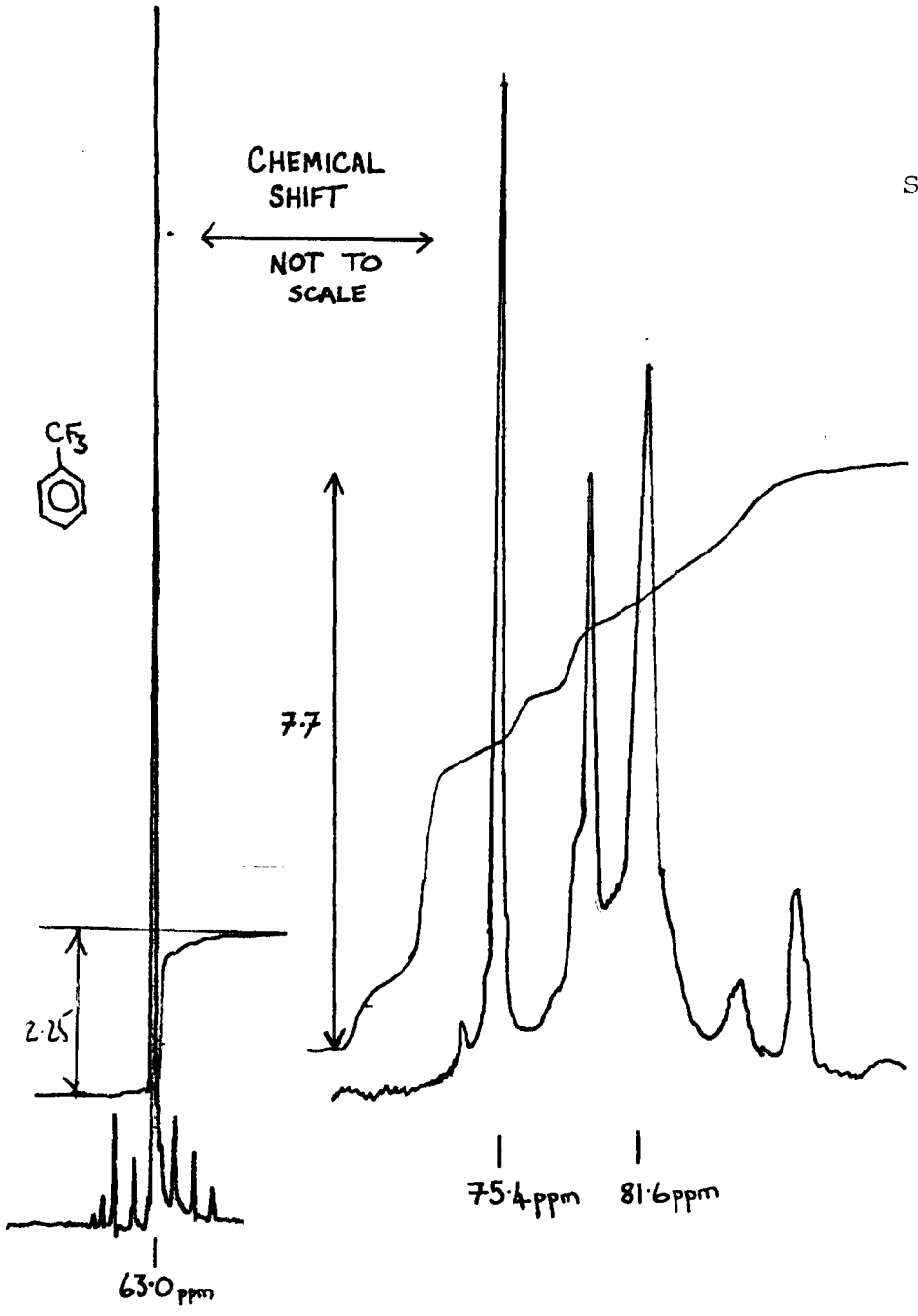
$$x = \frac{3 \times 13.2}{2.25 \times 5}$$

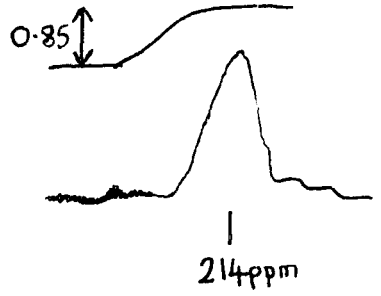
$$\therefore \quad x = 3.52$$

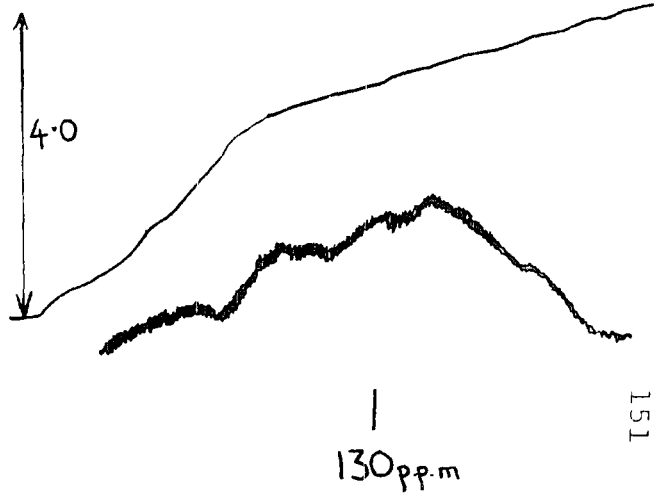
Having adjusted the integral of the trifluoromethylbenzene by a factor x, it is possible to obtain a fluorine: hydrogen ratio for the product by altering the total ^{19}F integral for the product, by the same factor x.



SPECTRA i


CHEMICAL SHIFT
NOT TO SCALE
CF3
7·7
2·25
63·0ppm
75·4ppm
81·6ppm


0·85
214ppm


4·0
130pp.m

From the spectra:

^{19}F product integral = 12.55

^{19}F corrected integral = 12.55(x)

= 12.55 × 3.52

= 44.2

^{1}H product integral = 5.95

∴ For the product F:H = 44.2:5.95 ≃ 44:6.

However the total number of hydrogen and fluorine atoms in the product is 26 ($C_{12}F_nH_mO_2$ [n+m = 26]. Normalising the ratio 44:6 gives:

F:H = 0.88 : 0.12.

Thus 88% of the 26 sites are occupied by fluorine atoms and 12% of the 26 sites by hydrogen atoms.

No. of fluorine atoms = $\frac{88}{100}$ x 26

= 22.88

No. of hydrogen atoms = $\frac{12}{100}$ x 26

= 3.12

∴ Av. formulae of the product = *ca.* $C_{12}F_{23}H_3O$.

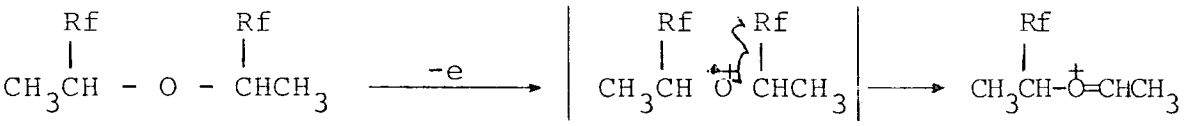
It is assumed that no structural alteration of the original substrate has occurred. The spectral evidence suggests that this is a reasonable assumption.

(b) Mass Spectrometry/g.l.c. Technique

This technique was developed specifically for the di-adduct (14) fluorination reactions. The product of the fluorination reactions for (14) could be resolved into

isomeric components (typically 20 to 30 components) using g.l.c.

The electron impact mass spectra of partially fluorinated branched ethers has been discussed in Chapter Five. The highest mass peak produced is derived from β cleavage of the ether link resulting in the loss of the polyfluoroalkyl side chain



(Rf = CF_2CFHCF_3)

The fluorination occurs such that the last hydrogen atom to be replaced by fluorine is the one in the polyfluoroalkyl side chain. Therefore it is possible to produce Table 23 which indicates the m/e value corresponding to each partially fluorinated isomer.

TABLE 23

Isomer	Mwt.	Side Chain lost	M/e of resulting fragment
$C_{10}F_{18}H_4O$	482	CF_2CFHCF_3	331
$C_{10}F_{17}H_5O$	464	CF_2CFHCF_3	313
$C_{10}F_{16}H_6O$	446	CF_2CFHCF_3	295
$C_{10}F_{15}H_7O$	428	CF_2CFHCF_3	277
$C_{10}F_{14}H_8O$	410	CF_2CFHCF_3	259
$C_{10}F_{13}H_9O$	392	CF_2CFHCF_3	241
$C_{10}F_{12}H_{10}O$	374	$CF_2CFH\ CF_3$	223

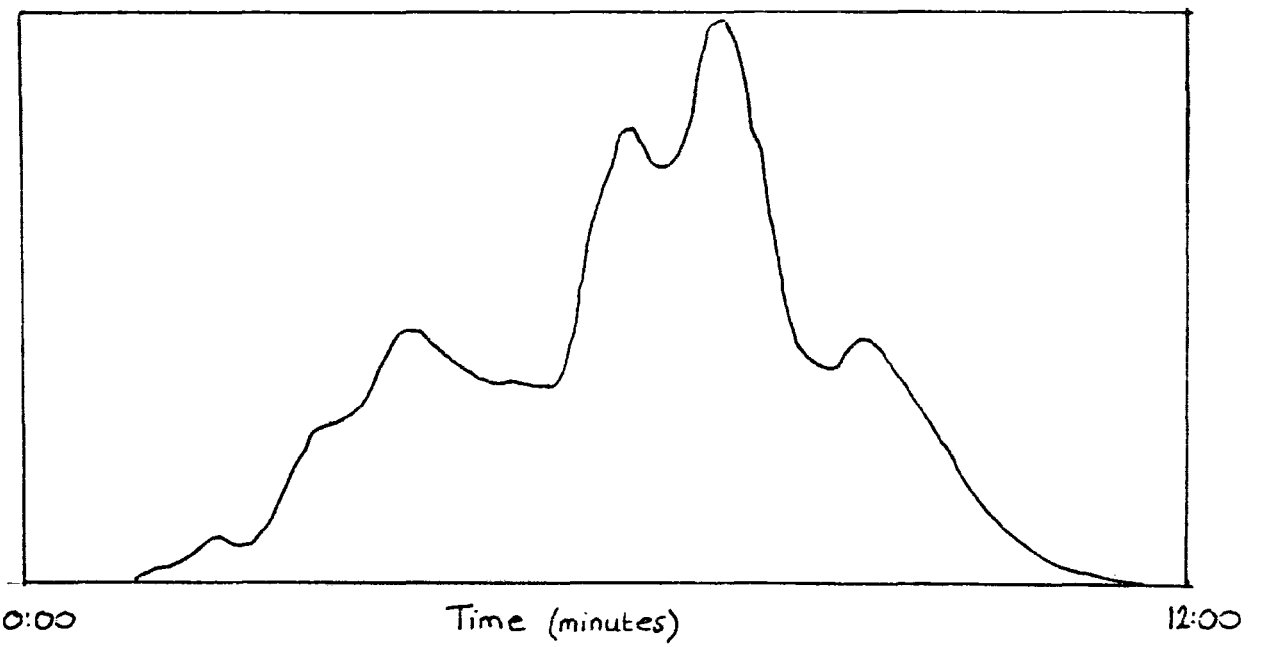
The percentage composition of each isomer, once identified, is calculated by comparing the peak areas of the chromatogram (using a gas density balance detector). The following example clearly illustrates this technique.

Example 2

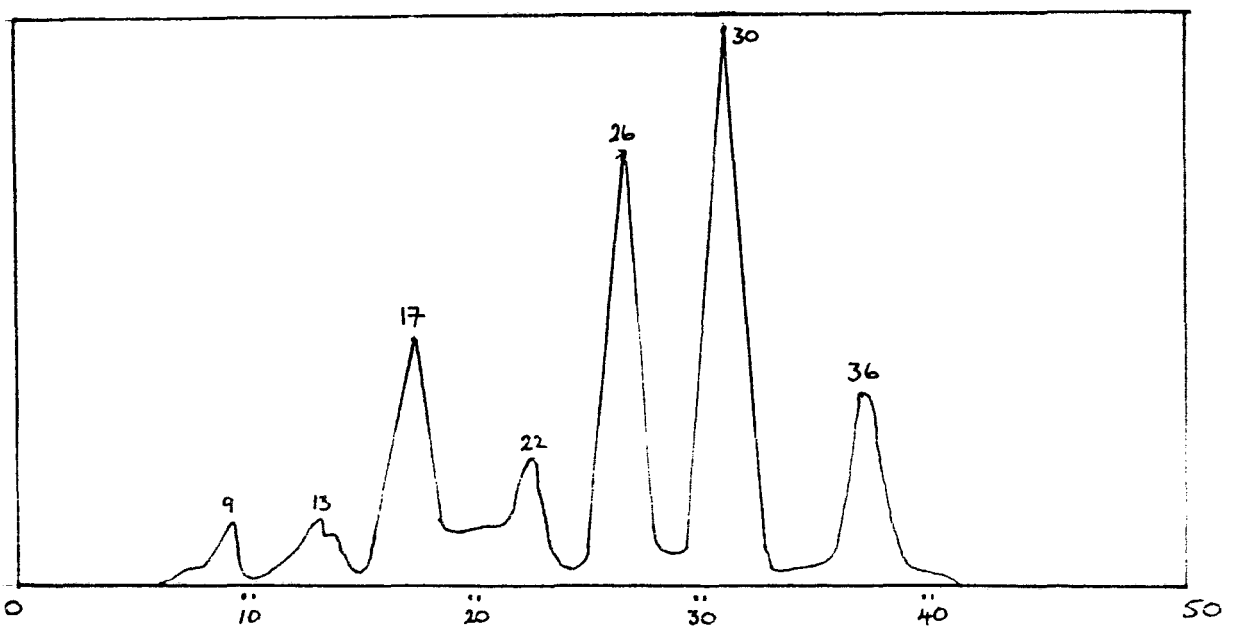
Capillary fluorination of (14) (see B.)

G.L.C. chromatograms.

1. using column SE30 (5%)



2. Computer mass maxed chromatogram.



Peak 36

PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	8.82	19	95.07	23.43
2	29.12	48.03	20	113.06	10.21
3	29.99	6.26	21	115.09	15.55*
4	32.02	8.82	22	127.07	80.05
5	33.13	7.66	23	129.08	3.71
6	43.12	12.76	24	133.10	3.48
7	45.19	8.58	25	145.10	19.26
8	49.00	3.48	26	151.04	16.71
9	50.97	60.71*	27	155.12	2.55*
10	61.02	13.23*	28	161.02	3.25
11	63.13	100.00*	29	175.12	2.55*
12	64.12	3.25	30	177.07	22.51*
13	65.10	8.35	31	181.07	6.26*
14	68.95	35.96*	32	195.11	4.64*
15	77.05	32.71*	33	197.05	11.69
16	80.96	11.60	34	213.12	3.02*
17	83.03	3.25*	35	259.15	5.80
18	93.05	2.55*	36	277.16	4.64

Peak 30

PEAK NO.	MASS	%HT. BASE	PEAK NO.	MASS	%HT. BASE
1	27.25	7.99	31	113.04	17.25*
2	29.12	30.67	32	115.07	12.50*
3	29.99	7.29	33	119.02	1.39
4	32.01	6.83	34	127.07	63.08*
5	33.12	5.90	35	129.06	3.24*
6	43.12	13.77*	36	131.03	2.20
7	45.18	6.25	37	133.08	24.31*
8	46.17	2.20*	38	141.06	2.43*
9	47.14	4.63	39	143.09	1.27
10	49.00	5.21	40	145.10	39.70
11	50.96	100.00*	41	146.12	1.97
12	52.06	1.27*	42	151.01	21.30*
13	61.01	7.64*	43	155.11	1.39
14	62.08	1.39	44	159.04	3.24*
15	63.13	32.06	45	161.02	3.59*
16	64.12	2.08*	46	163.05	3.82
17	65.09	39.70*	47	175.08	2.31*
18	68.95	46.87	48	177.07	24.65*
19	75.07	1.50*	49	178.07	1.27
20	77.05	26.97*	50	181.06	6.37*
21	78.02	1.39*	51	183.10	6.83
22	78.95	1.74*	52	193.10	4.17
23	80.96	17.25*	53	195.08	10.53
24	81.99	2.43*	54	197.06	13.77*
25	83.03	4.98	55	213.11	11.69*
26	93.05	2.20*	56	215.11	2.66
27	95.05	34.03*	57	259.15	3.36*
28	96.06	1.50*	58	277.12	16.55*
29	100.98	2.89	59	278.11	1.27
30	109.00	1.50	60	295.13	5.56

Peak 26

MASS	%HT. BASE	MASS	%HT. BASE		
48.99	3.66*	109.01	1.39*	163.09	3.91
50.96	100.00*	113.04	21.46*	175.12	2.40*
61.01	8.08*	114.07	1.39*	177.07	10.10
63.12	15.03	115.10	2.40	191.07	6.19*
64.11	2.40*	118.99	1.52	193.07	5.37*
65.09	9.97	123.08	1.52*	193.11	5.05*
68.95	56.19*	127.08	10.86	195.05	16.16*
75.07	1.26*	131.03	11.99	197.09	5.30
77.04	6.34	133.08	37.50*	213.12	8.46*
78.95	1.64*	134.11	6.39*	215.08	4.29*
80.95	19.95*	141.01	1.89*	225.11	2.90*
81.99	1.89*	143.02	1.77	243.15	1.64
83.03	17.42	145.07	60.61*	277.12	6.31
93.04	2.15*	146.10	2.40	295.16	14.63*
95.06	29.55	181.01	19.32	297.20	2.19*
100.98	3.64*	161.06	2.40		

Peak 9

MASS	%HT. BASE	MASS	%HT. BASE
28.12	100.00	313.17	5.29*
28.99	11.07	375.28	1.58*
32.02	18.58	413.26	3.90*
33.12	8.30		
43.13	4.74		
50.97	35.97*		
61.01	16.21*		
69.01	54.15*		
95.13	9.49*		
101.02	5.93		
113.09	19.76*		
145.15	4.35		
151.05	10.28*		
201.11	5.14*		
287.45	11.86		

Peak 13

MASS	%HT. BASE	MASS	%HT. BASE
28.12	74.48	118.99	7.12
28.99	10.98	127.07	4.45
32.02	15.13	131.03	9.20*
33.12	4.45	133.08	20.18*
43.12	10.68	145.09	27.30
45.17	5.64*	151.06	14.54*
50.97	95.25	161.08	3.56*
61.02	8.31	163.11	9.79
63.13	5.04	177.13	4.15*
65.13	7.42	181.06	3.86*
68.95	100.00	183.09	7.42
77.05	5.34*	195.11	5.34
80.95	4.15*	201.03	16.32*
83.03	13.65*	211.08	3.26
95.05	24.63	213.11	3.86
100.98	6.82	281.12	3.86
113.04	42.43*	313.11	4.67
115.02	3.26		

Peak 17

MASS	%HT. BASE	MASS	%HT. BASE
43.12	11.56*	133.08	13.32*
45.17	2.90*	145.12	31.66
49.00	7.34*	149.02	3.12*
50.97	100.00*	151.03	17.57*
61.02	8.69	161.05	2.12
63.13	6.37	163.08	5.98
69.13	17.57	177.12	7.14
69.95	78.74*	181.06	4.05*
77.05	8.11	183.09	10.92*
93.96	3.28*	193.13	2.32*
92.02	2.70*	196.07	6.88*
63.04	1.9%	197.11	4.05
95.07	28.01*	211.08	9.25
100.98	7.77	213.15	1.74
113.06	33.78*	215.07	2.32
115.09	5.98	243.14	5.98*
119.00	4.83	295.19	2.90
127.09	18.78	313.14	5.91
131.05	4.05		

Peak 22

MASS	%HT. BASE	MASS	%HT. BASE
45.19	6.42*	151.03	21.04*
50.97	100.00*	163.08	12.80*
61.02	3.47	177.12	5.64
63.13	3.98	181.06	2.17
65.13	10.20	183.12	2.47
68.95	73.80	193.07	5.63*
77.05	10.70	195.07	3.46
80.94	.90	197.08	4.12
84.03	8.88	213.10	3.25
95.07	27.67	215.11	2.82
100.98	7.83	253.09	6.39*
113.06	14.20	315.23	7.47*
115.09	3.25	413.50	2.61*
119.00	5.09*		
127.09	16.27		
131.05	3.04		
133.03	26.03		
145.12	41.87*		

By comparing the EI spectra for each g.l.c. peak with the values given in Table 23 an estimate of the empirical formula may be made,

e.g. Peak 36, m/e 277, av. formula equals $C_{10}F_{15}H_7O$

Peaks 30 and 26, m/e 295, av. formula equals $C_{10}F_{16}H_6O$

Peaks 9,13,17 and 22, m/e 313, av. formula equals $C_{10}F_{17}H_5O$

Percentage composition of the mixture is based on g.l.c. peak areas and found to be isomers $C_{10}F_{15}H_7O$, 6.4%; isomers $C_{10}F_{16}H_6O$, 59.4%; isomers $C_{10}F_{17}H_5O$, 32.1%. The average number of hydrogen remaining in the ether is given by the equation:

$$\underline{\text{Av.}}\ \text{No. of hydrogens} = \sum_{n=1}^{10} \frac{n(\%C_{10}F_{12+(10-n)}H_nO)}{100}$$

where n = no. hydrogens remaining in each isomer

$$\therefore \text{Av. No. of hydrogens remaining} = 7 \times \frac{6.4}{100} + 6 \times \frac{59.4}{100} + 5 \times \frac{32.1}{100}$$

$$= \underline{\underline{5.6}}$$

$\therefore$ Av. formulae of (63) = $C_{10}F_{16.4}H_{5.6}O$.

B. Direct Fluorination using the Copper Tube System

Unless otherwise stated the copper tube reactions were carried out using the following general procedure.

1. General Procedure

The reactor, assembled as illustrated in diagram 4, was charged with the adduct, at point (A), and purged with dry, oxygen free nitrogen for twenty minutes. The flow of nitrogen was then terminated and a flow of a nitrogen/fluorine mixture used to purge the reactor at approximately 200ml/minute. The temperature was controlled using ice baths or thermostatically controlled mineral oil baths. After five hours, having used 12.0g (0.32mol.) of fluorine, the reaction was terminated and the reactor purged with nitrogen for twenty minutes. The products were recovered by eluting the reactor with arcton 113 and then removing the solvent.

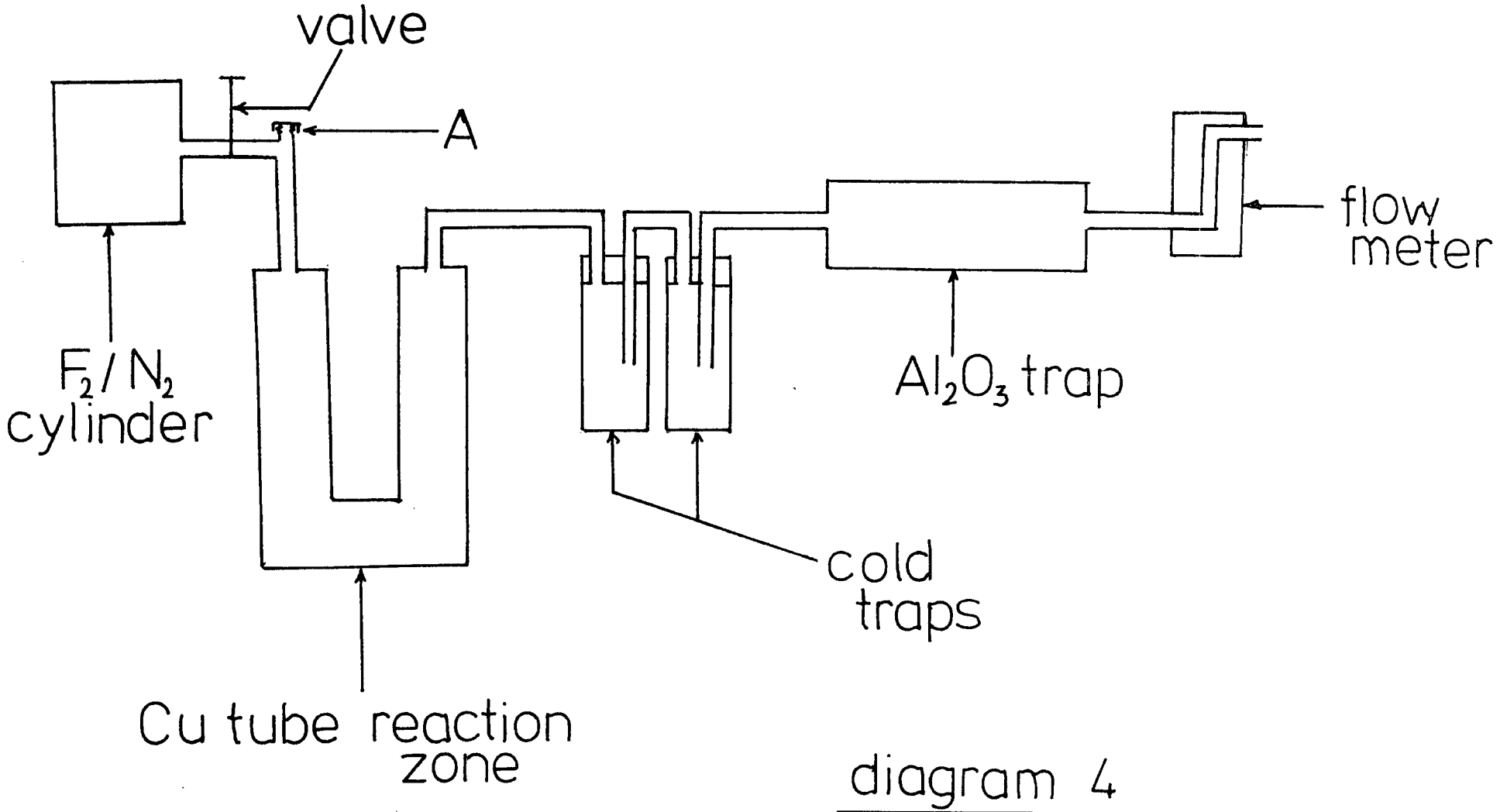

valve
A
flow meter
F_2/N_2 cylinder
Al_2O_3 trap
cold traps
Cu tube reaction zone

diagram 4

2. Direct fluorination of adduct 1,1,1,2,3,3-hexafluoro-4-methyl-5,8-dioxadecane (7)

(a) At 0°C

The adduct (7) (3.3g, 12.3mmol) was directly fluorinated in the copper tube reactor, at 0°C, for 5 hours, using a 10% fluorine in nitrogen mixture. The products were recovered by elution of the reactor with arcton 113. Removal of the solvent gave an inseparable mixture of partially fluorinated ethers averaging to $C_9F_{8.8}H_{11.2}O_2$ (64) (82%). The average molecular formula was calculated by comparing the relative integrals of n.m.r. signals with those of an internal standard (trifluoromethyl benzene).

(b) At 20°C

The adduct (7) (3.0g, 11.2mmol) was directly fluorinated in the copper tube reactor at 20°C using a 10% fluorine in nitrogen mixture. The products (1.05g), recovered by elution of the reactor with arcton 113, were an inseparable mixture of partially fluorinated ethers of average molecular formula $C_9F_{14}H_8O_2$ (55) (25%). The average molecular formula was calculated from relative integrals of NMR signals of an internal standard.

(c) From 0°C to 20°C

The adduct (7) (3.0g, 11.2mmol) was directly fluorinated at 0°C using a 10% fluorine in nitrogen mixture, for 2½ hours in the copper tube reactor. The temperature of the reactor was then elevated to 20°C for a further 2½ hours, after which the reactor was purged with nitrogen and the products (1.66g)

extracted from the reactor with arcton, 113. Removal of the solvent gave an inseparable mixture of partially fluorinated ethers averaging to $C_9H_{9.5}F_{12.5}O_2$ (56) (40%). The average molecular formula was calculated by comparing relative integrals of n.m.r. signals with those of an internal standard.

3. Direct Fluorination of 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-5,8-dioxadodecane (10)

(a) At 0°C

The adduct (10) (3.0g, 7.2mmol) was directly fluorinated at 0°C for 5 hours, using a 10% fluorine in nitrogen mixture, in the copper tube reactor. The reactor was then purged with nitrogen, and the products recovered by eluting the reactor with arcton 113. Removal of the solvent gave an inseparable mixture of partially fluorinated ethers averaging to $C_{12}F_{15.5}H_{11.5}O_2$ (57) (95%). The average molecular formula was calculated by comparing relative integrals of n.m.r. signals with those of an internal standard.

(b) From 0°C to 20°C

The adduct (10) (3.0g, 7.2mmol) was directly fluorinated at 0°C for 2½ hours, using a 10% fluorine in nitrogen mixture, in the copper tube reactor. The temperature of the reactor was then elevated to 20°C for a further 2½ hours, after which the reactor was purged with nitrogen and the products recovered by eluting with arcton 113. Removal of the solvent gave an inseparable mixture of partially fluorinated ethers averaging to $C_{12}H_{7.5}F_{18.5}O_2$ (58) (70%). The average molecular formula was calculated by comparing relative integrals of n.m.r. signals with those of an internal standard (trifluoromethyl benzene).

(c) $0^{o}C$ to $52^{o}C$

The adduct (10) (3.0g, 7.2mol) was directly fluorinated at $0^{o}C$, for 2.5 hours, using a 10% fluorine in nitrogen mixture, in the copper tube reactor. The temperature of the reactor was then elevated to $20^{o}C$, for a further 2.5 hours, then to $52^{o}C$ for a final 2.5 hour period. The reactor was then purged with nitrogen and the products recovered by elution with arcton 113. Removal of the solvent gave an inseparable mixture of partially fluorinated ethers averaging to $C_{12}H_5F_{21}O_2$ (59) (25%). The average molecular formula was calculated by comparing relative integrals of n.m.r. signals with those of an internal standard. (trifluoromethyl benzene).

C. Direct Fluorination using the Capillary Apparatus

The capillary system is illustrated in diagram 5 . The following procedure was used to directly fluorinate adducts with this apparatus.

1. General Procedure

The adduct was placed in the glass vessel, into which dipped a stainless steel capillary tube for the passage of fluorine, and the system purged with dry, oxygen-free nitrogen for twenty minutes. The nitrogen flow was then terminated and a flow of a nitrogen/fluorine mixture begun. The temperature of the glass vessel was regulated using a thermostatically controlled mineral oil bath. The resulting products were recovered from the glass vessel and examined with

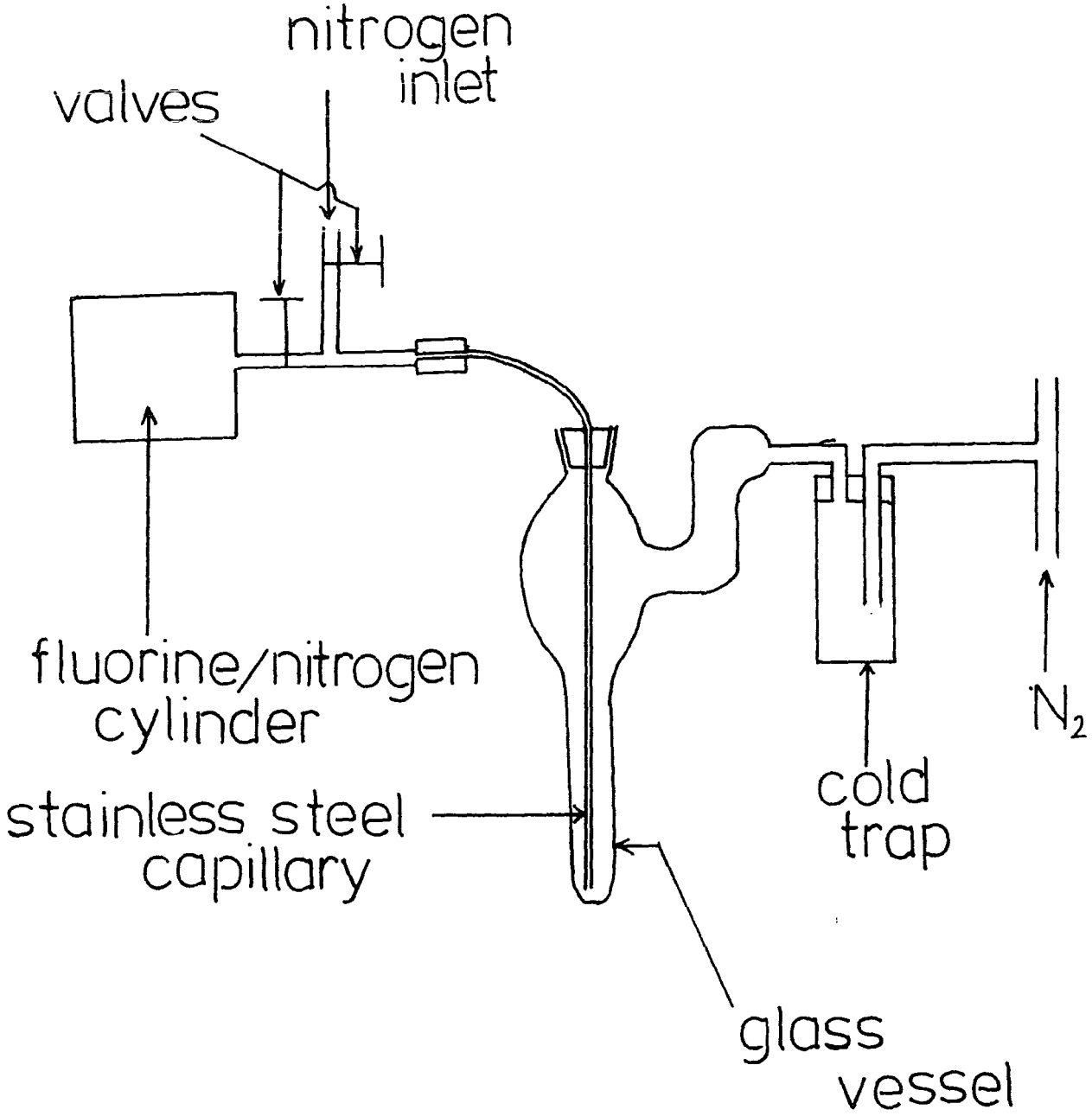

nitrogen
inlet
valves
fluorine/nitrogen
cylinder
stainless steel
capillary
cold
trap
N_2
glass
vessel

DIAGRAM 5

N.M.R. or mass spectra/g.l.c. techniques to estimate the percentage fluorination.

2. Direct fluorination of 1,1,1,2,3,3-hexafluoro-4-methyl-6-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadecane (9)

The adduct (9) (4.04g, 9.7mmol) was directly fluorinated, at 20°C, for 2 hours, then at 50°C for 3 hours using 10% fluorine in nitrogen in the capillary apparatus. The product (3.9g), a clear viscous liquid, was an inseparable mixture of partially fluorinated ethers averaging to $C_{12}H_9F_{17}O_2$ (59) (79%). The average molecular formula was calculated by comparing relative n.m.r. signals with those of an internal standard (trifluoromethyl benzene).

3. Direct fluorination of 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-5,8-dioxadodecane (10)

(a) From 20°C to 50°C

The adduct (10) (4.1g, 9.8mmol) was directly fluorinated, at 20°C, for 2 hours, then at 50°C for 3 hours, using a 10% fluorine in nitrogen mixture, in the capillary apparatus. The system was then purged with nitrogen and the products (3.95g) recovered to give an inseparable mixture of partially fluorinated ethers averaging to $C_{12}H_{10}F_{16}O_2$ (60) (82%). The average molecular formula was calculated by comparing relative n.m.r. signals with those of an internal standard (trifluoromethyl benzene).

(b) From 20°C to 110°C

The adduct (10) (3.9g, 9.33mmol) was directly fluorinated at 20°C for 2 hours, then at 50°C for a further 2 hours and

finally at 70°C for 2 hours, using a 10% mixture of fluorine in nitrogen in the capillary apparatus. The 10% fluorine/nitrogen mix was then replaced with a flow of 25% fluorine in nitrogen and the fluorination continued at 20°C for two hours, then at 70°C for 2 hours and finally at 110°C for 2 hrs. The system was then purged with nitrogen and the products recovered as a mixture of partially fluorinated ethers, averaging to $C_{12}F_{23}H_3O_2$ (6%). The average molecular formula was calculated by comparing the relative integrals of the n.m.r. signals with those of an internal standard (trifluoromethyl benzene).

4. Direct Fluorination of the tri-hexafluoropropene ethyldiglyme adducts (35) between 20°C and 100°C

The mixture of adducts (35) (3.7g, 6.1mmol) was directly fluorinated at 20°C for 3 hours, then at 50°C for 2 hrs. and finally at 70°C for 2 hours, in the capillary apparatus using a 10% fluorine in nitrogen mixture. The 10% fluorine/nitrogen mixture was then replaced with a flow of 25% fluorine in nitrogen and the fluorination continued at 20°C for 1.5 hours, then at 50°C for 2 hours and finally at 100°C for 2 hrs. The system was then purged with nitrogen and the products recovered as a mixture of partially fluorinated ethers averaging to $C_{17}F_{29.0}H_7O_3$ (61) (4%). The average molecular formula was calculated by comparing the relative n.m.r. integrals with those of an internal standard (trifluoromethyl benzene).

5. Direct Fluorination of Di-[1-methyl-2,2,3,4,4,4-hexafluorobutyl]Ether (14)

The adduct (14) (4.2g, 0.011 mmol) was directly fluorinated (using a 25% fluorine in nitrogen mix) at 20°C for 2 hours, then at 50°C for a further 3 hours, in the capillary apparatus. At this stage the liquid product was an inseparable multicomponent mixture averaging to $C_{10}F_{14}H_8O$(62) as estimated by mass spectroscopy g.l.c. techniques. The fluorine concentration was then raised to 50%, the temperature lowered to 20°C for 2 hours and then raised to 50°C for 3 hours. The resulting liquid product (4.1g) was an inseparable multicomponent mixture. The average formula was estimated as $C_{10}F_{16.1}H_{5.9}O$ (63) (82%), by mass spec./glc techniques.

Further fluorination of (63) using 100% fluorine at 20°C for 2 hrs., then 50°C for 2 hours and finally 110°C for 4 hrs. yielded an inseparable complex mixture averaging to $C_{10}F_{19.5}H_{2.5}O$ (64) (10%). The average molecular formula was estimated by mass spec./glc. techniques.

D. Sealed System Fluorination Reactions

1. Condensation of Fluorine

A stainless steel cylinder (1.5 litre) fitted with fluorine (1.5g, 39mmol) was connected *via* a "T" junction to a nickel tube, fitted with a valve, which was evacuated to high vacuum (Diagram 8). The interconnecting copper tubing was evacuated through the "T" junction and a valve on the junction sealed. Fluorine (0.86g, 22.6mmol) was condensed

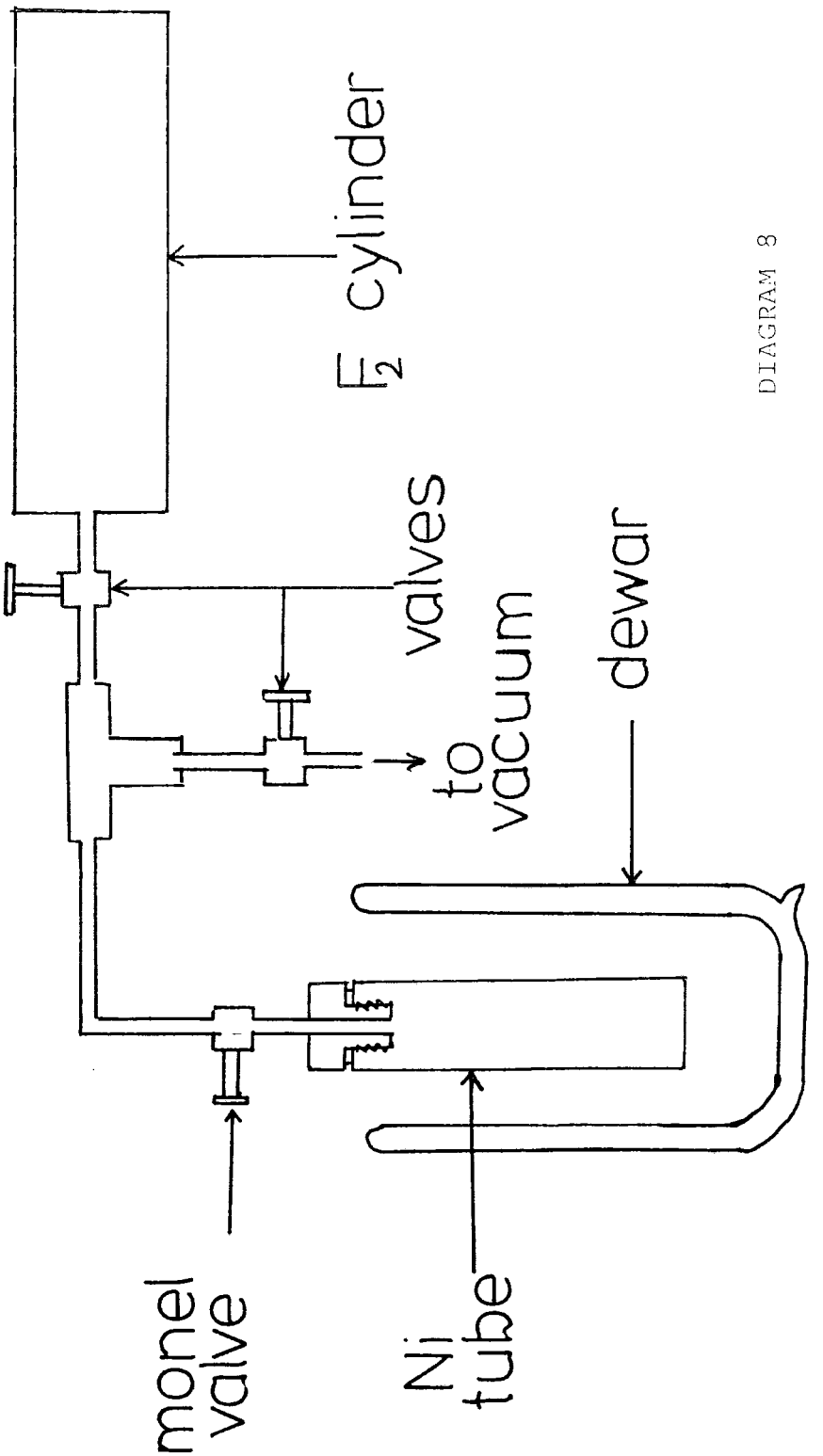


DIAGRAM 8

into the nickel tube by cooling in liquid nitrogen and opening the valves to the stainless steel cylinder. After 20 minutes the valves were sealed, the nickel tube disconnected from the "T" junction and allowed to warm to room temperature.

2. Sealed System Fluorination of $C_{10}F_{16}H_6O$ (63)

(a) At 20°C

The mixture $C_{10}F_{16}H_6O$ (63) (0.59g, 1.32mmol) was sealed in a nickel tube (70ml.) and fluorine (0.86g, 22.6mmol) condensed into the tube as previously described. The tube was allowed to warm to 20°C and left for 24 hours. The tube was then vented and opened. The liquid product was found to have the average formula $C_{10}F_{19}H_3O$ (65) using the mass spec/glc technique outlined at the beginning of this chapter.

(b) At 40°C

The product (63) (0.59g, 1.32mmol) was sealed in a nickel tube (70 ml.) and fluorine (0.86g, 22.6mmol) condensed into the tube as previously described. The tube was allowed to warm to 20°C and left for 10 hours. After this period the remaining fluorine and hydrogen fluoride were vented, the tube evacuated, then refilled with fluorine (0.86g, 22.6 mmol) and heated to 40°C for 20 hours. The tube was then cooled to 20°C, vented and opened. The liquid product (0.44g) was separated by preparative glc. (column A, 45°C) to yield: perfluoro-1-methylbutyl isopropyl ether (66), (10%); b.p.114°C; identified by a combination of NMR and mass spectra; IR, NMR and mass spectra 52; perfluoro-1-methylbutyl butyl ether (43), (14%); b.p. 126°C; (Found: C, 21.6; F, 74.8. $C_9F_{20}O$ requires:

C, 21.4; F, 75.4%); IR, NMR and mass spectra 36; and perfluoro-di-(1-methylbutyl) ether (38), (38%); b.p. 136°C (lit. 125 136°C); (Found: C, 21.4; F, 75.8. Calc. for $C_{10}F_{22}O$: C, 21.6; F, 75.4%). IR, NMR and mass spectra 34.

3. Sealed tube fluorination of the mixture $C_{12}F_{16}H_{10}O_2$ (56)

The mixture $C_{12}F_{16}H_{10}O_2$ (56) (0.40g, 0.85mmol) was sealed in a nickel tube (70 ml.) and fluorine (0.86g, 22.6mmol) condensed into the tube. The mixture was allowed to warm to 20°C, left for 10 hours, then vented, re-evacuated and re-filled with fluorine (0.86g, 22.6mmol). The tube was then heated to 40°C for 20 hours before cooling to 20°C, and the gaseous products vented. The liquid product separated by preparative scale g.l.c. to give: perfluoro-4,9-dimethyl-5,8-dioxadodecane (43), (15%). IR, NMR and mass spectra 38, and a mixture of partially fluorinated products (40%).

4. Sealed System Fluorination of 1,1,1,2,3,3,10,10,11,-12,12,12-dodecafluoro-4,9-dimethyl-6-[1,1,2,3,3,3-hexafluoropropyl]-5,8-dioxadodecane (11)

(a) Prefluorination in the capillary apparatus

Prior to a sealed system fluorination the adduct(11),(4.0g,7.0mmol) was directly fluorinated in the capillary apparatus using a mixture of 25% fluorine in nitrogen at 20°C for 2 hours, then at 50°C for 3 hours, after which the 25% fluorine/nitrogen mixture was replaced with a flow of 50% fluorine in nitrogen and the reaction continued at 20°C for 2 hrs., then at 50°C for 3 hrs. The reactor was then purged with nitrogen and the product (81), (3.5g) recovered. The product, a clear

viscous liquid, was not examined at this stage.

(b) Sealed System Fluorination of mixture (81) at 40°C

The mixture (81) (0.4 g) was sealed in a nickel tube (70 ml.) and fluorine (0.86g, 22.6mmol) condensed into the tube. The mixture was allowed to warm to 20°C and left for 10 hours. After this period the tube was vented, refilled with fluorine (0.86g, 22.6mmol) and heated to 40°C for 20 hours. The tube was then cooled to 20°C, vented and opened. The liquid products were separated by preparative scale g.l.c. (Column A, 70°C) to give: perfluoro-4,9-dimethyl-6-propyl-5,8-dioxadodecane (44), (10%); IR, NMR and mass spectra 39; and a mixture of partially fluorinated compounds (42%) that could not be separated.

(c) Sealed System Fluorination of mixture (81) at 65°C

The mixture (81) (0.4g) was sealed in a nickel tube (70ml.) and fluorine (0.86g, 22.6mmol), condensed into the tube. The mixture was allowed to warm to 20°C and left for 10 hours. After this period the tube was vented, refilled with fluorine (0.86g, 22.6mmol) and heated to 65°C for 20 hours. The tube was then cooled to 20°C, vented and opened. The liquid products were separated by preparative scale glc (Column A, 70°C) to give: perfluoro-4,9-dimethyl-6-propyl-5,8-dioxadodecane (44), (28%), IR, NMR and mass spectra 39; and a mixture of volatile compounds (12%) that were not investigated.

E. Miscellaneous Sealed Tube Reaction

The following general procedure was used for all sealed tube reactions.

1. General Procedure

The adduct, sealed in a nickel tube fitted with a monel valve, was degassed using freeze thaw cycles under vacuum. The evacuated tube was cooled (-78°C) and pressurised with the desired fluorine/nitrogen mixture. On completion of the reaction the tube was vented, opened and the liquid products recovered. The percentage fluorination was measured using either NMR or mass spectra/glc techniques.

2. Sealed tube fluorination of di-[1-methyl-2,2,3,4,4,4-hexafluorobutyl]ethyl ether (14).

(a) Attempt at using Neat Fluorine

The adduct (14) (0.41g, 1.09mmol) was sealed into a tube cooled to -198°C. Fluorine (0.86g, 22.7mmol) was condensed into the tube and the tube allowed to warm to 20°C over 10 hours. After a further 10 hours at 20°C the tube was vented, opened and purged with nitrogen. The products were recovered as a layer of carbonised material.

(b) Using 30% Fluorine

The adduct (14) (1.69g, 4.5mmol) was fluorinated in a nickel tube, using a 30% mixture of fluorine in nitrogen at three atmospheres of pressure. The temperature of the tube was maintained at -78°C for 4 hrs., then allowed to warm to room temperature for 4 hrs. and then heated to 80°C for a final 4 hours. The tube was vented, opened, purged with

nitrogen and the products recovered to give an inseparable multicomponent mixture averaging to $C_{10}FH_9O$ (67) (95%). The average molecular formula was estimated using mass spec./ glc. techniques.

(c) Using 30% Fluorine in Nitrogen and irradiating with gamma rays

The adduct (14) (1.64g, 4.8mmol) was fluorinated in a nickel tube, using a 30% mixture of fluorine in nitrogen at three atmospheres of pressure. The temperature of the tube was maintained at -78°C for 4 hours, then allowed to warm to room temperature for 4 hours. The tube was then irradiated with gamma rays for 24 hrs. (200krads. hr^{-1}) before being vented, opened and purged with nitrogen. The products were recovered as an inseparable, multicomponent mixture averaging to $C_{10}F_{13.5}H_{8.5}O$ (68) (93%). The average molecular formula was estimated using mass spec./glc techniques.

3. Sealed Tube Fluorination of the mixture $C_{10}F_{16.1}H_{5.9}O$ (11) from experiment B6

(a) Using neat Fluorine and irradiating with gamma rays over 10 hrs.

The mixture $C_{10}F_{16.1}H_{5.9}O$ (63) (0.56g, 1.25mmol) was sealed into a tube cooled to -198°C. Fluorine (0.88g, 22.7mmol) was condensed into the tube and the tube allowed to warm to room temperature over a period of 10 hours. The tube was then irradiated with gamma rays for 24 hrs. (200 krds. hr^{-1}) before being vented, opened and purged with nitrogen. The products were recovered as an inseparable multicomponent mixture averaging to $C_{10}F_{17}H_3O$ (69) (62%). The average molecular formula was estimated using mass spec. glc/techniques.

(b) Attempt at using neat Fluorine and irradiating with gamma rays over 120 hrs.

The mixture $C_{10}F_{16.1}H_{5.9}O$ (63) (0.61g, 1.6mmol) was sealed into a tube cooled to -198°C. Fluorine (0.88g, 22.7mmol) was condensed into the tube and the tube allowed to warm to room temperature over a period of 10 hours. The tube was then irradiated with gamma rays for 120 hours (200 krads.hr^{-1}) before being vented, opened and purged with nitrogen. The products were recovered as inextrudable carbonised material.

CHAPTER TWELVE

EXPERIMENTAL TO CHAPTER SIX

A. Preparation of hexafluoropropene/polyether adduct

1. Preparation of Polyethylene Glycol Diethyl Ether (Av.mol.wt. 456).

Sodium hydride (4.0g, 0.096mol, 60% immersion in oil was suspended in toluene (25ml.) in a dry flask fitted with a reflux condenser, dropping funnel and nitrogen inlet. The flask was constantly purged with nitrogen. Dry polyethylene glycol (av.mol.wt. 400) [PEG 400] (20.06g, 0.05mol) in toluene (50ml.) was slowly added to the flask, while constantly stirring, *via* a dropping funnel. The di-sodium salt, a viscous brown liquid, began to form immediately. The mixture was stirred at 20°C for one hour, then 110°C for 2 hrs. to ensure complete reaction. The toluene was removed by distillation *in vacuo* to leave the di-sodium salt of PEG 400 in quantitative yield. Ethyl iodide (25.2g, 0.16mol.) was added to the di-sodium salt slowly, at 20°C and immediate vigorous reaction occurred. After the reaction had subsided the mixture was heated under reflux for three hours. Excess ethyl iodide was distilled from the flask to leave a brown liquid, purification of which, by dissolution in CH_2Cl_2 and passing over alumina, yielded polyethylene glycol diethyl ether (av.mo.wt.456) (70), (73%); IR, and NMR Spectra 47.

2. Free Radical Addition of Polyethylene glycol diethyl ether to Hexafluoropropene

A nickel tube (70 mol.), fitted with a valve, charged with polyethylene glycol diethyl ether (av.mol.wt. 456) (5.3g, 0.011mol.) and di-tertiarybutyl peroxide (1.5g, 0.01 mol.) was cooled (-196°C liquid air) and evacuated to high vacuum.

The contents were degassed using freeze thaw cycles under vacuum. Hexafluoropropene (40g, 0.26mol.) was transferred into the tube under vacuum and the tube sealed. The tube was heated to 140°C for 30 hrs. while rocking. After which the tube was cooled (-196°C, liquid air), opened to a vacuum system, and the volatile components transferred to a cold trap by allowing the tube to warm to room temperature. The residual liquid product was purified by dissolving in $CHCl_3$ and passing over alumina. Removal of the chloroform yielded a mixture of polyadducts averaging to $C_{40}F_{36}H_{46}O_{10}$ (71) (95%); (average formula calculated by comparing ^1H and ^{19}F NMR integrations of (71) with those of an internal standard trifluoromethyl benzene); (Found: C, 32.9, H, 3.1; F, 51.7. $C_{40}F_{36}H_{46}O_{10}$ requires: C, 35.0, H, 3.3; F, 49.0%); IR, NMR and mass spectrum

B. Fluorination of hexafluoropropene/polyether adduct

1. Capillary Fluorination of $C_{40}F_{36}H_{46}O_{10}$ (71)

The mixture (71) (2.1g, 1.5mmol) was directly fluorinated in the capillary apparatus using a flow of 25% fluorine in nitrogen (50ml./min.) for 2 hrs. at 20°C, then 3 hrs. at 50°C, after which a 50% fluorine in nitrogen mixture was used (50ml./min.) dropping the temperature to 20°C for 2 hrs. then raising to 50°C for 3 hrs. The product was recovered as a clear viscous liquid (72), (69%); which averaged to $C_{40}F_{45}H_{37}O_{10}$ (as calculated by comparing ^1H and ^{19}F NMR integrations with those of an internal standard trifluoromethyl benzene).

2. Sealed System Fluorination of $C_{40}F_{45}H_{37}O_{10}$ (72)

The mixture (72), 0.6g, 0.4 mmol) was sealed in a nickel tube (70 ml.) fitted with a monel valve, the system evacuated to high vacuum and the valve sealed. Fluorine (0.86g, 22.6mmol) was condensed into the tube as previously described and the tube allowed to warm to room temperature where it remained for 10 hrs. The tube was then vented, re-evacuated and fluorine (0.86g, 22.6mmol.) condensed into the tube, the tube was heated to 40°C for 15 hrs. After which the tube was once again vented, re-evacuated and refilled with fluorine (0.86g, 22.6 mmol) and heated to 60°C for 10 hrs. The tube was finally vented, opened, and purged with nitrogen and the products extracted with 1,1,2-trichlorotrifluoro-ethane. The product was a clear viscous liquid of average formula $C_{40}F_{82}O_{10}$ (73), (38.4%); Found: C, 24·1 ; F, 64.5; $C_{40}F_{82}O_{10}$ requires C, 21.8, F, 70.8%); IR and NMR spectra 49

CHAPTER THIRTEEN

EXPERIMENTAL TO CHAPTER SEVEN

A. Attempted Dehydrodimerisation Reactions

1. 3 -[1,1,2,2-tetrafluoroethyl]-2,5-dioxahexane (3)

The adduct (3) (1.97g, 10.4mmol) and di-tertiary-butyl peroxide (0.73g, 5mmol) were placed in a 70 ml. pyrex tube and degassed using freeze thaw cycles under vacuum. The tube was sealed, heated to 140°C for 20 hrs., then cooled (-196°C) and opened to a vacuum. Volatile by-products were transferred, under vacuum, from the tube to another vessel by allowing the tube to warm to room temperature. The products (1.8g) of liquid were purified using preparative scale glc (column K, 130°C) to give (3) (91%). Identified by comparison of NMR and IR spectra with those of the starting material. IR, NMR and mass spectra 30.

2. 1,1,2,2-tetrafluoro-4,7-dioxaoctane (4)

The adduct (4) (2.08g, 10.9mmol) and di-tertiary-butyl peroxide (0.74g, 5.06mmol) were placed in a 70 ml pyrex tube and degassed using freeze thaw cycles under vacuum. The tube was sealed, heated to 140°C for 20 hours, then cooled (-196°C) and opened to a vacuum. Volatile by-products were transferred, under vacuum,from the tube to another vessel by allowing the tube to warm to room temperature. The products (1.8g) of liquid were purified using preparative scale glc (column K, 130°C) to give 1,1,2,2-tetrafluoro-4,7-dioxaoctane (4) (87%). Identified by comparison of NMR and IR spectra with those of the starting material; IR, NMR and mass spectra 31.

B. Attempted Polymerisation of 2-[1,1,2,3,3,3-hexafluoropropyl]-1,4-dioxan (76)

1. Free radical addition of 1,4-dioxan to hexafluoropropene

A mixture of 1,4 dioxan (9.12g, 10.4mmol) and hexafluoropropene (30.8g, 205mmol) were irradiated, in a nickel tube, with gamma rays for 72 hrs. (200 krads $hr.^{-1}$), using the general procedure described in Chapter Nine. The liquid products were distilled to give 2-[1,1,2,3,3,3-hexafluoropropyl]-1,4-dioxan (76) (90%), $b.p._{46}$ 80°C. Identified by comparison of NMR and mass spectra with those of an authentic sample.

2. Attempted Polymerisation of (76) using SbF_5

The adduct (78) (1.64g, 6.9mmol) was placed in a dry flask, which was constantly purged with nitrogen and situated in an ice bath at 0°C. Antimony pentafluoride (0.6g, 2.7mmol) was added, dropwise, over a period of *ca.* 5 minutes with no vigorous reaction. After 4 hours the temperature was gradually increased until the mixture began to reflux and this was maintained for a further two hours. The mixture was then cooled, washed with water and the organic layer (1.4g) recovered. The products were distilled under vacuum to give 2-[1,1,2,3,3,3-hexafluoropropyl]-1,4-dioxan (76) (85%) identified by comparison of NMR and IR with those of the starting material.

C. Dehydrofluorination of 1,1´-di-1-[1,2,2,3,4,4-hexafluorocyclobutyl]ethyl ether (20)

The adduct (20) (1.71g, 4.3mmol) and potassium hydroxide (2.5g, 44mmol) in 5 ml water were heated, while stirring, in a flask constantly flushed with nitrogen, to 110°C for 9 hrs. The organic layer (0.7g) was then recovered and the products isolated using preparative scale glc (Column 10% SE30, 120°C) to give di-1-[perfluorocyclobut-1-enyl]-ethyl ether (77), (27%); (Found: C, 40.5; H, 2.8; $C_{12}F_{10}H_8O$ requires, C, 40.2; H, 2.8%); IR, NMR and mass spectra 50 ; and a mixture of isomers $C_{12}F_{11}H_9O$ (78),(79) (24%); (Found: C, 37.9; H, 2.08; $C_{12}F_{11}H_9O$: requires C, 38.0; H, 2.9%); IR, NMR and mass spectra 51 .

APPENDIX ONE

INFRA RED SPECTRA

1. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether.
2. Di-(2,2,3,4,4,4-hexafluoro-1-methylbutyl) ether
3. 1-(1,2,3,3,4,4-Hexafluorocyclobutyl)ethyl ethyl ether
4. Di-1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether
5. 1-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)ethyl ethyl ether
6. Di-1-(1,2,2,3,3,4,4,5,5-octafluorocyclopentyl)ethyl ether
7. 1-(1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexyl)ethyl ethyl ether
8. Di-1-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)ethyl ether
9. 3-Chloro-2,2,3-trifluoro-1-methylpropyl ethyl ether
10. Telomeric mixture of $CH_3CH_2OCH(CH_3)[CF_2CFCl]_nH$ (where n=2 or 3)
11. 2,2,3-trifluoro-1-methylpropyl ethyl ether
12. Telomeric mixture of $CH_3CH_2OCH(CH_3)[CF_2CFH]_nH$ (where n=2 or 3)
13. 4-(1,1,2,3,3,3-Hexafluoropropyl)-3,6-dioxaoctane
14. 1,1,1,2,3,3-Hexafluoro-4-methyl-5,8-dioxadecane
15. 1,1,1,2,3,3-Hexafluoro-4-methyl-6-(1,1,2,3,3,3-hexafluoropropyl)-5,8-dioxadecane
16. 1,1,1,2,3,3,10,10,11,12,12,12-Dodecafluoro-4,9-dimethyl-5,8-dioxadodecane
17. 1,1,1,2,3,3,10,10,11,12,12,12-Dodecafluoro-4,9-dimethyl-6-(1,1,2,3,3,3-hexafluoropropyl)-5,8-dioxadodecane
18. A mixture of mono-adducts of F-cyclopentene and ethyl glyme
19. 2,4-Di-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxaoctane
20. 2,7-Di-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxaoctane
21. 2,4,7-Tri-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxaoctane
22. A mixture of mono-adducts of cyclobutene and ethyl glyme
23. A mixture of di-adducts of cyclobutene and ethyl glyme
24. A mixture of mono-adducts of hexafluoropropene and ethyl diglyme
25. A mixture of di-adducts of hexafluoropropene and ethyl diglyme

26. A mixture of tri-adducts of hexafluoropropene and ethyl diglyme

27. A mixture of tetra-adducts of hexafluoropropene and ethyl diglyme

28. 1,1,1,2,3,3-Hexafluoro-5,8-dioxanonane

29. 3-(1,1,2,3,3,3-Hexafluoropropyl)-2,4-dioxahexane

30. 3-(1,1,2,2-Tetrafluoroethyl)-2,5-dioxahexane

31. 1,1,2,2-Tetrafluoro-4,7-dioxaoctane

32. Telomeric adducts of tetrafluoroethene and monoglyme

33. Perfluoro-1-methylbutyl ethyl ether

34. Perfluoro-di-(1-methylbutyl) ether

35. Perfluoro-4-methyl-5,8-dioxadecane

36. Perfluoro-1-methylbutyl butyl ether

37. Perfluoro-4-methyl-6-propyl-5,8-dioxadecane

38. Perfluoro-4,9-dimethyl-5,8-dioxadodecane

39. Perfluoro-4,9-dimethyl-6-propyl-5,8-dioxadodecane

40. Perfluoro-1-cyclobutylethyl ethyl ether

41. Perfluoro-di-(1-cyclobutylethyl) ether

42. Perfluoro-di-(1-cyclopentylethyl) ether

43. Perfluoro-1-methylhexyl-1-cyclopentylethyl ether

44. Perfluoro-di-(1-cyclohexylethyl) ether

45. Perfluoro-1-chlorobutane

46. Perfluoro-3-chloro-1-methylpropyl ethyl ether

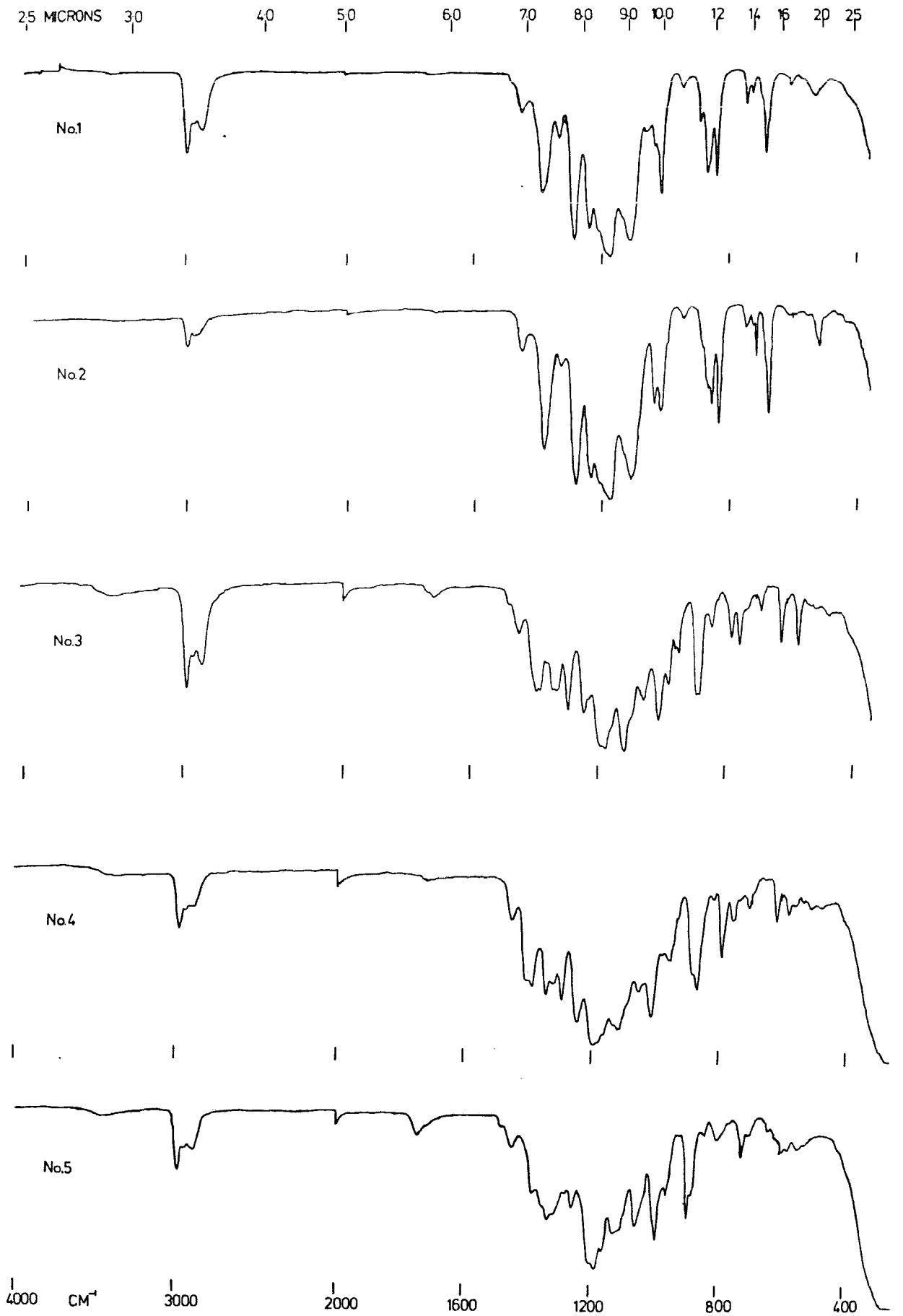
47. Polyethyleneglycol diethyl ether (av.molecular weight 456)

48. Polyethyleneglycol diethyl ether (456) hexafluoropropene heptaadduct (*ca.* $C_{40}F_{36}H_{36}O_{10}$)

49. Perfluoropolyether (*ca.* $C_{40}F_{82}O_{10}$)

50. Di-1-(cyclobut-1-enyl)ethyl ether

51. 1-Perfluorocyclobut-1-enylethyl 1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether.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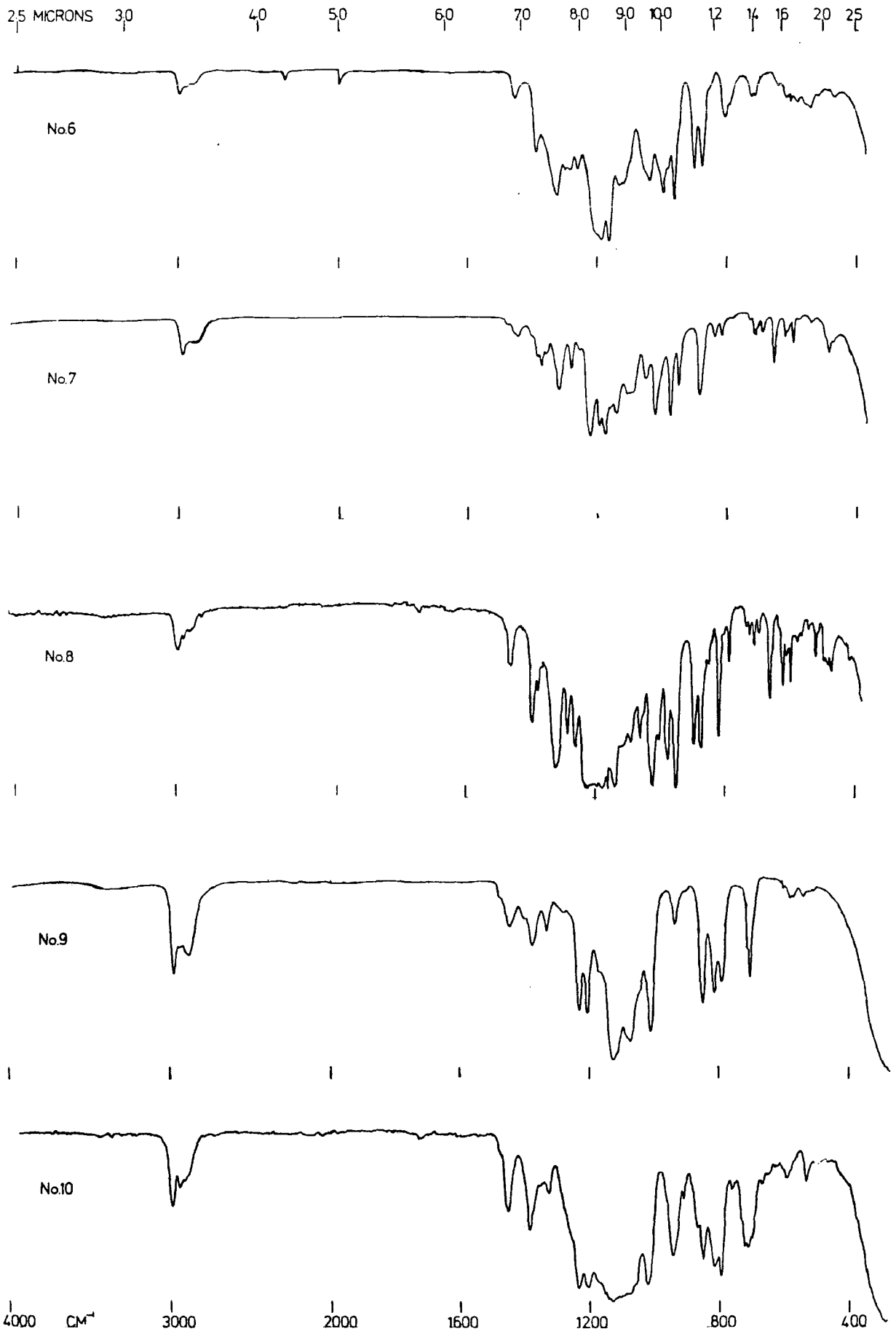
No.1
No.2
No.3
No.4
No.5
4000 CM⁻¹ 3000 2000 1600 1200 800 400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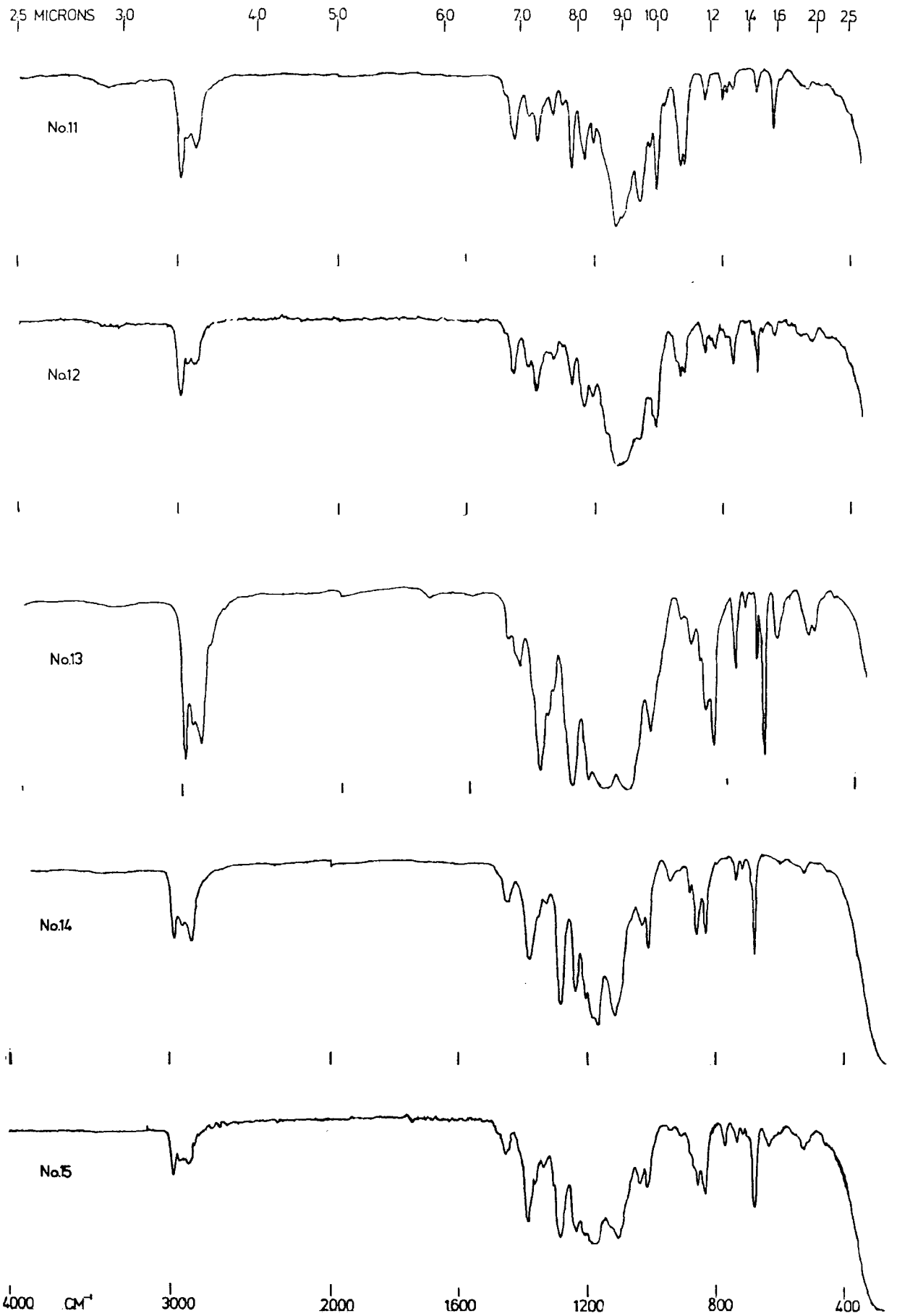
No.6
No.7
No.8
No.9
No.10
4000 CM⁻¹ 3000 2000 1600 1200 800 400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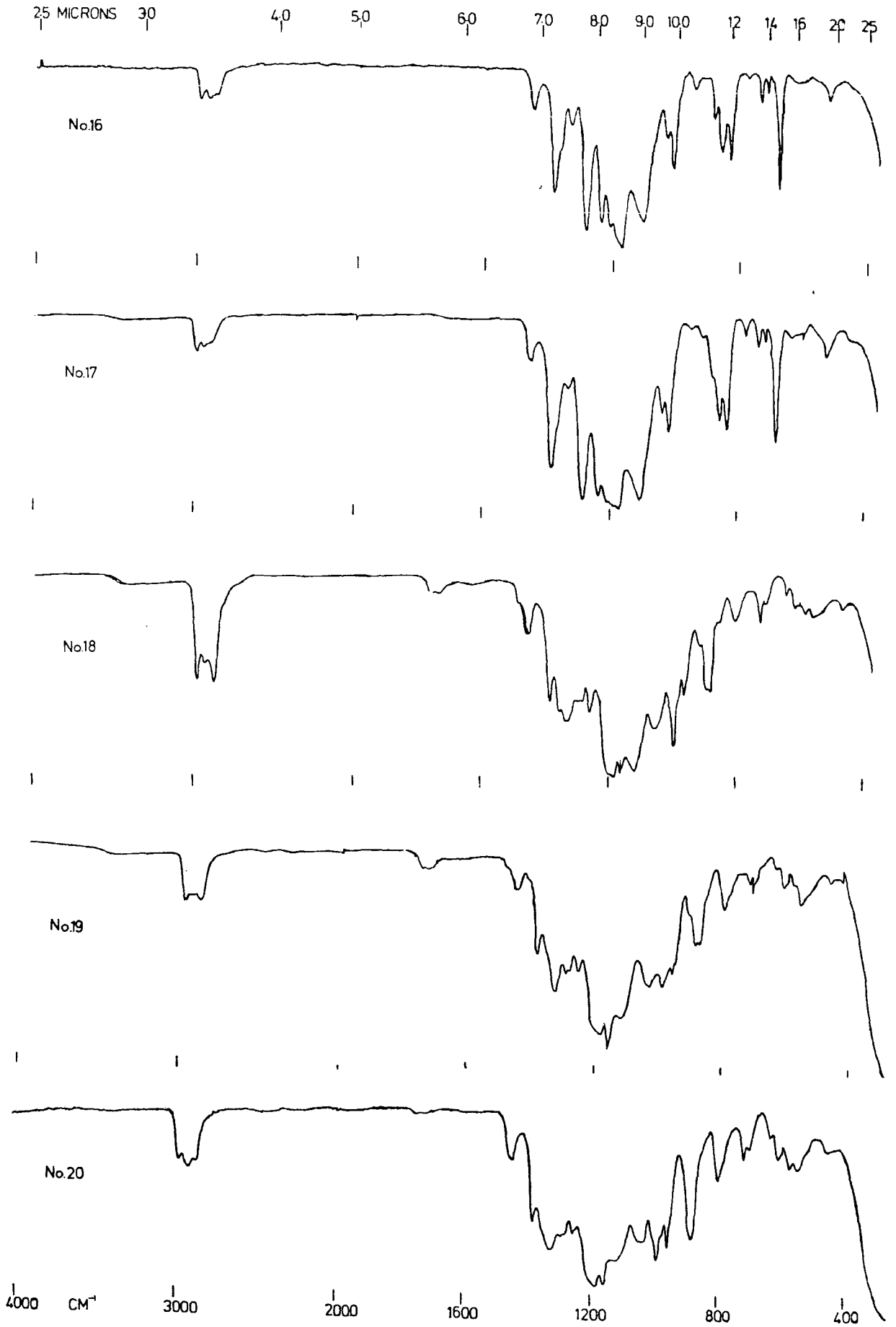
No.11
No.12
No.13
No.14
No.15
4000 CM⁻¹ 3000 2000 1600 1200 800 400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No.16
No.17
No.18
No.19
No.20
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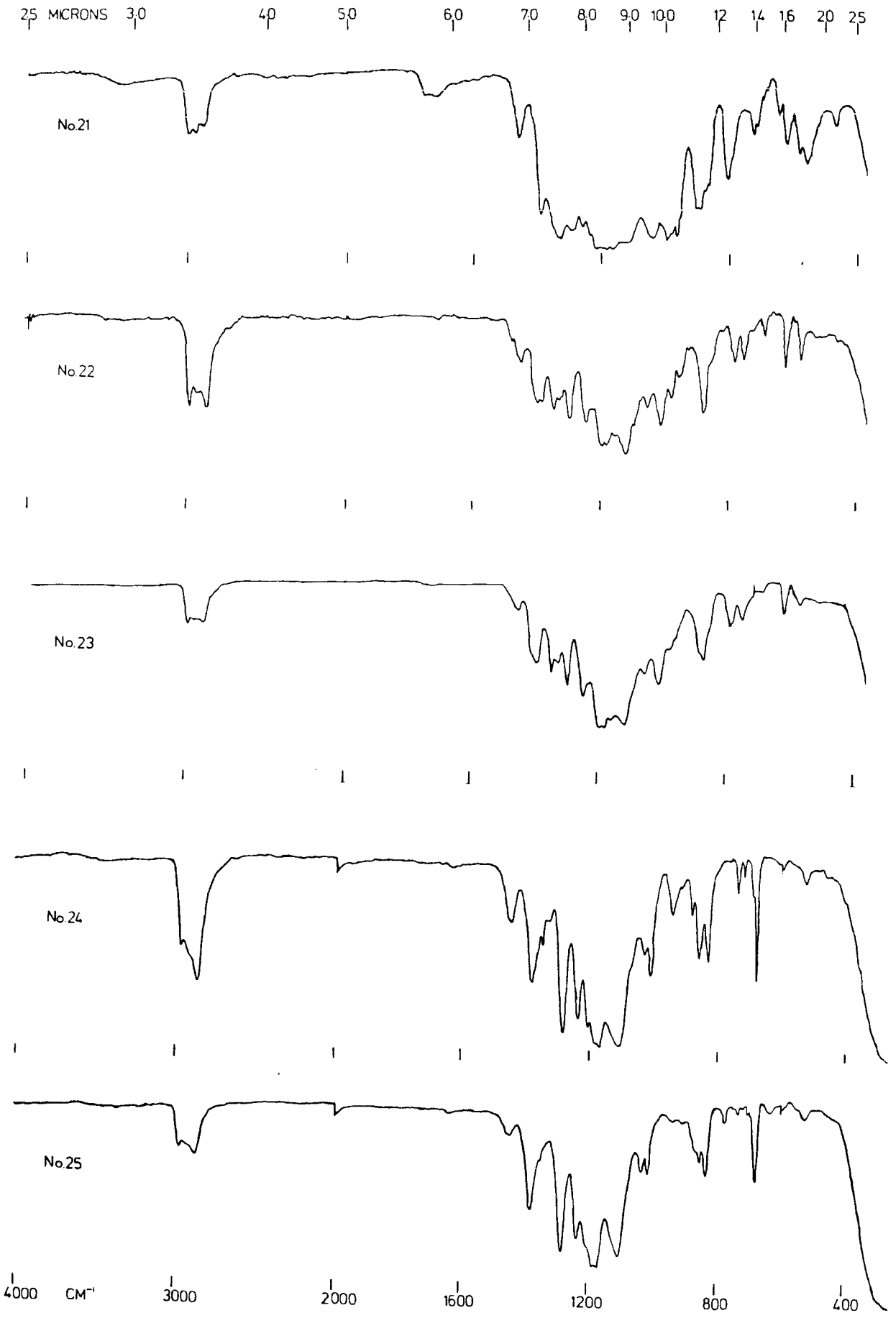
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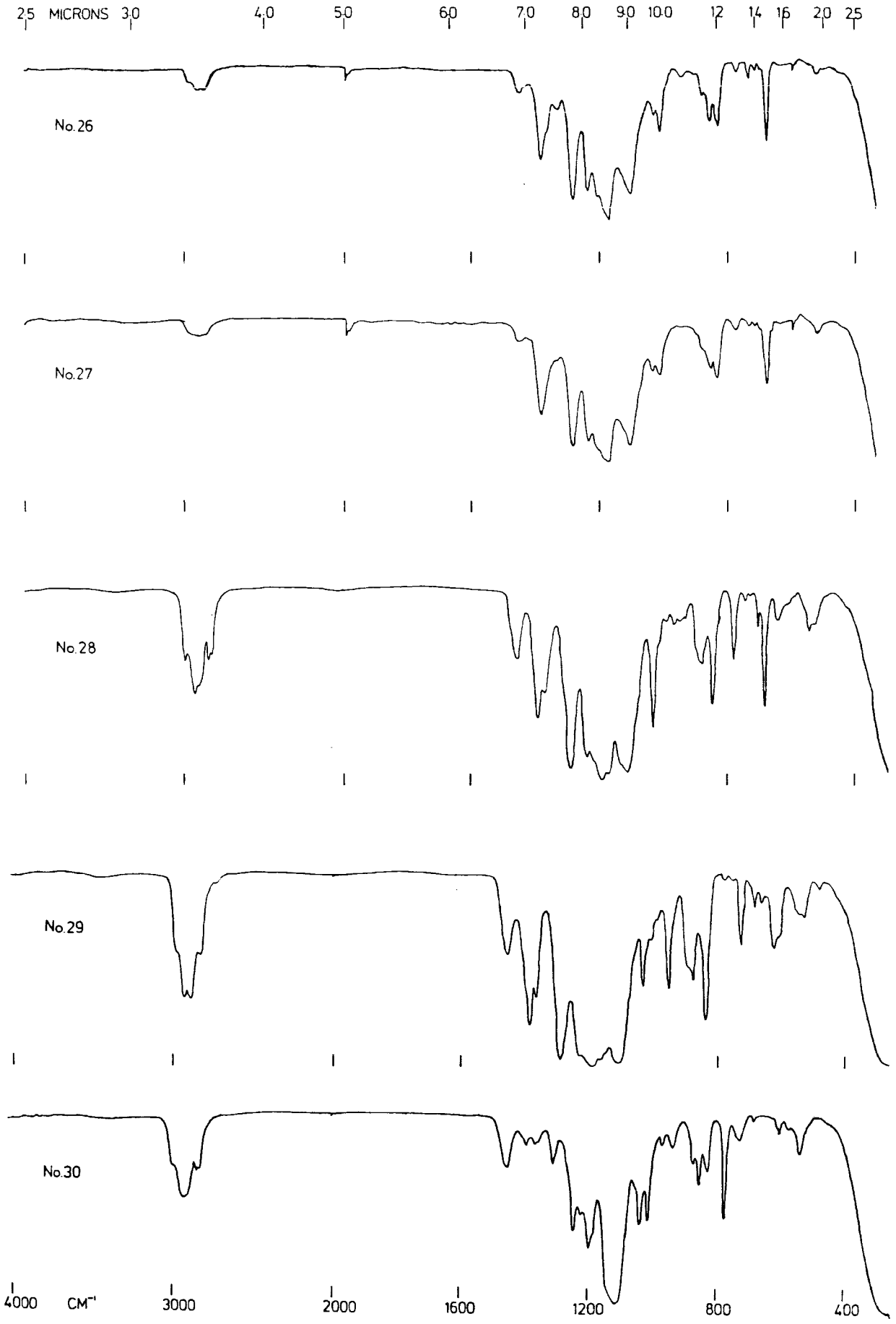
No.21
No.22
No.23
No.24
No.25
4000 CM⁻¹ 3000 2000 1600 1200 800 400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No.26
No.27
No.28
No.29
No.30
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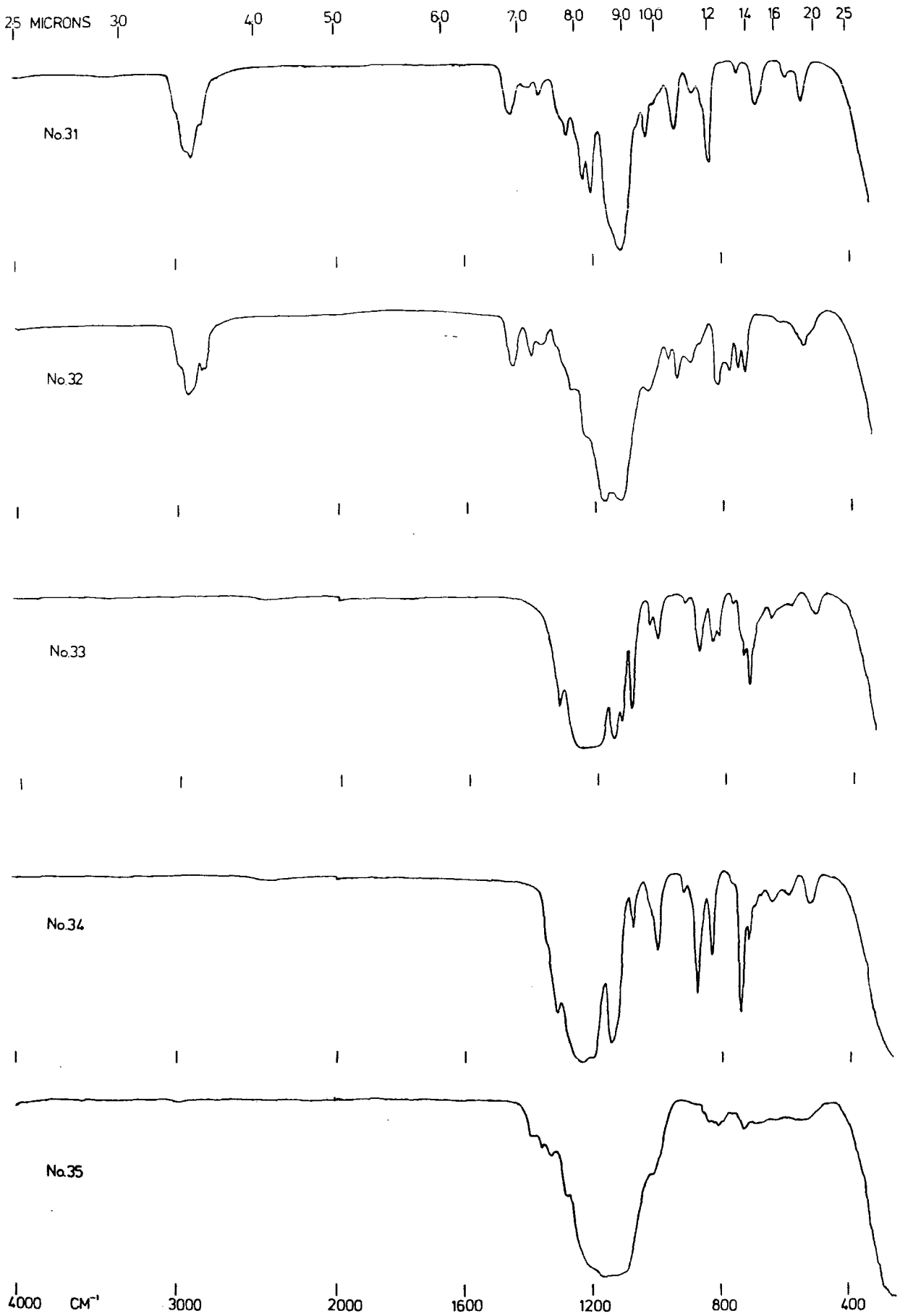
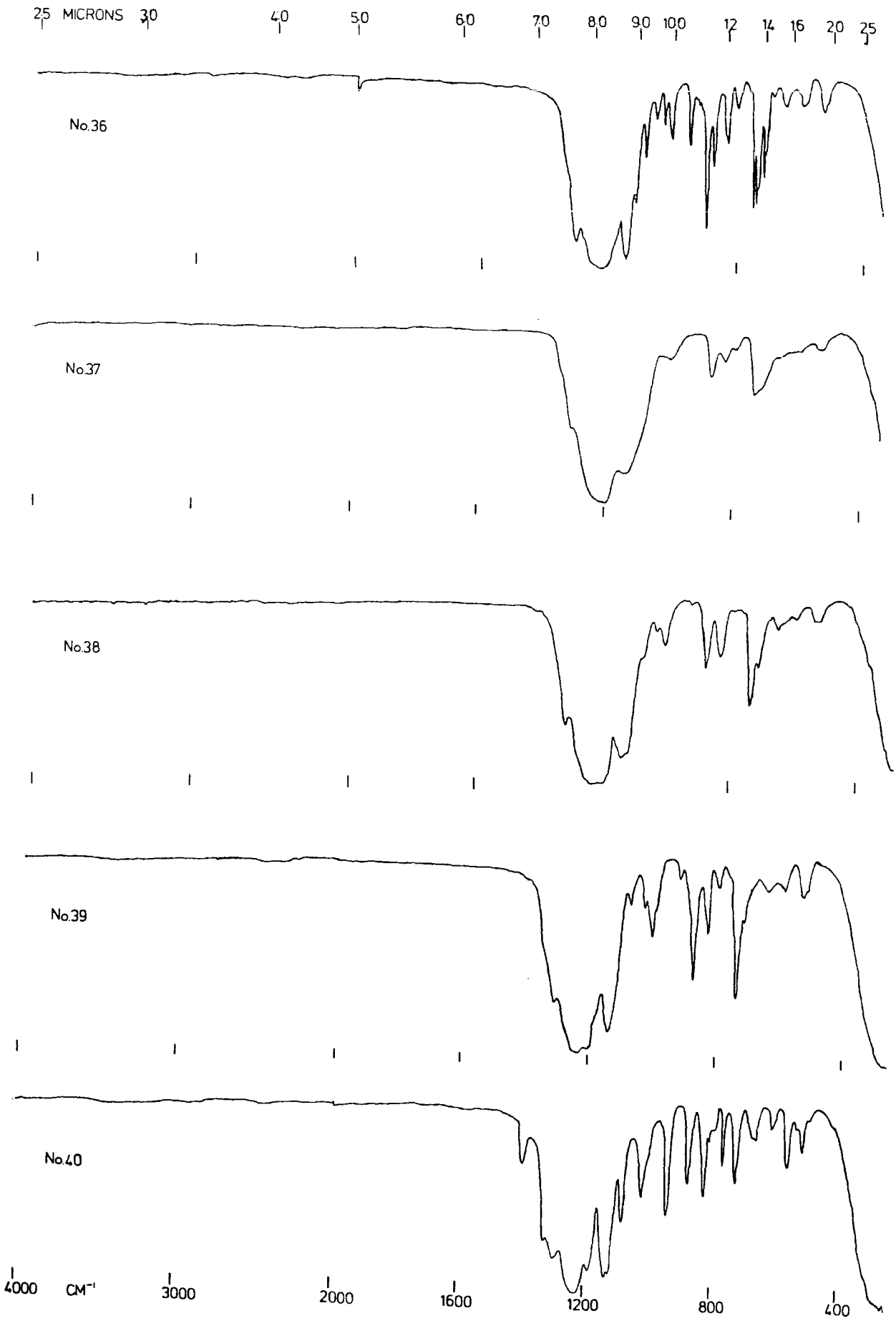

25 MICRONS 30 40 50 60 70 80 90 100 12 14 16 20 25
No.31
No.32
No.33
No.34
No.35
4000 CM⁻¹ 3000 2000 1600 1200 800 400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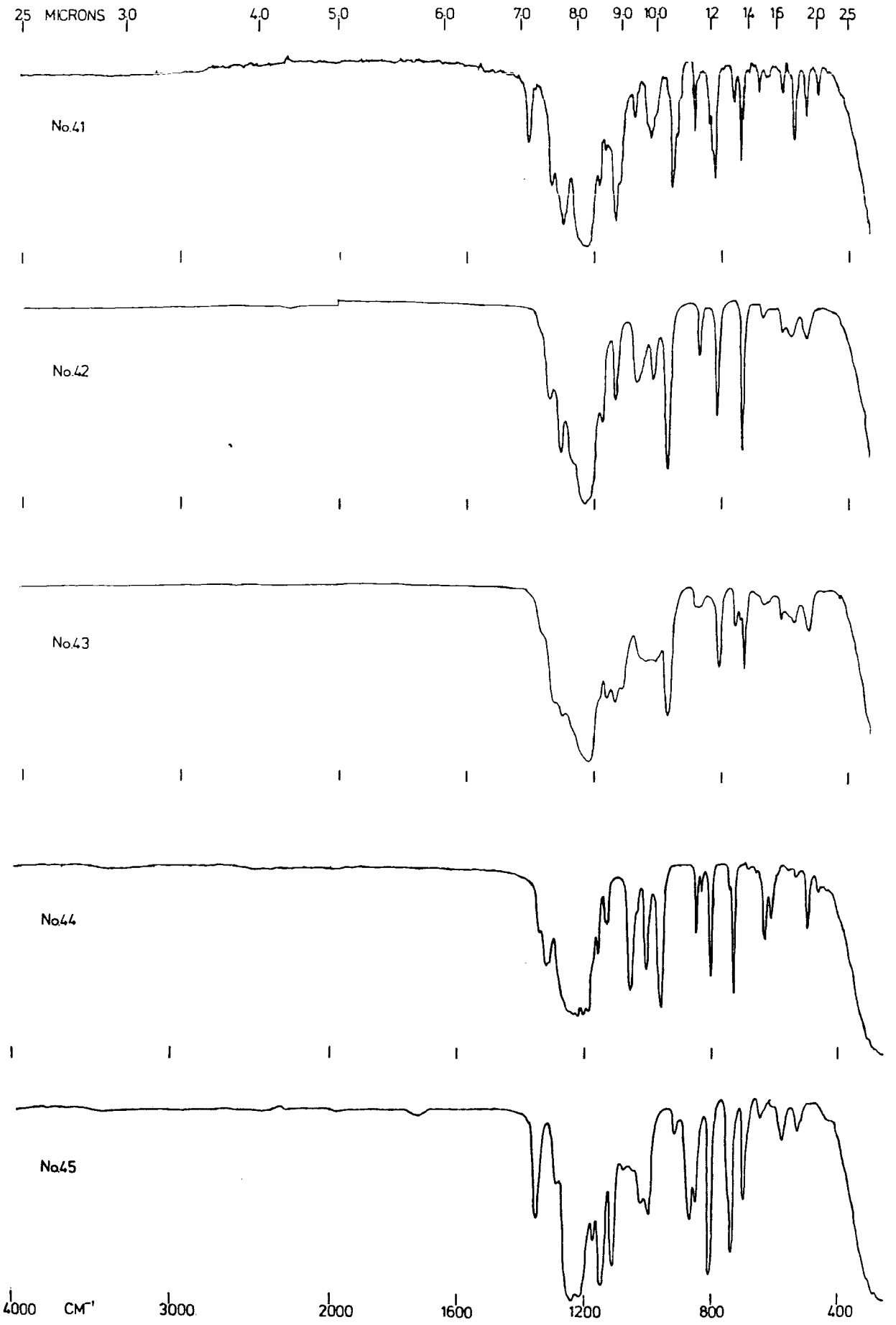
No.37
No.38
No.39
No.40
4000 CM⁻¹ 3000 2000 1600 1200 800 400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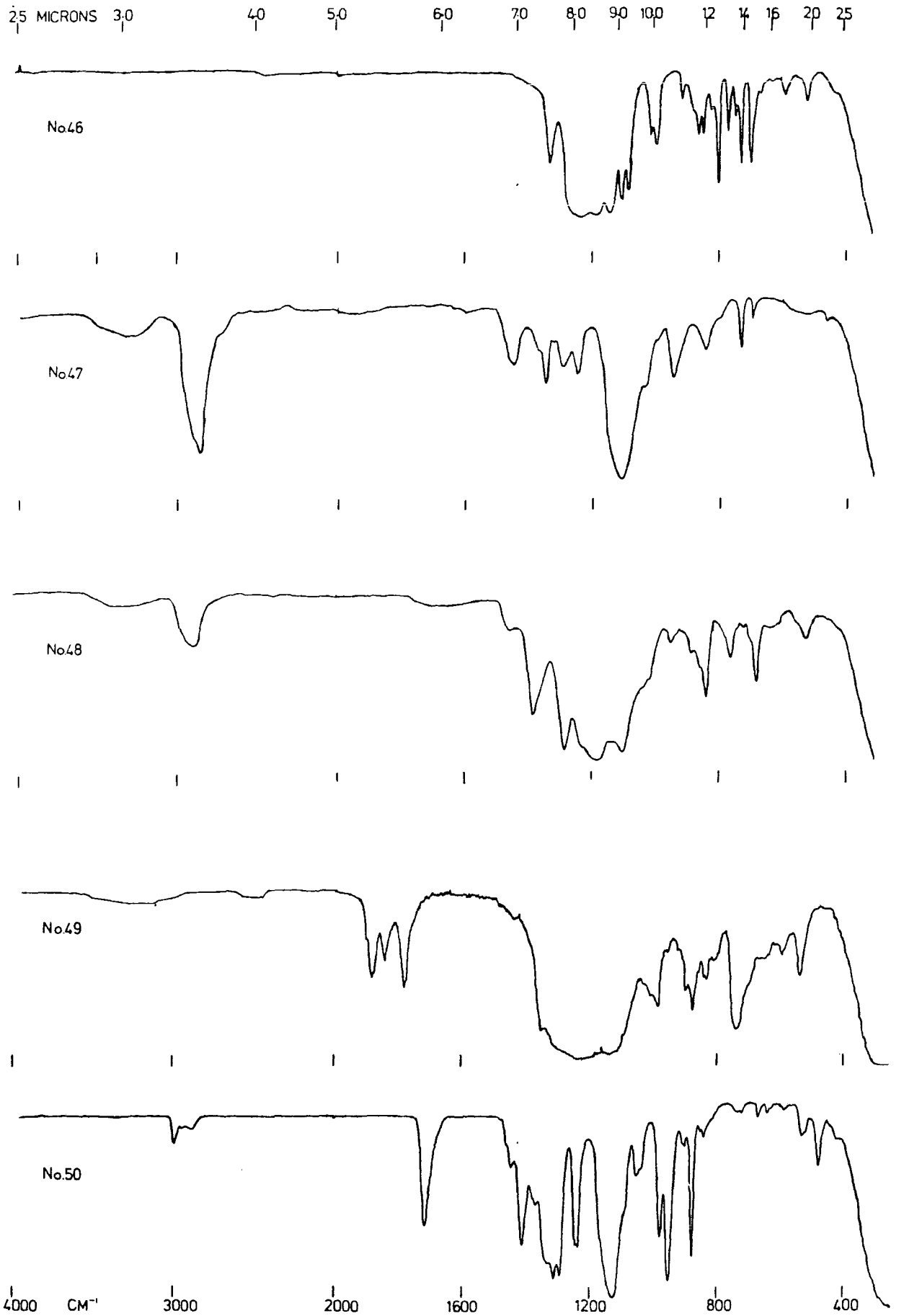
No.41
No.42
No.43
No.44
No.45
4000 CM⁻¹ 3000 2000 1600 1200 800 400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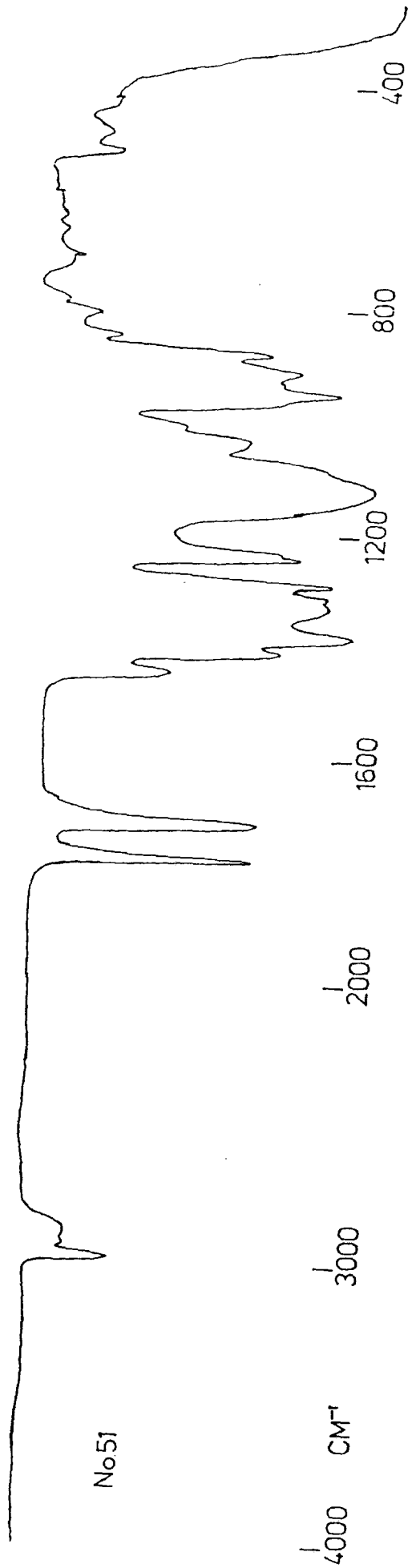
No.46
No.47
No.48
No.49
No.50
4000 CM⁻¹ 3000 2000 1600 1200 800 400


No.51
4000
3000
2000
1600
1200
800
400
CM⁻¹

APPENDIX TWO

N.M.R. SPECTRA

1. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether
2. Di-2,2,3,4,4,4-hexafluoro-1-methylbutyl ether
3. 1-(1,2,3,3,4,4-Hexafluorocyclobutyl)ethyl ethyl ether
4. Di-1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether
5. 1-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)ethyl ethyl ether
6. Di-1-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)ethyl ether
7. 1-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)ethyl ethyl ether
8. Di-1-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)ethyl ether
9. 3-Chloro-2,2,3-trifluoro-1-methylpropyl ethyl ether
10. Telomeric adducts of chlorotrifluoroethene and ethyl ether
11. 2,2,3-Trifluoro-1-methylpropyl ethyl ether
12. Telomeric adducts of trifluoroethene and ethyl ether
13. 4-(1,1,2,3,3,3-Hexafluoropropyl)-3,6-dioxahexane
14. 1,1,1,2,3,3-Hexafluoro-4-methyl-5,8-dioxadecane
15. 1,1,1,2,3,3-Hexafluoro-4-methyl-6-(1,1,2,3,3,3-hexafluoropropyl)-5,8-dioxadecane
16. 1,1,1,2,3,3,10,10,11,12,12,12-Dodecafluoro-4,9-dimethyl-5,8-dioxadodecane
17. 1,1,1,2,3,3,10,10,11,12,12,12-Dodecafluoro-4,9-dimethyl-6-(1,1,2,3,3,3-hexafluoropropyl)-5,8-dioxadodecane
18. Mixture of mono-adducts of F-cyclopentene and ethyl glyme
19. 2,4-Di(1,2,3,3,4,4,5,5-octafluorocyclopentyl-3,6-dioxahexane
20. 2,7-Di(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxahexane
21. 2,4,7-Tri(1,2,3,3,4,4,5,5-octafluorocyclopentyl-3,6-dioxahexane
22. Mixture of mono-adducts of F-cyclobutene and ethyl glyme
23. Mixture of di-adducts of F-cyclobutene and ethyl glyme
24. Mixture of mono-adducts of hexafluoropropene (HFP) and ethyl diglyme
25. Mixture of di-adducts of HFP and ethyl diglyme
26. Mixture of tri-adducts of HFP and ethyl diglyme
27. Mixture of tetra-adducts of HFP and ethyl diglyme

28. 1,1,1,2,3,3-Hexafluoro-5,8-dioxanonane

29. 3-(1,1,2,3,3,3-Hexafluoropropyl)-2,4-dioxahexane

30. 3-(1,1,2,2 -Tetrafluoroethyl)-2,5-dioxahexane

31. 1,1,2,2-Tetrafluoro-4,7-dioxaoctane

32. A mixture of telomeric adducts of tetrafluoroethylene and monoglyme

33. Perfluoro-1-methylbutyl ethyl ether

34. Perfluoro-di (1-methylbutyl) ether

35. Perfluoro-4-methyl-5,8-dioxadecane

36. Perfluoro-1-methylbutyl butyl ether

37. Perfluoro-4-methyl-6-propyl-5,8-dioxadecane

38. Perfluoro-4,9-dimethyl-5,8-dioxadodecane

39. Perfluoro-4,9-dimethyl-6-propyl-5,8-dioxadodecane

40. Perfluoro-1-cyclobutylethyl ethyl ether

41. Perfluoro-di(1-cyclobutylethyl)ether

42. Perfluoro-di(1-cyclopentylethyl)ether

43. Perfluoro-1-cyclopentylethyl 1-methylhexyl ether

44. Perfluoro-di(1-cyclohexylethyl)ether

45. Perfluoro-1-chloro-n-butane

46. Perfluoro-3-chloro-1-methylpropyl ethyl ether

47. Polyethylene glycol diethyl ether (456)

48. Polyethylene glycol diethyl ether/hexafluoropropene hepta adduct

49. Perfluoropolyether

50. Di-1-(perfluorocyclobut-1-enyl)ethyl ether

51. 1-Perfluorocyclobut-1-enyl)ethyl 1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether.

52. Perfluoro-1-methylbutyl isopropyl ether

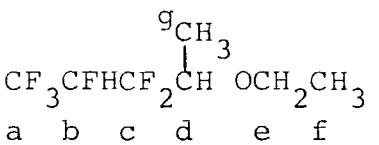
53. Perfluoro-n-hexane

54. Perfluoro-n-octane.

The following abbreviations are used in this appendix: S, singlet; D, doublet; T, triplet; Q, quartet; M, multiplet.

Chemical shifts are quoted in parts per million relative to the external standards $CFCl_3$(δF) and TMS(δH). Shifts upfield of $CFCl_3$ are quoted as positive, as are shifts downfield of TMS.

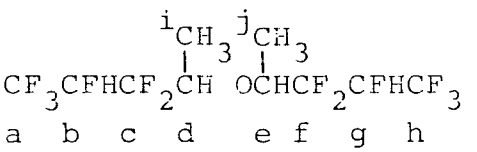
1. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether



Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment
δF			
76.7	M	)	
		) 3	) a
77.3	M	)	)
121.3,125.9	AB, J_{FF}=230Hz	)	)
		) 2	) c
127.0,131.7	AB,J_{FF}=230Hz	)	)
216.1	D of M J_{FH}=40Hz	)	)
		) 1	) b
219.2	D of M J_{FH}=40Hz	)	)
δH			
0.8	T, J_{HH} = 6Hz	3	f
0.9	D, J_{HH} = 5Hz	3	g
3.1	Q, J_{HH} = 7Hz	)	)
		) 3	) d,e
3.3	Q, J_{HH} = 7Hz	)	)
4.7	D of M, J_{HF} = 40Hz	1	b

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

2. Di-2,2,3,4,4,4-hexafluoro-1-methylbutyl ether



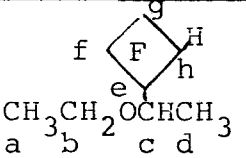
δF

76.1	M	3	a,h
121.6,123.3 127.0,128.3	unresolved Abs.	2	c,f
214.2	D of M, J_{FH} = 40Hz	1	b,g

δH

1.1	D, J_{HH} = 6Hz	3	i,j
3.8	M	1	d,e
4.8	D of M, J_{HF} = 40Hz	1	b,g

3. 1-(1,2,3,3,4,4-Hexafluorocyclobutyl)ethyl ethyl ether



δF

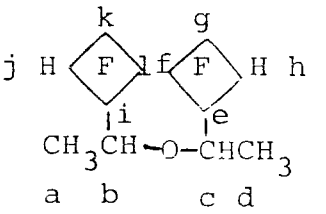
114.8 118.1 129.1 129.8 133.7 136	M	4	g,f
186.3 202.1	M	1	e
215.5 219.2 222.9	D of M J_{FH} = 51Hz	1	h

δH

1.2 1.3	D, J_{HH} = 3.5Hz T, J_{HH} = 4.5Hz	6	a,d
3.6	M	3	b,c
5.1	D of M, J_{HF} = 47Hz	1	h

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

4. Di-1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether



δF

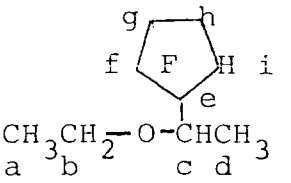
117.6	M	)		
		)		
121.6	M	)		
		)		
129.0	M	)		
		)		
131.3	M	)		
		)	4	k,l,g,f
135.0	M	)		
		)		
139.0	M	)		
190.0	M	)		
		)	1	i,e
205.3	M	)		
216.8	D of M, J_{FF} = 47Hz	)		
		)	1	j,h
224.1	D of M, J_{FF} = 47Hz	)		

δH

1.0	D of M, J_{HH} = 5.1Hz	3	a,d
3.8	M	1	b,c
4.7	D of M, J_{HF} = 47Hz	1	j,h

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

5. 1-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)ethyl ethyl ether



δF

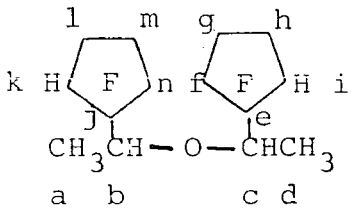
111.2, 114.2	Overlapping ABs.	6	f,g,h
118.1, 119.4			
120.9, 121.0			
122.9, 124.9			
125.5, 125.9			
127.0, 128.4			
129.0, 129.5			
130.3, 131.6			
132.7, 133.5			
189.5	M	1	e
191.3	M		
195.2	M		
209.5	D of M, J_{FH} = 43Hz	1	i
210.9	D of M, J_{FH} = 43Hz		
224.6	D of M, J_{FH} = 43Hz		
228.7	D of M, J_{FH} = 43Hz		

δH

1.2	T of M, J_{HH} = 9Hz	6	a,d
1.4	D of M, J_{HH} = 7Hz		
3.5	M (broad)	3	b,c
5.0	D of M, J_{FH} = 41Hz	1	i

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

6. Di-1-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)ethyl ether



δF

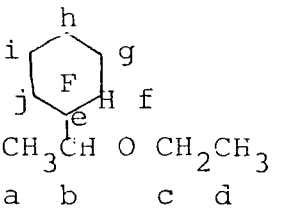
114,8, 117.6 119.9, 123.0 124.9, 127.6 129.0, 130.0	overlapping ABs.	6	l,m,n,f,g,h
189.3 193.3 194.7	M M M	1	e,j
210.0 226.6 228.6	M M M	1	k,i

δH

1.4	M	3	a,d
4.1	M	1	b,c
4.8	D of M, J_{HF} = 40Hz	1	k,i

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

7. 1-(1,2,3,3,4,4,5,5,6,6-dodecafluorocyclohexyl)ethyl ethyl ether



δF

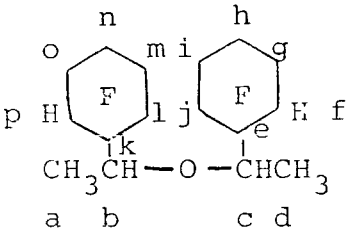
117.4, 119.4	overlapping ABs and M		g,h,i
121.2, 122.5			
123.7, 124.6			
125.8, 128.4			
129.3, 131.0			
133.6, 141.0			
142.3, 145.0			
193.4	M		e
197.3	M		
211.4	M		f
226.2	M		

δH

1.1	T, J_{HH} = 10Hz	6	a,d
1.4	M		
3.5	M	3	b,c
3.8	M		
5.3	D of M, J_{HF} = 50Hz	1	f

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

8. Di-1-(1,2,3,3,4,4,5,5,6,6-dodecafluorocyclohexyl)ethyl ether



δF

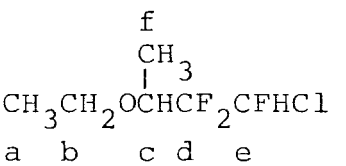
120.1, 121.5	overlapping ABs and Ms		g,h,i,j,l, m,n,o
122.4, 123.6			
126.1, 127.2			
127.6, 128.6			
129.3, 129.7			
130.1, 129.6			
140.7, 144.0			
190.0	M		p,f
191.1	M		
214.6	M		e,k
232.6	M		

δH

1.4	M	3	a,d
4.4	M	1	b,c
5.2	D of M, J_{HF} = 50Hz	1	f,p

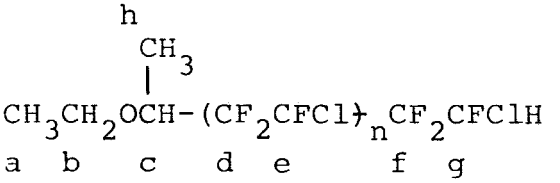
Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

9. 3-Chloro-2,2,3-Trifluoro-1-methylpropyl ethyl ether



δF			
127.8	M	2	d
155.0	D of T, J_{FH} = 43Hz, J=13Hz	1	e
161.8	D of T, J_{FH} = 43Hz, J=13Hz		
δH			
1.0	T of M, J_{HH} = 6Hz	6	a
1.8	D of M, J_{HH} = 6Hz		f
3.4	M	3	b,c
6.2	D of M, J_{HF} = 43Hz	1	e

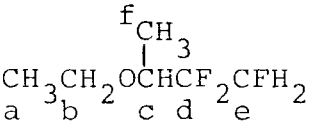
10. Telomeric mixture of $C_2H_5OCH(CH_3)(CF_2CFCl)_nH$ (n=1,2)



δF			n = 1,2
116	M	-	d,e,f
121	M (broad)		
125	M		
126.6	M		
151.6	M	-	g
154.0	M (broad)		
160.0	M		
δH			
1.0	overlapping D and T	3	a,h
1.16			
1.3			
3.6	M	3	c
4.0	M		
6.3	D of M, J_{HF} = 50Hz	1	g

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

11. 2,2,3-Trifluoro-1-methylpropyl ethyl ether



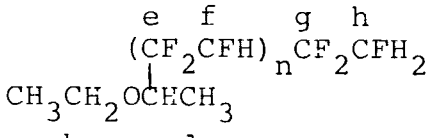
δF

118.1, 127.6	AB, J_{FF} = 284Hz		d

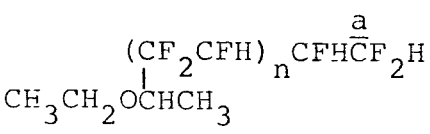
δH

0.9	M	6	a,f
3.4	M	3	b,c
4.4	D of M, J_{HF} = 54Hz	2	e

12. A mixture of Telomeric Adducts of trifluoroethene and diethyl ether



A



B

n = 1 or 2

δF

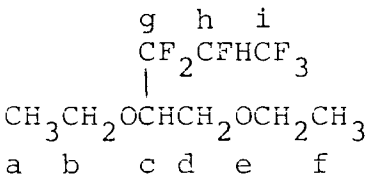
115.3, 120.6 122.2, 124.2 125.8, 128.8 134.3, 135.0	overlapping ABs. and Ms.	4	e,g
218.0	D of M	1	f

δH

0.9	T, J_{HH} = 7Hz	6	b
1.0	D, J_{HH} = 7Hz		d
3.25	M	7.6	e,g
4.3	D of M, J_{HF} = 48Hz		f,h
5.7	T of M, J_{HF} = 52Hz	minor intensity	a isomer B.

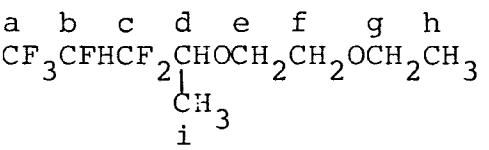
Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

13. 4-(1,1,2,3,3,3-Hexafluoropropyl)-3,6-dioxooctane



δF			
76.4	M	3	i
121.7, 124.7	AB, J_{FF} = 230Hz	2	g
125.3, 127.9	AB, J_{FF} = 230Hz		
215.1	D of M, J_{FH} = 40Hz	1	h
217.0	D of M, J_{FH} = 40Hz		
δH			
0.87	T, J_{HH} = 6Hz	6	a,f
3.2	M	7	b,c,d,e
4.9	D of M, J_{FH} = 40Hz	1	h

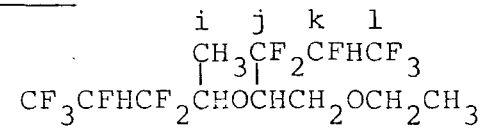
14, 1,1,1,2,3,3-Hexafluoro-4-methyl-5,8-dioxadecane



δF			
75.9	M	3	a
76.4	M		
120.3, 125.3	AB, J_{FF} = 250 Hz	2	c
129.0, 135.8	AB, J_{FF} = 255Hz		
215.0	D of M, J_{FH} = 40Hz	1	b
218.6	D of M, J_{FH} = 40Hz		
δH			
0.8	T, J_{HH} = 6Hz	6	h
0.9	D, J_{HH} = 7Hz		i
3.1	M	7	d,e,f,g
3.2	M		
4.7	D of M, J_{HF} = 40Hz	1	b

Shift p.p.m.	Fine Structure Constant Coupling	Relative Intensity	Assignment

15. 1,1,1,2,3,3-Hexafluoro-4-methyl-6-(1,1,2,3,3,3-Hexafluoropropyl)-5,8-dioxadecane



a b c d e f g h i j k l

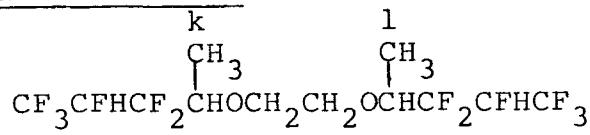
δF

75.2	M	3	a,l
115.6, 118.4 121.6, 122.8 125.3	) overlapping) unresolved) ABs.	2	c,j
211.0 213.1	M M	1	b,k

δH

0.7	T, J_{HH} = 6Hz	3	i
0.8	D, J_{HH} = 5Hz		h
2.8 3.1 3.2	M M M	3	d,e,f,g
4.6	D of M, J_{HF} = 46Hz	1	b,k

16. 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-5,8-dioxadodecane



a b c d e f g h i j k l

δF

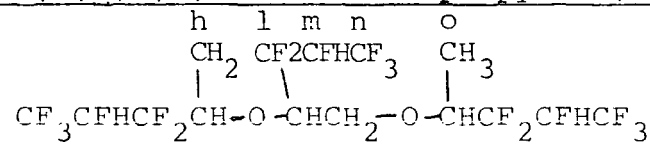
76.5 76.9	M M	3	a,j
125 130	M M	2	c,h
215 218.9	M M	1	b,i

δH

1.1	D, J_{HH} = 5Hz	3	k,l
3.4	M	6	d,e,f,g
4.8	D of M, J_{HF} = 40Hz	1	b,i

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

17. 1,1,1,2,3,3,10,10,11,12,12,12-dodecafluoro-4,9-dimethyl-6-(1,1,2,3,3,3-hexafluoropropyl)-5,8-dioxadodecane



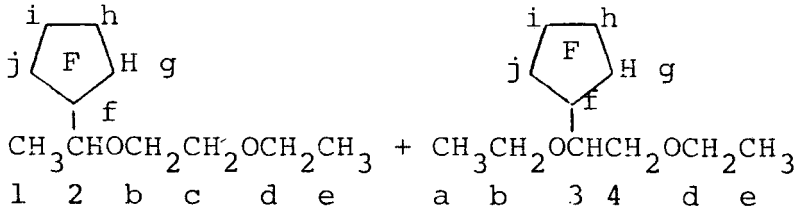
δF

75.4	M	3	a,j,n
126	M	2	c,h,l
128	M		
217	M	1	b,i,m

δH

1.1	D of M, J_{HH} = 5Hz	3	k,o
3.6	M	4	d,e,f,g,h
4.8	D of M, J_{HF} = 52Hz		b,m,i

18. F-cyclopentene/ethyl glyme mono-adduct isomers



δF

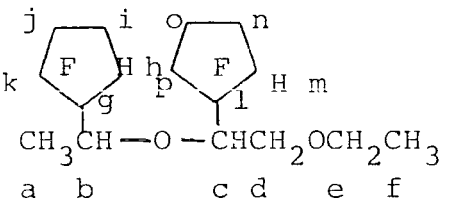
116.9, 119.8 120.1, 120.5 121.6, 124.0 125.1, 125.6 126.5, 127.7 128.6, 129.1 129.4, 129.9 130.2, 130.5 131.7, 132.4 132.9, 133.3 134.6, 135.7	overlapping ABs. and Ms.		j,i,h
191.6	M		f
194.8	M		
185.3	M		
197.3	M		
210.6	D of M, J_{FH} = 47Hz		g
212.4	D of M, J_{FH} = 47Hz		
230.4	D of M, J_{FH} = 47Hz		

δH

1.0	T of M, J_{HH} = 7Hz	6	a,e
1.2	D of M, J_{HH} = 8Hz		1
3.4	M (broad)	8	2,3,4,b,c,d
5.0	D of M, J_{HF} = 48Hz		g

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

19. 2,4-Di-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxaoctane



δF

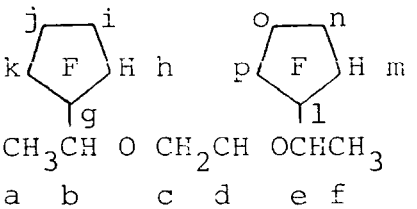
118.0, 121.0	)		
121.5, 122.1	)		
122.9, 123.5	) overlapping ABs. and M	6	k,i,j,n,o,p
127.1, 130.6	)		
135.0	)		
190.1	M)		
192.2	M)	1	g,l
209.1	D of M, J_{FH} = 50Hz)		
210.9	D of M, J_{FH} = 50Hz)	1	h,m
219.2	D of M, J_{FH} = 50Hz)		

δH

1.1	M	3	a,f
3.5	M)		b,c,d,e
4.8	M)	4	h,m

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

20. 2,7-Di(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxaoctane



δF

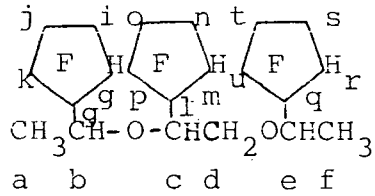
121.8, 123.2 124.5, 125.6 127.8, 129.0 130.6, 132.6 133.3, 135.3 137.1, 138.3	overlapping ABs and M	6	i,j,k, n,o,p
192.0	M		
194.6	M	1	g,l
197.0	M		
211.6	D of M, J_{FH} = 47Hz		
213.6	D of M, J_{FH} = 47Hz	1	h,m
224.6	D of M, J_{FH} = 47Hz		

δH

1.1	M	6	a,f
3.5	M	5	b,c,d,e
5.1	D of M, J_{HF} ≃ 50Hz	2	h,m

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

21. 2,4,7-Tri(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxaoctane



δF

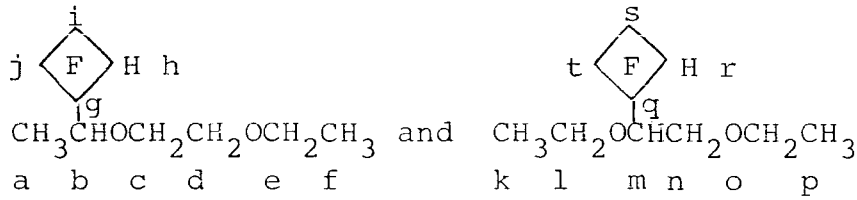
115.3, 120.2 121.3, 126.3 128.0, 129.2 131.0, 135.8	overlapping ABs and Ms	6	k,j,i,n,o, p,s,t,u
190.7	M		
194.6	M	1	g,l,q
198.0	M		
212.0	M		
220.6	M	1	h,m,r

δH

1.2	M (broad)	3	a,f
3.7	M (broad)	4	b,c,d,e
5.0	D of M, $J_{HF} \simeq 40$Hz		h,m,r,

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

22. Mixture of F-cyclobutane/ethyl glyme mono-adducts



δF

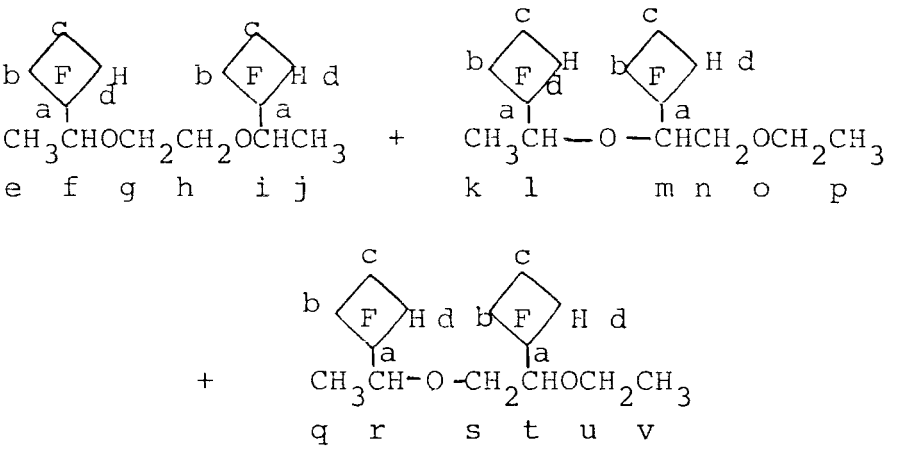
120.6, 124.8 125.5, 128.8 130.6, 132.0 133.0, 135.0	Overlapping ABs and Ms	4	t,s,i,j
189.3	M	1	g,q
189.6	M		
216.4	D of M, J_{FH} = 51Hz	1	h,r
217.8	D of M, J_{FH} = 51Hz		

δH

0.8	T of M, J_{HH} = 10Hz	3	f,k,p
0.9	D of M, J_{HH} = 8Hz		a
3.3	M	4	c,d,e,l,m,n,o
4.9	D of M, J_{HF} = 50Hz		h,r

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

23. Mixture of F-cyclobutene/ethyl glyme di-adducts



δF

116.6, 121.6 125.8, 129.8 131.2, 135.5 137.0, 139.3	overlapping ABs and Ms	4	b,c
189.0	M	1	a
202.3	M		
205.6	M		
214.6	M	2	d
216.0	M		
217.6	M		

δH

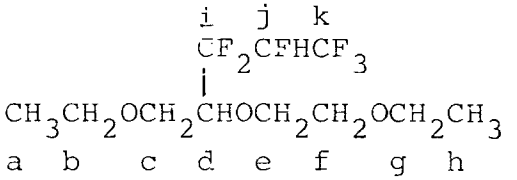
0.9	T of M, J_{HH} = 6Hz	3	p,v
1.2	D of M, J_{HH} = 7Hz		e,j,q
3.5	M	3	f,g,h,i,l,m,n,o, r,s,t,u
4.9	M	1	d

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

24. Hexafluoropropene/ethyl diglyme mono-adducts

Empirical Formula = $C_{11}F_6H_{18}O_3$

Typical structure



a b c d e f g h

δF

75.3	M	3	k
121.0, 123.6 126.6, 130.0	unresolved ABs	2	i
214.0 218.5	M M	1	j

δH

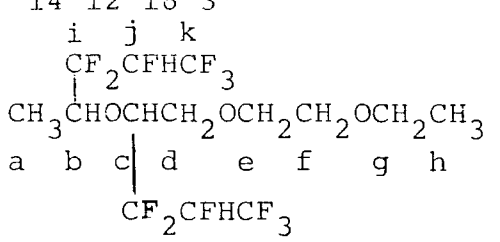
0.8 0.9	T, J_{HH} = 6.5Hz D, J_{HH} = 6.0Hz	6	a,h Rf CH_3CH-
3.5 5.0	M (broad D of M, J_{HF} = 45Hz	12	b,c,d,e,f,g

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

25. Hexafluoropropene/ethyl diglyme di-adducts

Empirical Formula= $C_{14}F_{12}H_{18}O_3$

Typical Structure:



δF

74.8	M	3	n,k
121.3 124.3 129.3	M M M	) 2	i,l
214.0	M	1	j,m

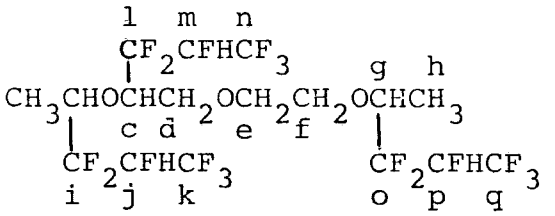
δH

1.0	M (broad)	6	a,h
3.4	M (broad)	10	b,c,d,e,f,g
5.0	D of M, J_{HF} = 48Hz	2	j,m

26. Hexafluoropropene/ethyl diglyme tri-adducts

Empirical Formula: $C_{17}F_{18}H_{18}O_3$

Typical Structure:



δF

74.3	M	3	k,n,q
124.0	M (broad)	2	i,l,o
213.0	M	/	j,m,p

δH

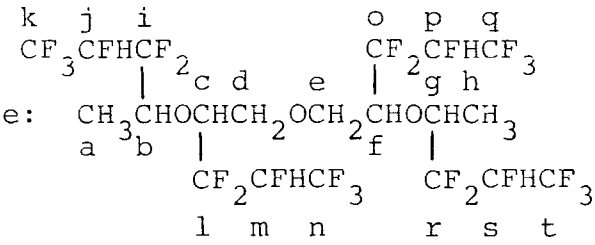
1.4	M	6	a,h
3.8	M (broad)	9	b,c,d,e,f,g
5.1	D of M, J_{HF} = 43Hz	3	j,m,p

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

27. Hexafluoropropene/ethyl glyme tetra-adducts

Empirical Formula = $C_{20}F_{24}H_{18}O_3$

Typical Structure:



δF			
74.3	M	3	k,n,q,t
124.0	M (broad)	2	i,l,o,r
213.0	M	1	j,n,p,s
δH			
1.3	M	6	a,h
3.9	M	8	b,c,d,e,f,g
5.0	D of M, J_{HF} = 49Hz	4	j,m,p,s

28. 1,1,1,2,3,3-Hexafluoro-5,8-dioxanonane

$CF_3CFHCF_2CH_2OCH_2CH_2OCH_3$
a b c d e f g

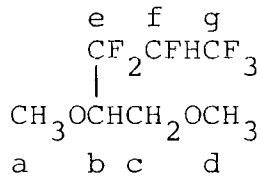
δF			
76.3	M	3	a
119.0	M	2	c
120.1	M		
212.1	M	1	b
214.0	M		

δH

Not available.

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

29. 3-(1,1,2,3,3,3-Hexafluoropropyl)-2,5-dioxahexane



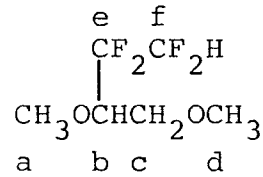
δF

75.4	M	3	g
118.6 121.7	M M	2	e
210.9 213.4	M M	1	f

δH

2.8	M	3	d
3.0 3.1 3.4 4.5	M M M D of M, J_{FH} = 42.7Hz	7	a b,c f

30. 3-(1,1,2,2-Tetrafluoroethyl)-2,5-dioxahexane



δF

127.5, 130.3	AB, J_{FF} = 273.4Hz	2	e
138.9, 142.3	D of AB, J_{FF} = 3 02Hz J_{FH} = 48.8Hz	2	f

δH

3.3	S		d
3.5	S		a
3.6	M		b,c
5.9	T of D of D, J_{1-2} = 49.2Hz J_{1-3} = 5Hz		f

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

31. 1,1,2,2-Tetrafluoro-4,7-dioxaoctane

a b c d e f
$HCF_2CF_2CH_2OCH_2CH_2OCH_3$

δF			
126.3	M	2	b
140.9	D of M, J_{FH} = 55Hz	2	a
δH			
2.9	S	3	f
3.5	M	))	
3.6	M	))	
3.9	M	) 7)	c,d,e
5.9	T of T, J_{1-3} = 5.3Hz, J_{1-2} = 53Hz	))	a

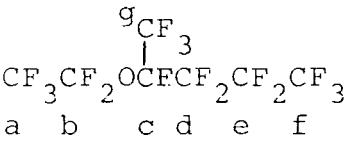
32. Telomeric adducts of tetrafluoroethylene and Monoglyme

e f g h
$(CF_2CF_2)_nCF_2CF_2H$
|
CH_3OCH_2CH O CH_3
a b c d n = 1,2,3 *etc.*

δF			
118.7, 123.7	AB, J_{FF} = 290Hz	-	e
124.9	M	-	f
131.0	M	-	g
138.1	D of M, J_{FH} = 48Hz	-	h
δH			
3.4	S		a
3.5	S		d
3.7	M	)	
3.8	M	)	b,c
6.1	T of T, J_{1-2} = 52.2Hz, J_{1-3} = 5.3Hz		h

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

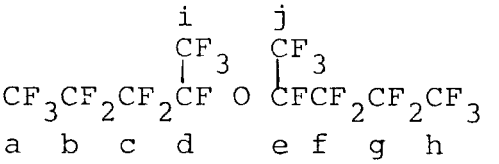
33. Perfluoro-1-methylbutyl ethyl ether



δF

80.6	M	3	g
81.7	T, J_{FF} 11Hz.	3	f
85.6	M	2	b
87.0	M	3	a
123.5	M	2	)
127.0	M	) 2	) e,d
128.0	M	)	)
141.3	M	1	c

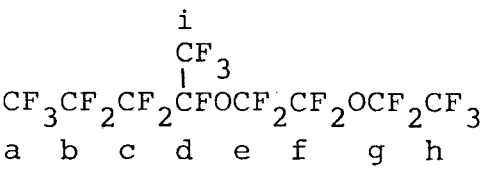
34. Perfluoro-di(1-methylbutyl) ether



δF

80.0	M	)	
81.6	M	) 3	i,j
84.7	T of M, J_{FF} 9.5Hz	3	a,h
118.6	M	2	)
127.5	M	)	) b,c,f,g
128.6	M	) 2	)
137.6	M	1	d,e

35. Perfluoro-4-methyl-5,8-dioxadecane

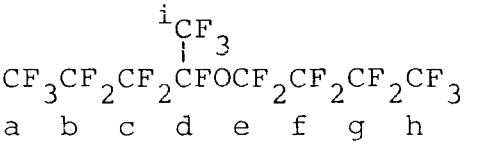


δF

80.3	M	3	i
83.8	T of M (J_{FF} = 10)	3	a
88.5	M	)	
90.0	M	) 6	e,f,g
91.0	M	3	h
123.0	M	)	
127.0	M	) 4	e,b
128.0	M	)	
141.3	M	1	d

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

36. Perfluoro-1-methylbutyl butyl ether

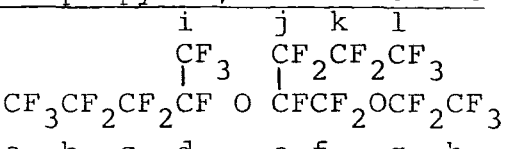


a b c d e f g h

δF

81.6	M	3	i
83.2	M	2	e
84.3	T of M, J_{FF} = 10Hz	6	a,h
123.8	M	2	c
128.3	M	6	b,f,g
129.0	M		
143.0	M	1	d

37. Perfluoro-4-methyl-6-propyl-5,8-dioxadecane

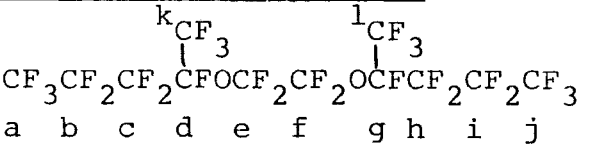


a b c d e f g h

δF

79.5	M	2	f
81.2	M	3	i
83.8	T of M, J_{FF} = 9Hz	6	a,l
87.5	M	2	g
89.7	M	3	h
123.3	M	4	j,k,c,b
128.0	M		
136.6	M	2	d,e

38. Perfluoro-4,9-dimethyl-5,8-dioxadodecane



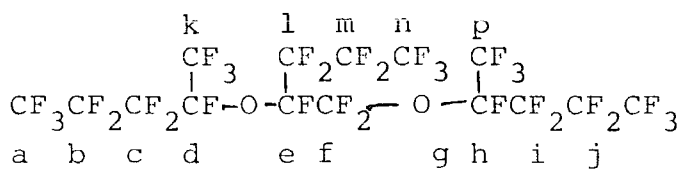
a b c d e f g h i j

δF

80.8	M	3	k,l
84.0	T of M, J_{FF} = 11Hz	3	a,j
87.8	M	2	e,f
123.3	M	4	b,c,h,i
127.3	M		
127.8	M		
141.8	M	1	d,g

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

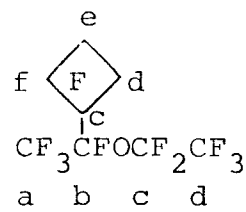
39. Perfluoro-4,9-dimethyl-6-propyl-5,8-dioxadodecane



δF

79.6	M	3	k or p
80.3	M	2	f
81.3	M	3	p or k
84.0	T of M, J_{FF} = 10Hz	9	a, j, n
122.0	M	6	b,c,h,i,l,m
127.8	M	6	
135.2	M	2	d,e
143.5	M	1	g

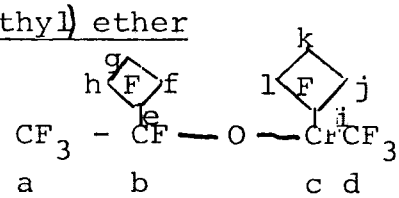
40. Perfluoro-1-cyclobutylethyl ethyl ether



δF

80.6	M	3	a
89.4	M	2	g
90.1	M	3	h
131.9	M	4	f,d
132.6	M		
134.4	M	2	e
134.8	M		
138.6	M	1	b
192.4	M	1	c

41. Perfluoro-di-1-(cyclobutylethyl) ether

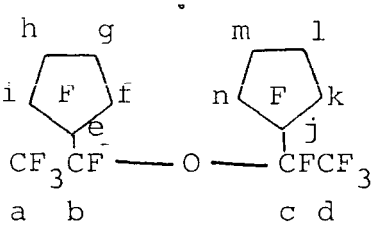


δF

79.2	M	3	a,d
80.7	M	3	
132.4	M	12	f,g,h, j,k,l
133.5	M		
134.3	M		
134.8	M	2	b,c
135.4	M		
190.3	M	2	e,i
191.7	M		

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

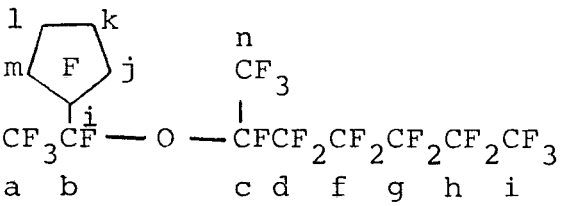
42. Perfluoro-di-(1-cyclopentylethyl) ether



δF

84.7	M	6	a,d
123.1 123.9 125.5 126.7 127.1	overlapping ABs	16	f,g,h,i,k,l, m,n
137.1	M	2	b,c
188.9	M	2	e,j

43. Perfluoro-1-cyclopentylethyl 1-methyl ether

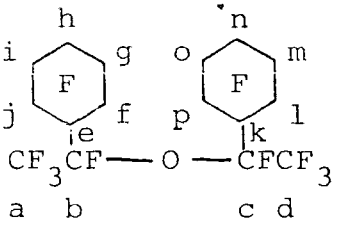


δF

78.7 79.3	M M	3 3	a,n
127.3 129.9	M M	16	j,k,l,m, d,e,f,g
138.8 139.9	M M	2	b,c
183.5	M	1	i

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

44. Perfluoro-di-1-(cyclohexylethyl) ether



δF

83.5	M	3	a,d
117.6) 121.0) 122.8) 126.2) 128.0) 129.5) 139.1) 141.0)	Overlapping ABs and Ms	))))))))	20	f,g,h,i,l,m n,o,p
144.1) 147.0)	M M	)	2	b,c
187.6	M, J=15Hz	2	e,k

45. Perfluoro-1-chloro-n-butane

a b c d
$CF_3CF_2CF_2CF_2Cl$

δF

70.3	M	2	d
83.2	M	3	a
122.0	M	2	c
126.7	M	2	b

46. Perfluoro-3-chloro-1-methylpropyl ethyl ether

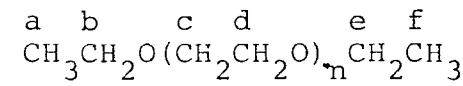
f
CF_3
$CF_3CF_2OCFCF_2CF_2Cl$
a b c d e

δF

68.3	M	2	e
81.2	M	3	f
87.8	M	2	b
89.4	M	3	a
120.8	M	2	d
141.6	M	1	c

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

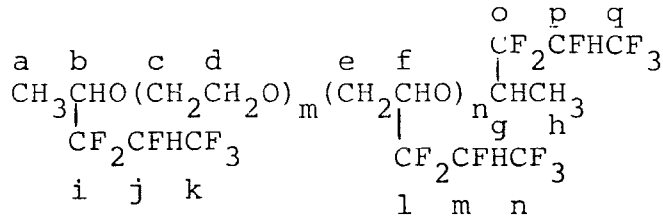
47. Polyethylene glycol diethyl ether (av.mol wt. 456)



δH

0.7	T, J_{HH} = 7Hz	3	a,f
2.4	M (broad)	20	b,c,d,e

48. Polyethylene glycol/hexafluoropropene hepta-adduct



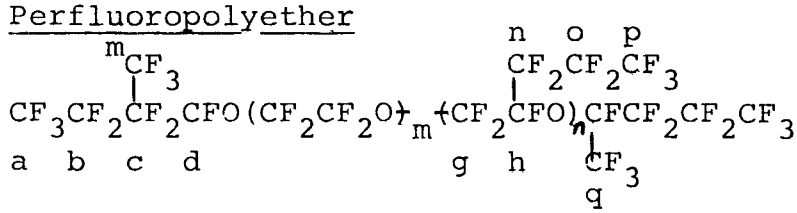
δF

75.6	M	3	k,n,q
123.3	M	2	i,l,o
214.0	M	1	j,m,p

δH

0.9	M	3	a,h
3.8	M	22	b,c,d,e,f,g
4.05	M		
5.2	D of M, J_{HF} = 40Hz		j,m,p

49. Perfluoropolyether

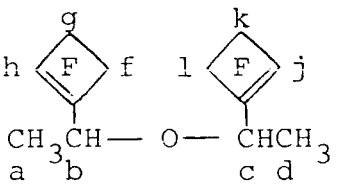


δF

81.8	M	7	a,m,e,f g,p,l
83.6	M		
85.5	M		
121.9	M	5	b,c,n,o,j,k
123.0	M		
124.8	M		
127.0	M		
140.6	M (broad)		d,h,i

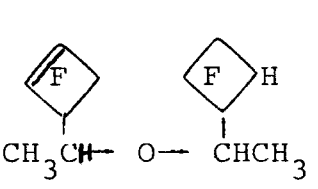
Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

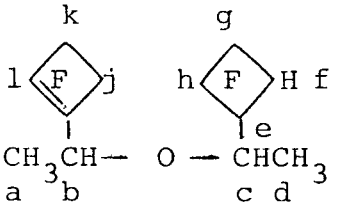
50. Di-1-(perfluorocyclobut-1-enyl)ethyl ether



δF			
115.3	M	1	h,j
118.2	M	2	l,f or g,k
120.9	M	2	g,k or l,f
δH			
1.0	D, J_{HH} = 6Hz	3	a,d
3.8	M	1	b,c

51. 1- Perfluorocyclobut-1-enyl)ethyl 1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether

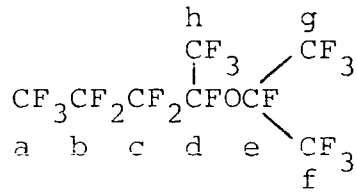




	impurity		
δF			
114.9			1
118.1		)	
118.8		)	g,h,j,k
121.3		)	
133.5	M		e
172.2	D of M, J = 7OHz		f
δH			
1.2	M	3	a,d
4.12	M)	1	b,c
4.5	M)		f

Shift p.p.m.	Fine Structure Coupling Constant	Relative Intensity	Assignment

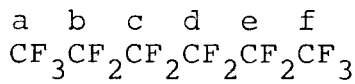
52. Perfluoro-1-methylbutyl isopropyl ether



δF

81.5	M	3	a or h
83.5	M	3	h or a
85.0	M	6	g,f
124.6	M	)	
128.5	M	) 4	b,c
130.0	M	)	
137.5	M	1	e
143.6	M	1	d

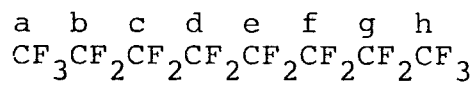
53. Perfluoro-n-hexane



δF

83.5	M	3	a,f
125.2	M	2	b,e
128.7	M	2	c,d

54. Perfluoro-n-octane



δF

82.1	M	3	a,h
125.0	M	2	b,h
127.8	M	)	
		) 4	c,d,e,f
128.7	M	)	

APPENDIX THREE

MASS SPECTRA

1. 2,2,3,4,4,4-Hexafluoro-1-methylbutyl ethyl ether
2. Di-2,2,3,4,4,4-hexafluoro-1-methylbutyl ether
3. 1-(1,2,3,3,4,4-Hexafluorocyclobutyl)ethyl ethyl ether
4. Di-1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether
5. 1-(1,2,3,3,4,4,5,5-Octafluorocyclopentyl)ethyl ethyl ether
6. Di-1-(1,2,3,3,4,4,5,5-octafluorocyclopentyl)ethyl ether
7. 1-(1,2,3,3,4,4,5,5,6,6-Decafluorocyclohexyl)ethyl ethyl ether
8. Di-1-(1,2,3,3,4,4,5,5,6,6-decafluorocyclohexyl)ethyl ether
9. 3-Chloro-2,2,3-trifluoro-1-methylpropyl ethyl ether
10. Telomeric adducts of chlorotrifluoroethene and ethyl ether
11. 2,2,3-Trifluoro-1-methylpropyl ethyl ether
12. Telomeric adducts of trifluoroethene and ethyl ether
13. 4-(1,1,1,2,3,3-Hexafluoropropyl)-3,6-dioxahexane
14. 1,1,1,2,3,3-Hexafluoro-4-methyl-5,8-dioxadecane
15. 1,1,1,2,3,3-Hexafluoro-4-methyl-6-(1,1,2,3,3,3-hexafluoropropyl)-5,8-dioxadecane
16. 1,1,1,2,3,3,10,10,11,12,12,12-Dodecafluoro-4,9-dimethyl-5,8-dioxadodecane
17. 1,1,1,2,3,3,10,10,11,12,12,12-Dodecafluoro-4,9-dimethyl-6-(1,1,2,3,3,3-hexafluoropropyl)-5,8-dioxadecane
18. Mixture of mono-adducts of F-cyclopentene and ethyl glyme
19. 2,4-Di(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxahexane
20. 2,7-Di(1,2,3,3,4,4,5,5-octafluorocyclopentyl)-3,6-dioxahexane
21. 2,4,7-Tri(1,2,3,3,4,4,5,5-octafluorocyclopentyl-3,6-dioxahexane
22. Mixture of mono-adducts of F-cyclobutene and ethyl glyme
23. Mixture of di-adducts of F-cyclobutene and ethyl glyme
24. Mixture of mono-adducts of hexafluoropropene (HPF) and ethyl diglyme
25. Mixture of di-adducts of HFP and ethyl diglyme
26. Mixture of tri-adducts of HFP and ethyl diglyme
27. Mixture of tetra-adducts of HFP and ethyl diglyme

*28. 1,1,1,2,3,3-Hexafluoro-5,8-dioxanonane

29. 3-(1,1,2,3,3,3-Hexafluoropropyl)-2,4-dioxahexane

30. 3-(1,1,2,2-Tetrafluoroethyl)-2,5-dioxahexane

31. 1,1,2,2-Tetrafluoro-4,7-dioxaoctane

32. A mixture of telomeric adducts of tetrafluoroethylene and monoglyme

33. Perfluoro-1-methylbutyl ethyl ether

34. Perfluoro-di(1-methylbutyl) ether

35. Perfluoro-4-methyl-5,8-dioxadecane

36. Perfluoro-1-methylbutyl butyl ether

37. Perfluoro-4-methyl-6-propyl-5,8-dioxadecane

38. Perfluoro-4,9-dimethyl-5,8-dioxadodecane

39. Perfluoro-4,9-dimethyl-6-propyl-5,8-dioxadodecane

40. Perfluoro-1-cyclobutylethyl ethyl ether

41. Perfluoro-di(1-cyclobutylethyl)ether

42. Perfluoro-di(1-cyclopentylethyl)ether

43. Perfluoro-1-cyclopentylethyl 1-methylhexyl ether

44. Perfluoro-di(1-cyclohexylethyl)ether

*45. Perfluoro-1-chloro-n-butane

46. Perfluoro-3-chloro-1-methylpropyl ethyl ether

47.)
)
48.) Not measured
)
49.)

50. Di-1-(perfluorocyclobut-1-enyl)ethyl ether

* 51. 1-Perfluorocyclobut-1-enyl)ethyl 1-(1,2,3,3,4,4-hexafluorocyclobutyl)ethyl ether.

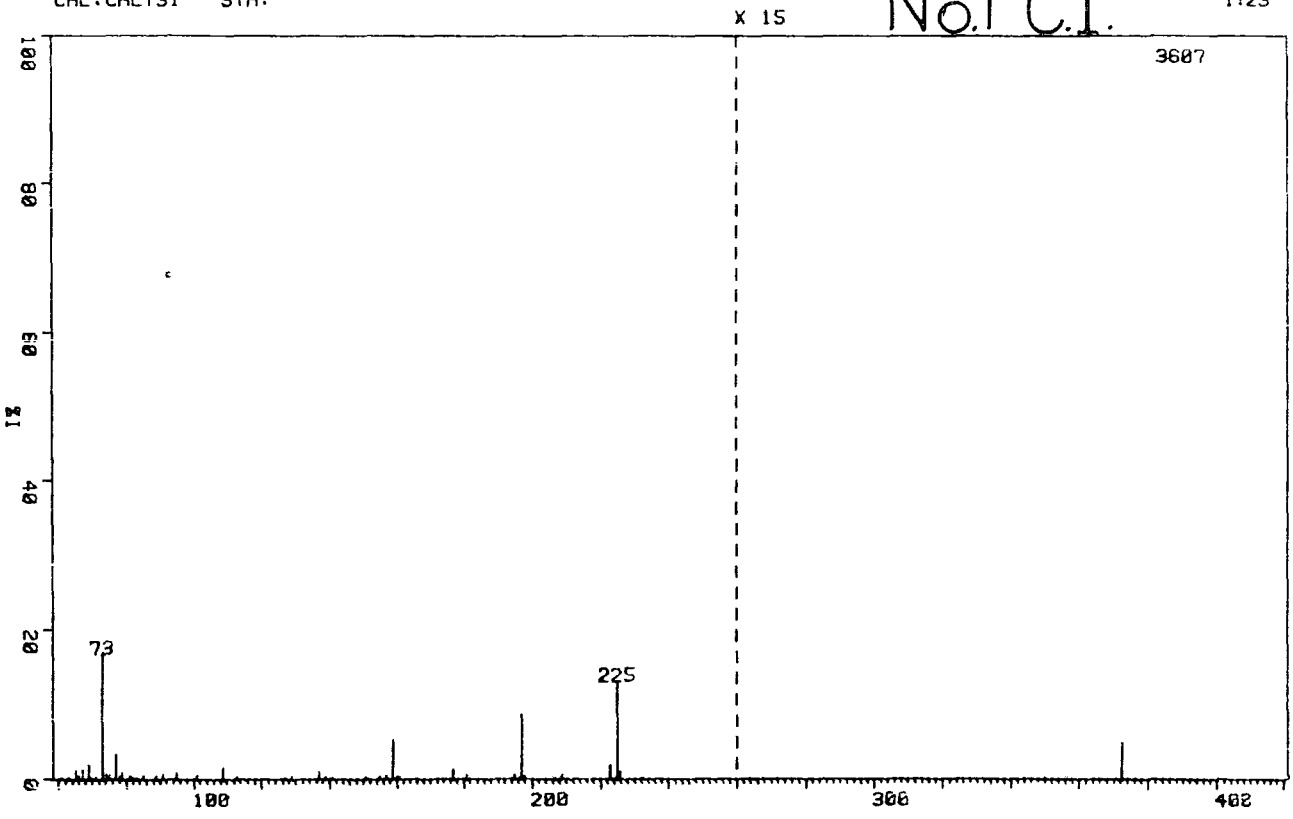
52. Perfluoro-1-methylbutyl isopropyl ether

* (not measured)

PT11X 9 P.T.TELFORD 1/1 C.I.
CAL:CALT31 STA:

26-MAR-85
1:25

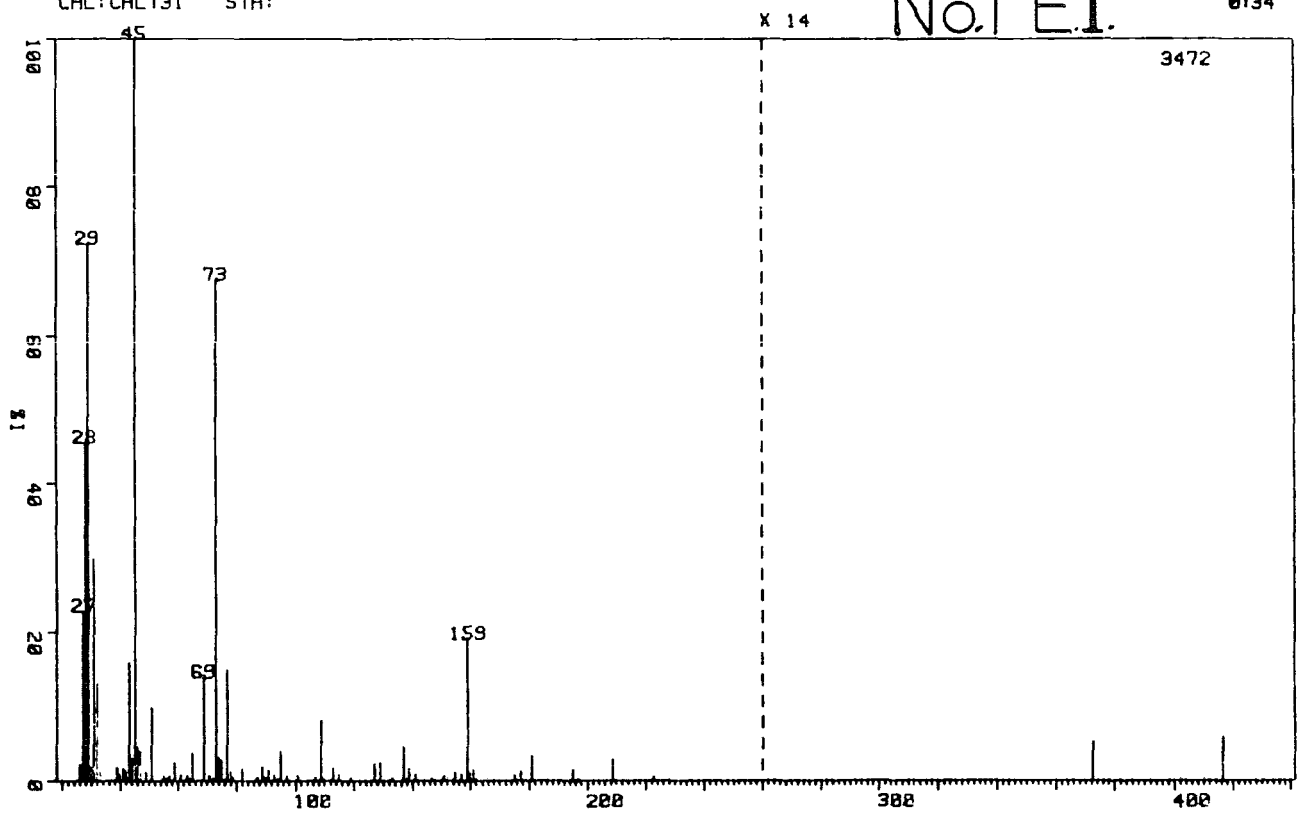
No.1 C.I.



MASS	%HT. BASE	MASS	%HT. BASE
60.90	0.22	156.86	0.47
63.01	0.30	158.80	5.35
65.03	1.25	159.84	0.39
66.05	0.47	160.83	0.33
67.03	1.36	176.86	1.41
68.92	2.05	180.81	0.58
69.92	0.30	194.87	0.67
70.94	0.47	196.91	8.84
73.02	16.80	197.90	0.53
74.04	0.83	206.88	0.33
75.00	0.64	208.85	0.67
76.97	3.41	222.90	2.00
77.95	0.53	224.93	13.17
78.92	1.03	225.92	1.05
80.92	0.55	372.55	0.33
81.90	0.33		
83.00	0.36		
85.03	0.64		
88.87	0.44		
90.87	0.80		
94.96	0.94		
100.94	0.69		
108.88	1.69		
112.92	0.44		
126.92	0.28		
128.85	0.47		
136.90	1.08		
138.85	0.42		
140.82	0.22		
150.78	0.30		
154.81	0.33		

PT11X 3 P.T.TELFORD 1/1 E.I.
CAL:CALT31 STA:

26-MAR-85
0:34

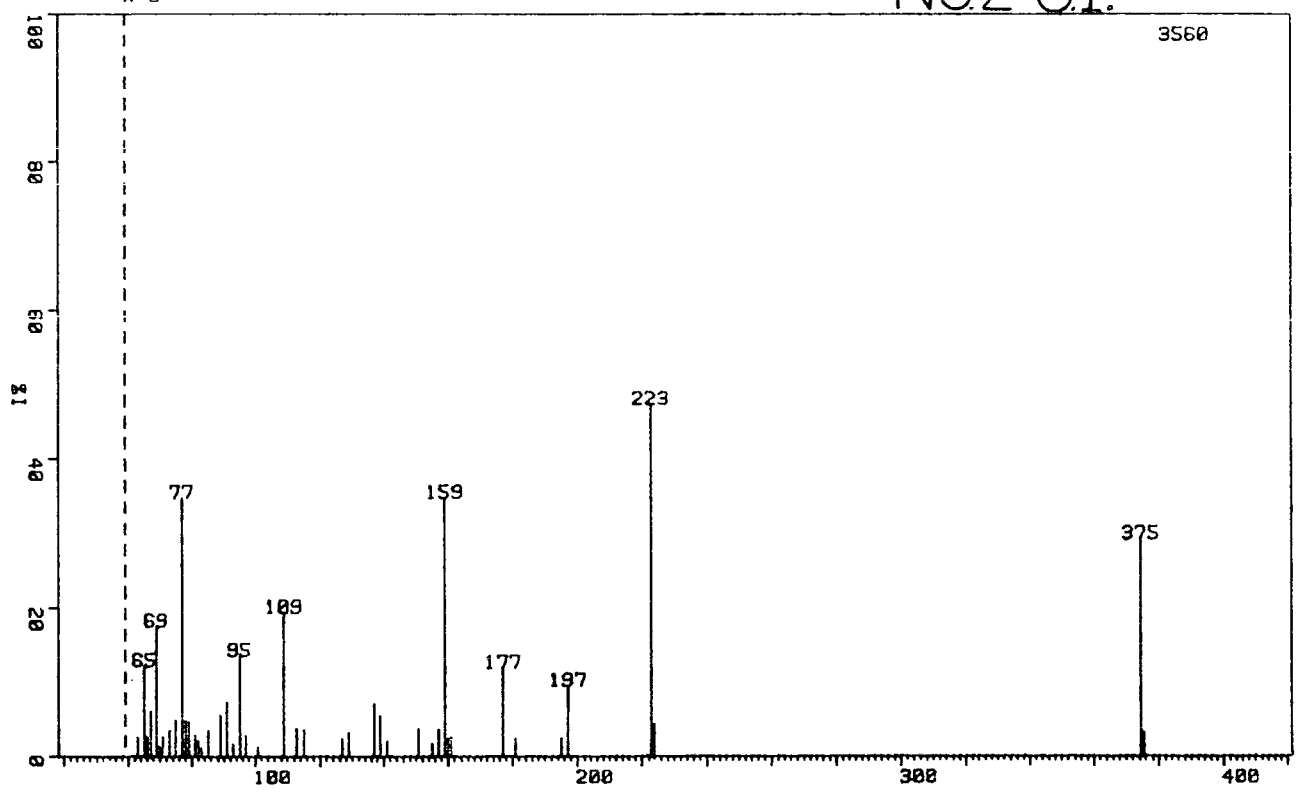


MASS	%HT. BASE	MASS	%HT. BASE		
26.30	2.16	63.04	0.78	132.96	0.37
27.23	22.81	64.06	0.40	136.96	4.64
28.11	45.56	65.07	3.83	137.94	0.32
28.13	4.98	68.94	13.94	138.90	1.73
28.97	6.65	70.96	0.69	140.88	0.98
29.00	72.32	72.03	0.35	146.97	0.32
29.80	0.43	73.07	67.48	150.90	0.60
29.83	2.02	74.09	3.17	154.96	1.18
30.88	29.93	75.05	2.79	156.97	1.01
31.97	13.16	76.04	0.26	158.93	19.18
32.00	0.37	77.02	14.92	159.90	1.09
33.07	1.41	77.99	1.35	160.90	1.56
38.95	1.81	78.95	0.40	161.94	0.29
39.79	0.86	81.95	1.70	174.95	0.72
40.93	1.70	87.00	0.43	176.96	1.24
41.98	1.24	88.92	1.93	180.88	3.25
42.03	0.58	89.88	0.43	194.94	1.56
43.05	15.99	90.92	1.47	196.95	0.32
43.10	2.02	92.96	0.86	208.90	2.88
44.09	3.08	93.99	0.35	222.95	0.60
45.12	100.00	94.99	4.03	372.67	0.37
46.12	4.58	96.98	0.72	416.60	0.43
47.08	4.00	100.88	0.78		
48.94	1.18	107.00	0.52		
50.92	9.85	108.95	8.21		
55.12	0.75	109.92	0.32		
56.12	0.32	112.97	1.81		
57.06	0.75	115.00	0.98		
57.10	0.58	118.93	0.37		
58.97	2.53	126.96	2.30		
60.95	0.81	128.90	2.51		

PT12X 8 P.T.TELFORD 1/2 C.I.
CAL:CALT31 STA:
X S

No.2 C.I.

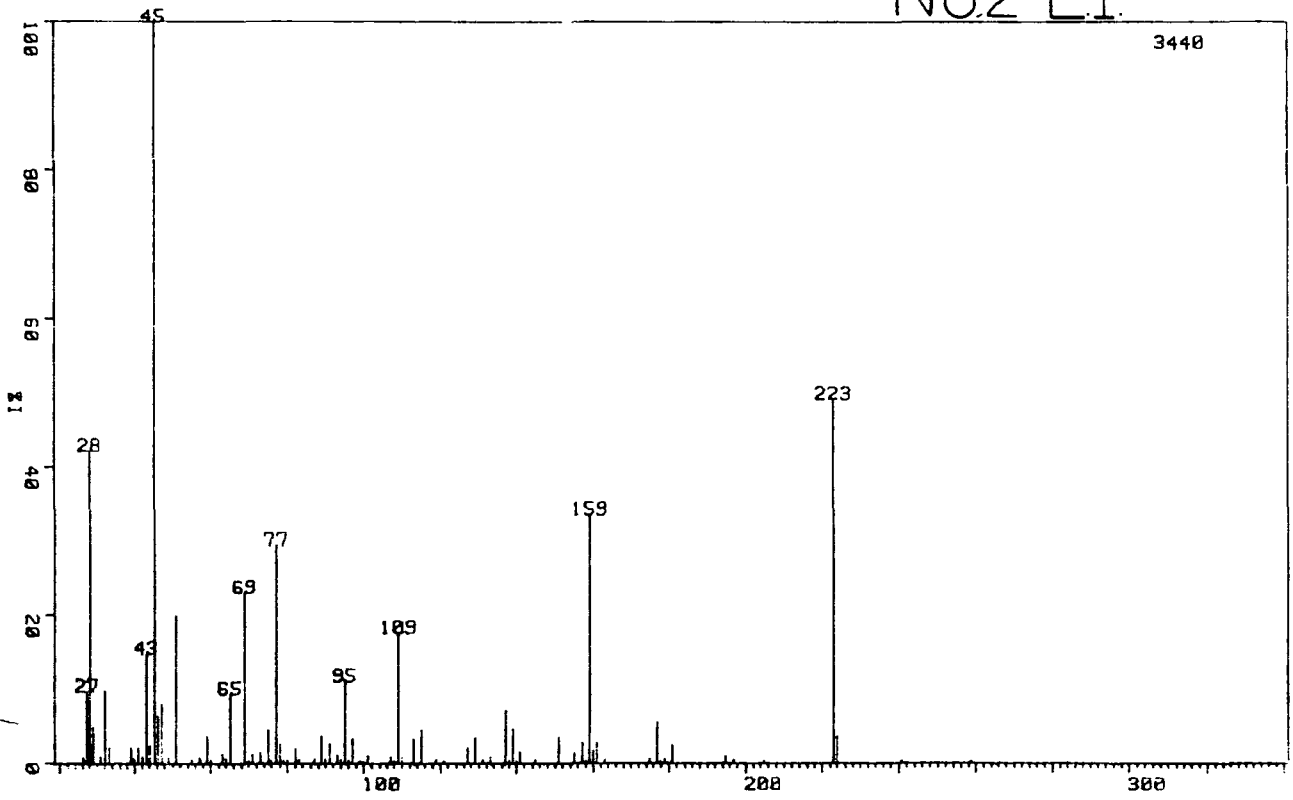
26-MAR-85
1:17



MASS	%HT. BASE	MASS	%HT. BASE
63.00	0.53	150.86	0.76
65.03	2.44	154.95	0.37
66.05	0.53	156.95	0.73
67.03	1.24	158.92	6.97
68.91	3.51	159.89	0.48
69.91	0.28	160.87	0.53
70.94	0.53	176.93	2.39
73.02	0.70	180.85	0.51
75.00	1.01	194.92	0.51
76.97	6.97	196.92	1.91
77.95	0.98	222.88	9.47
78.92	0.96	223.93	0.90
80.92	0.59	374.58	5.87
81.89	0.45	375.58	0.65
83.00	0.28		
85.04	0.70		
88.87	1.12		
90.90	1.46		
92.93	0.25		
92.97	0.37		
94.96	2.72		
96.96	0.59		
100.84	0.28		
108.88	3.88		
112.92	0.76		
114.95	0.73		
126.92	0.48		
128.86	0.65		
136.93	1.43		
138.89	1.12		
140.88	0.42		

PT12X 3 P.T.TELFORD 1/2 E.I. 26-MAR-85
CAL:CALT31 STA: 0.35

No.2 EI



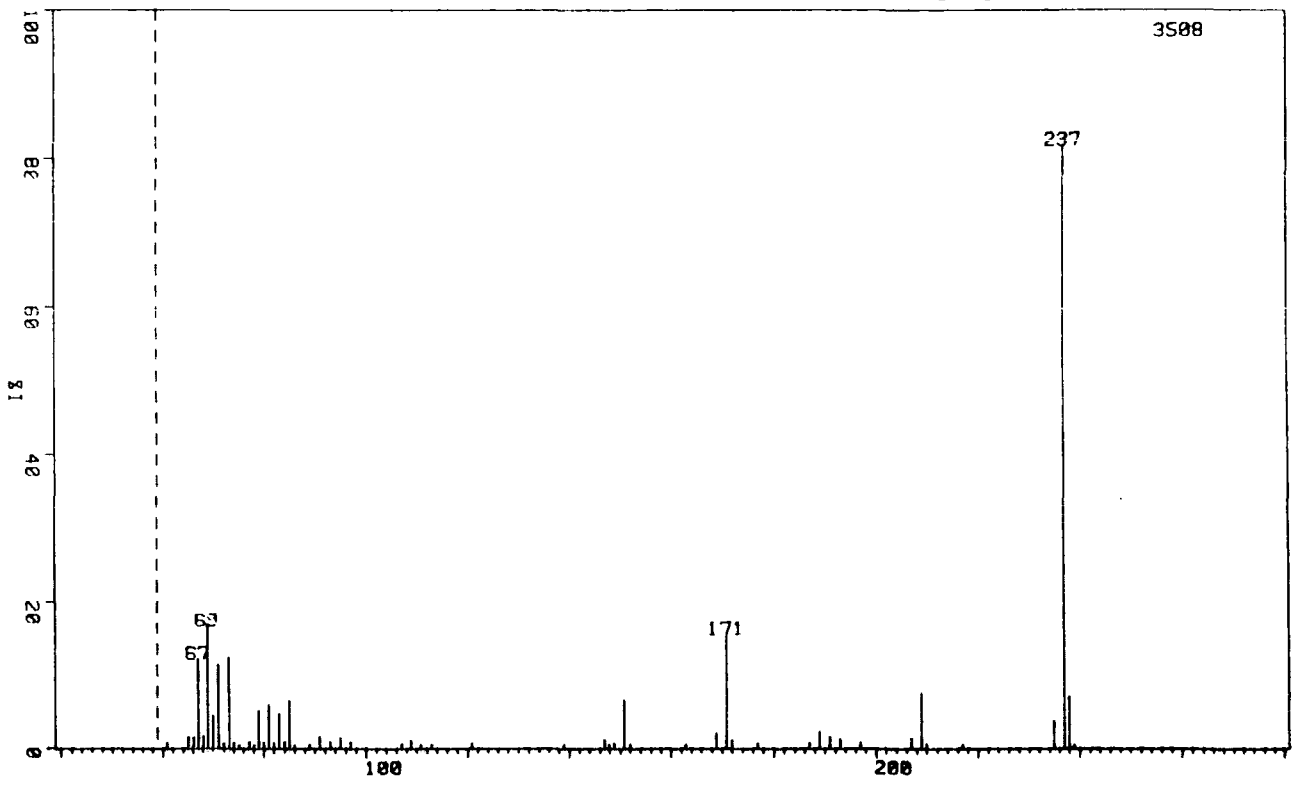
MASS	%HT. BASE	MASS	%HT. BASE		
26.30	0.81	70.96	1.31	128.91	3.55
27.23	9.74	73.07	1.54	130.39	0.52
28.11	42.18	75.05	4.51	132.97	0.90
28.13	2.38	76.04	0.47	136.98	7.18
28.96	4.97	77.02	29.48	137.98	0.38
29.00	1.57	77.99	2.62	138.93	4.71
30.87	0.96	78.95	0.47	139.90	0.32
31.96	9.74	79.87	0.35	140.91	1.60
33.07	2.21	81.95	2.06	144.96	0.44
38.95	2.18	82.98	0.55	150.89	3.58
39.79	0.67	87.00	0.70	154.98	1.54
40.93	2.09	88.92	3.78	156.98	2.82
41.98	0.84	89.88	0.78	157.96	0.29
42.03	0.96	90.95	2.65	158.93	33.52
43.06	14.85	92.99	1.16	159.90	1.80
44.09	2.47	94.02	0.55	160.89	2.99
45.12	100.00	95.02	11.13	162.96	0.44
46.12	6.45	96.01	0.44	174.97	0.61
47.08	8.11	97.01	3.40	176.97	5.61
48.94	0.87	98.94	0.35	177.95	0.32
50.92	20.00	99.87	0.26	178.93	0.58
55.13	0.44	100.92	1.13	180.89	2.56
57.05	0.90	107.00	0.96	194.94	1.05
57.10	0.49	107.97	0.38	196.95	0.52
58.97	3.66	108.95	17.59	204.95	0.29
59.90	0.52	109.91	0.90	222.92	49.16
63.04	1.37	112.97	3.28	223.94	3.72
64.06	0.76	115.00	4.53	240.84	0.38
65.07	9.39	118.93	0.61	258.81	0.32
68.94	23.02	120.93	0.29		
69.89	0.35	126.97	2.15		

PT971X 2 P.T.TELFORD 97/1 :-BU CI

CAL:CALT31 STA:

No.3 CI.

02-DEC-85
0:26

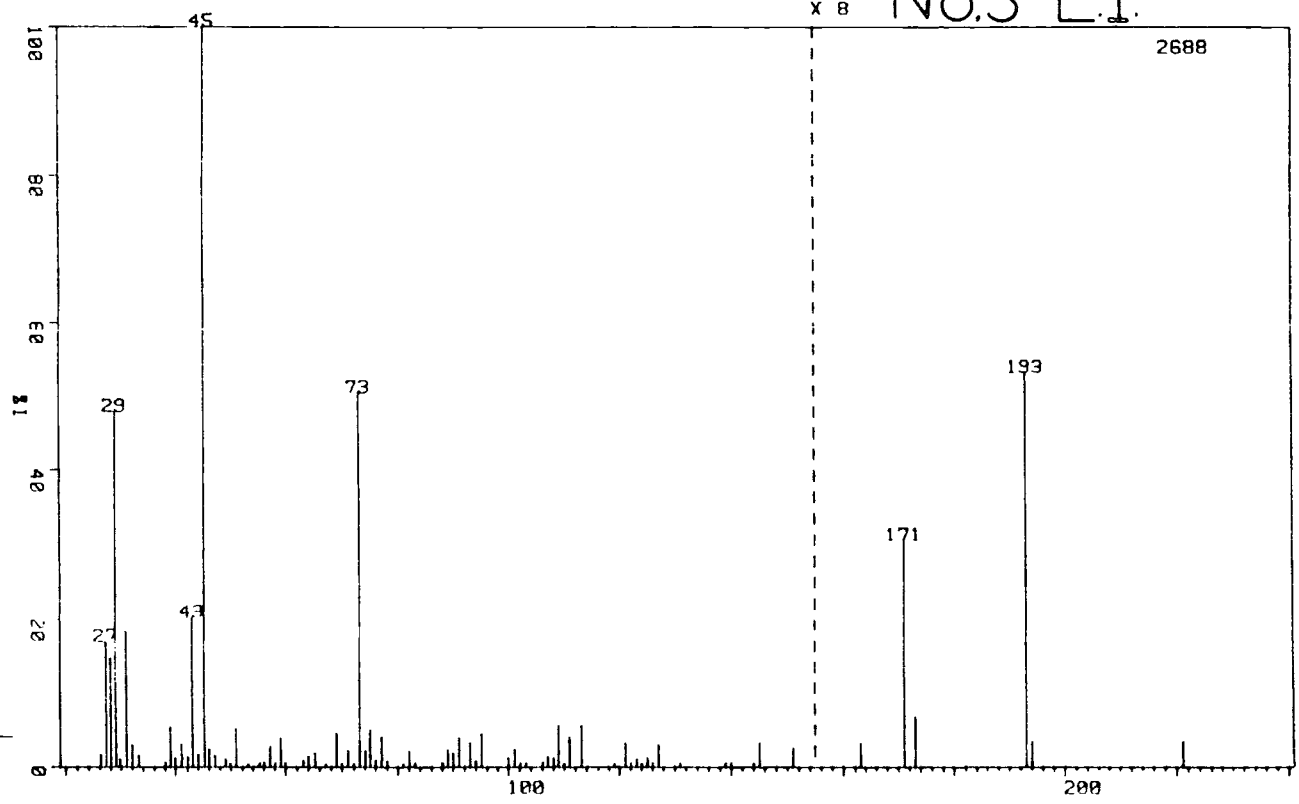


MASS	%HT. BASE	MASS	%HT. BASE
60.90	0.43	112.92	0.31
65.03	0.86	120.90	0.40
66.04	0.30	128.97	0.31
67.02	6.16	146.97	0.66
68.00	0.88	147.91	0.26
68.95	0.30	148.87	0.43
69.90	2.34	150.85	3.39
70.98	5.73	151.92	0.31
72.03	0.37	152.97	0.31
73.04	4.24	168.88	1.17
74.06	0.48	170.90	7.84
75.02	0.26	171.93	0.63
75.08	0.29	176.96	0.40
77.01	0.51	186.92	0.48
77.98	0.26	188.90	1.23
78.95	2.65	190.92	0.88
79.89	0.46	192.93	0.68
80.94	3.05	196.96	0.48
82.00	0.37	206.92	0.77
83.03	2.48	208.90	3.91
84.05	0.51	209.93	0.37
85.06	3.34	216.98	0.34
86.06	0.26	234.94	1.97
88.91	0.26	235.97	40.96
90.90	0.88	237.94	3.68
92.98	0.48	238.93	0.23
95.02	0.80		
97.03	0.51		
106.97	0.37		
108.91	0.60		
110.87	0.31		

PT971X S P.T.TELFORD EI 97/1
CAL:CALT31 STAR

No.3 E.I.

02-DEC-85
8:52



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.30	1.75	59.93	0.56	108.02	1.23
27.23	17.00	63.07	0.89	109.00	5.65
28.11	14.84	64.10	1.45	109.96	0.45
28.99	47.92	65.12	1.93	110.97	4.13
29.80	0.41	67.03	0.48	113.03	5.65
29.83	1.12	69.99	4.69	114.00	0.48
30.88	18.45	69.91	0.48	121.01	3.24
31.97	3.05	70.97	2.34	122.05	0.52
33.07	1.60	73.04	0.48	123.04	1.08
38.04	0.71	73.09	50.48	124.07	0.41
38.96	5.54	74.12	2.23	125.06	1.23
39.80	1.23	75.03	5.02	126.07	0.63
39.86	0.60	76.04	0.97	127.06	3.01
40.94	3.20	77.02	4.13	130.99	0.56
42.01	1.38	77.99	0.86	139.03	0.56
43.07	20.35	80.92	0.48	140.00	0.52
44.10	1.75	81.96	2.19	144.05	0.45
45.13	100.00	83.01	0.52	145.06	3.31
46.13	2.49	87.98	0.63	151.02	2.64
47.10	1.64	88.95	2.42	163.06	0.41
48.96	1.12	89.89	1.90	171.03	3.83
49.87	0.56	90.97	3.94	173.04	0.86
50.94	5.21	93.01	3.31	193.05	6.66
53.09	0.41	94.03	0.89	194.06	0.45
55.15	0.56	95.04	4.54	221.09	0.45
56.19	0.71	99.91	1.23		
56.15	0.41	100.97	2.42		
57.03	2.29	102.02	0.60		
57.13	0.67	104.06	0.56		
58.05	0.56	106.05	0.78		
59.00	3.93	107.04	1.45		

PT972X 4 P.T.TELFORD 97/2 I-BU CI

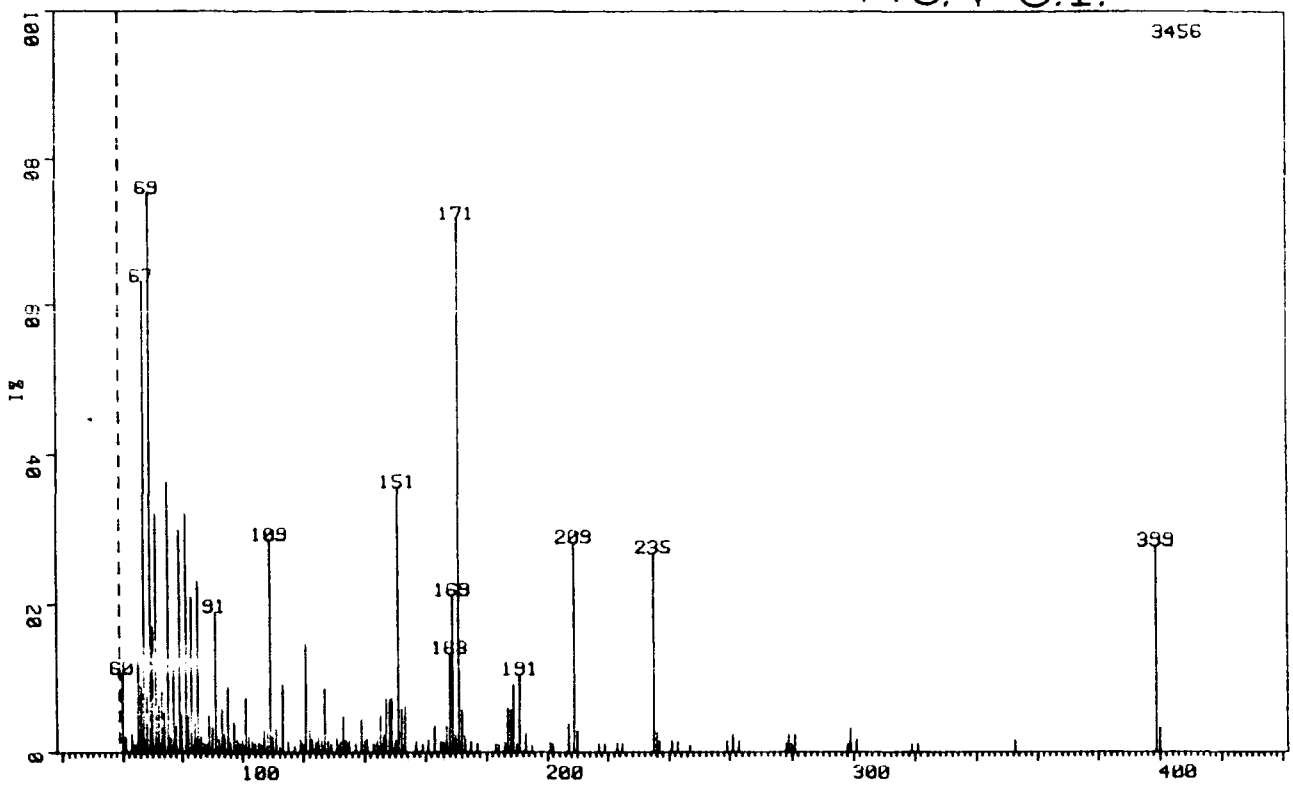
CAL:CALT31 STA:

X 4

No.4 C.I.

02-DEC-85

0:43

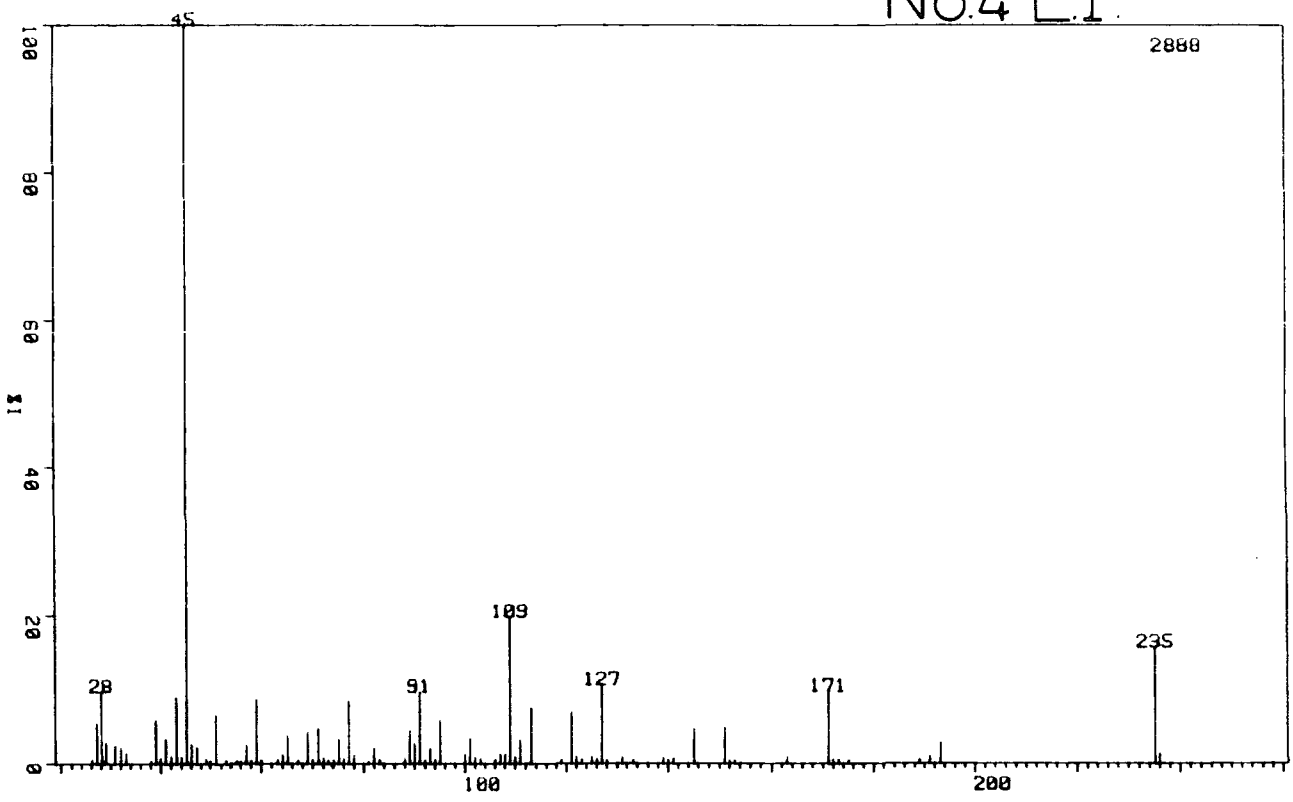


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT BASE		
60.93	0.55	99.91	0.49	143.97	0.52	208.93	7.06
63.00	0.64	100.93	1.85	144.97	1.30	209.92	0.75
64.01	0.29	101.97	0.67	146.01	0.67	214.99	0.32
65.03	3.15	103.01	0.55	147.02	1.82	218.96	0.32
66.04	2.26	104.02	0.38	147.97	1.82	222.99	0.32
67.03	15.77	105.05	0.52	148.94	1.88	224.95	0.32
68.00	2.00	106.00	0.38	149.89	0.46	234.96	6.71
68.96	18.81	107.03	0.78	150.90	8.91	235.95	0.67
69.90	4.28	107.99	0.78	151.93	1.50	236.94	0.38
70.96	8.07	108.96	7.15	152.97	1.56	240.87	0.41
72.00	1.91	109.92	0.55	156.95	0.41	242.93	0.38
73.02	2.11	110.96	0.84	158.94	0.32	246.99	0.26
74.05	1.42	112.06	0.23	160.95	0.43	258.89	0.41
75.05	9.11	112.97	2.29	162.96	0.93	260.88	0.61
76.04	0.58	115.03	0.38	164.98	0.38	262.94	0.38
76.98	3.01	117.02	0.26	165.97	0.38	277.91	0.32
77.97	0.95	118.97	0.46	166.94	0.93	278.86	0.61
78.93	7.49	119.90	0.32	167.94	3.36	279.89	0.32
79.87	1.33	120.95	3.67	168.92	5.30	280.89	0.61
80.96	8.07	121.99	0.78	169.89	0.64	297.95	0.29
81.99	1.30	123.03	0.49	170.92	17.94	298.94	0.81
83.04	5.27	124.03	0.38	171.94	1.48	300.94	0.46
84.06	1.07	125.00	0.67	172.97	0.58	318.94	0.29
85.09	5.82	126.00	0.52	175.00	0.38	320.99	0.32
86.07	0.61	126.98	2.17	176.99	0.32	352.92	0.43
87.00	0.35	127.99	0.43	183.00	0.29	398.93	6.94
87.97	0.32	128.97	0.32	184.03	0.29	399.94	0.84
88.92	1.30	130.93	0.52	185.97	0.38		
89.87	1.01	131.95	0.41	186.93	1.53		
90.95	4.75	132.99	1.24	187.95	1.48		
92.01	0.55	134.01	0.43	188.91	2.29		
93.02	1.48	135.04	0.55	189.91	0.32		
94.06	0.64	137.03	0.35	190.90	2.63		
95.05	2.23	138.98	1.13	192.95	0.67		
96.08	0.43	139.93	0.46	195.01	0.26		
97.06	1.04	140.94	0.49	200.94	0.35		
98.03	0.49	142.95	0.32	201.95	0.29		
98.98	0.41	143.02	0.29	206.94	0.98		

PT972X 4 P.T.TELFORD 97/2 EI
CAL:CALT31 STA:

No.4 E.I.

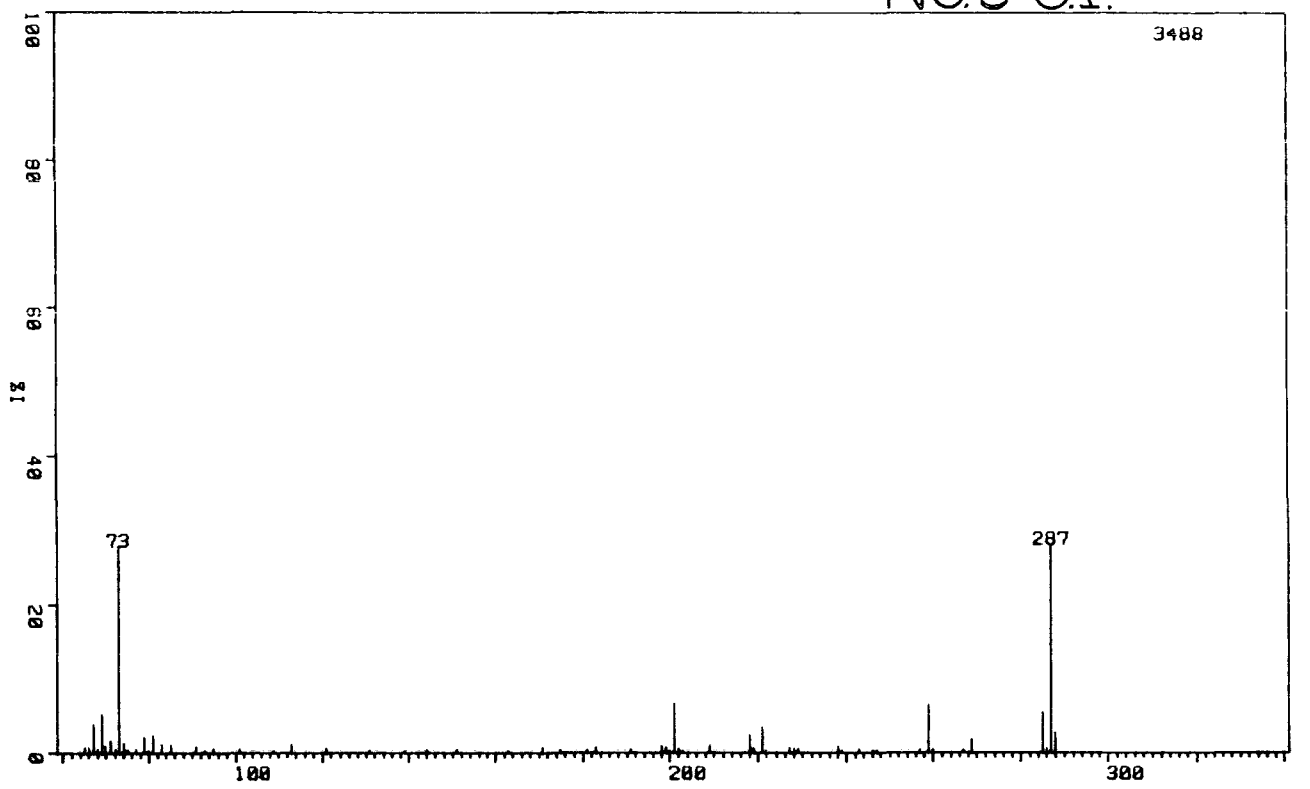
02-DEC-85
0:43



MASS	%HT. BASE	MASS	%HT. BASE		
26.30	0.55	63.07	0.52	108.04	1.39
27.23	5.44	64.10	1.35	109.01	19.81
28.11	9.73	65.09	3.81	109.97	0.93
28.13	1.18	67.03	0.42	110.99	3.22
28.97	2.87	68.97	4.26	113.05	7.58
29.00	1.70	69.93	0.59	119.01	0.45
30.88	2.46	70.99	4.88	121.03	7.03
31.97	2.22	72.05	0.87	122.07	1.00
33.08	1.49	73.06	0.35	123.07	0.66
38.04	0.42	73.09	0.42	125.06	0.97
38.96	5.92	74.13	0.45	126.08	0.69
39.80	0.73	75.07	3.39	127.06	10.70
39.86	0.52	76.08	0.73	128.06	0.45
40.95	3.39	77.06	8.48	131.00	0.90
42.00	0.48	78.03	1.18	133.10	0.38
42.04	0.93	80.95	0.31	139.03	0.83
43.08	9.00	82.01	2.08	140.02	0.52
44.11	0.93	83.05	0.62	141.05	0.73
45.14	100.00	88.02	0.73	145.08	4.81
46.13	2.60	88.98	4.43	151.04	4.99
47.10	2.22	89.94	2.74	152.07	0.38
48.96	0.66	90.99	9.73	153.09	0.45
49.88	0.38	92.04	0.45	163.06	0.93
50.95	6.61	93.03	2.11	171.05	9.80
53.10	0.52	94.05	0.59	172.08	0.69
55.15	0.35	95.06	5.96	173.08	0.55
56.11	0.35	99.93	1.42	175.10	0.45
57.09	2.53	100.99	3.53	189.06	0.52
57.14	0.52	102.03	0.97	191.06	1.07
58.05	0.48	103.07	0.73	193.07	2.94
59.00	8.69	106.07	0.52	235.13	15.72
59.94	0.52			236.11	1.39

PT951X 6 P.T.TELFORD 95/1 I-BU CI 04-DEC-85
CAL:CALT31 STA: 0:56

No.5 C.I.

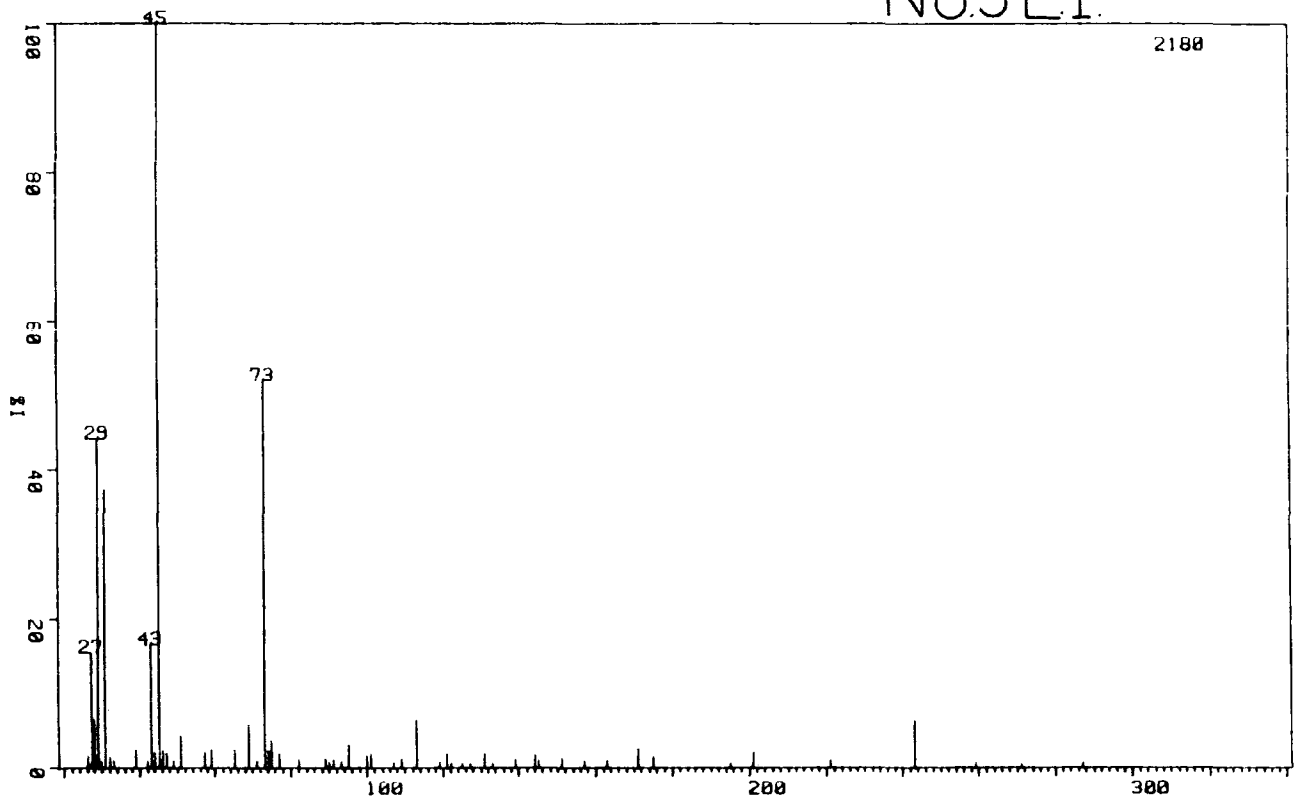


MASS	%HT. BASE	MASS	%HT. BASE
65.03	0.83	174.91	0.37
66.04	0.80	180.89	0.37
71.07	4.09	182.92	0.83
73.00	0.74	196.93	0.43
88.06	5.33	197.91	0.97
89.90	1.00	198.87	0.80
70.95	1.75	199.91	0.32
72.00	0.52	200.89	6.74
73.02	27.95	201.95	0.60
74.04	1.40	202.95	0.32
74.98	0.46	208.97	1.12
76.97	0.54	217.98	2.47
78.97	2.18	218.95	0.69
79.87	0.40	220.93	3.53
80.92	2.44	221.95	0.34
86.01	1.23	226.98	0.75
85.04	1.15	227.97	0.60
90.90	0.89	228.97	0.57
93.01	0.34	237.95	0.95
94.97	0.60	238.94	0.32
95.04	0.54	242.91	0.43
100.09	0.54	245.96	0.32
100.99	0.43	246.94	0.34
103.94	0.34	256.92	0.43
112.96	1.23	258.91	6.62
120.94	0.52	259.91	0.49
130.90	0.47	266.96	0.37
139.02	0.62	268.94	1.92
148.96	0.37	284.92	5.59
150.92	0.49	285.93	0.60
162.93	0.34	286.94	28.24
170.91	0.80	287.95	2.84

PT951X 7 P.T.TELFORD 95/1 EI
CAL:CALT31 STA:

No.5 E.I.

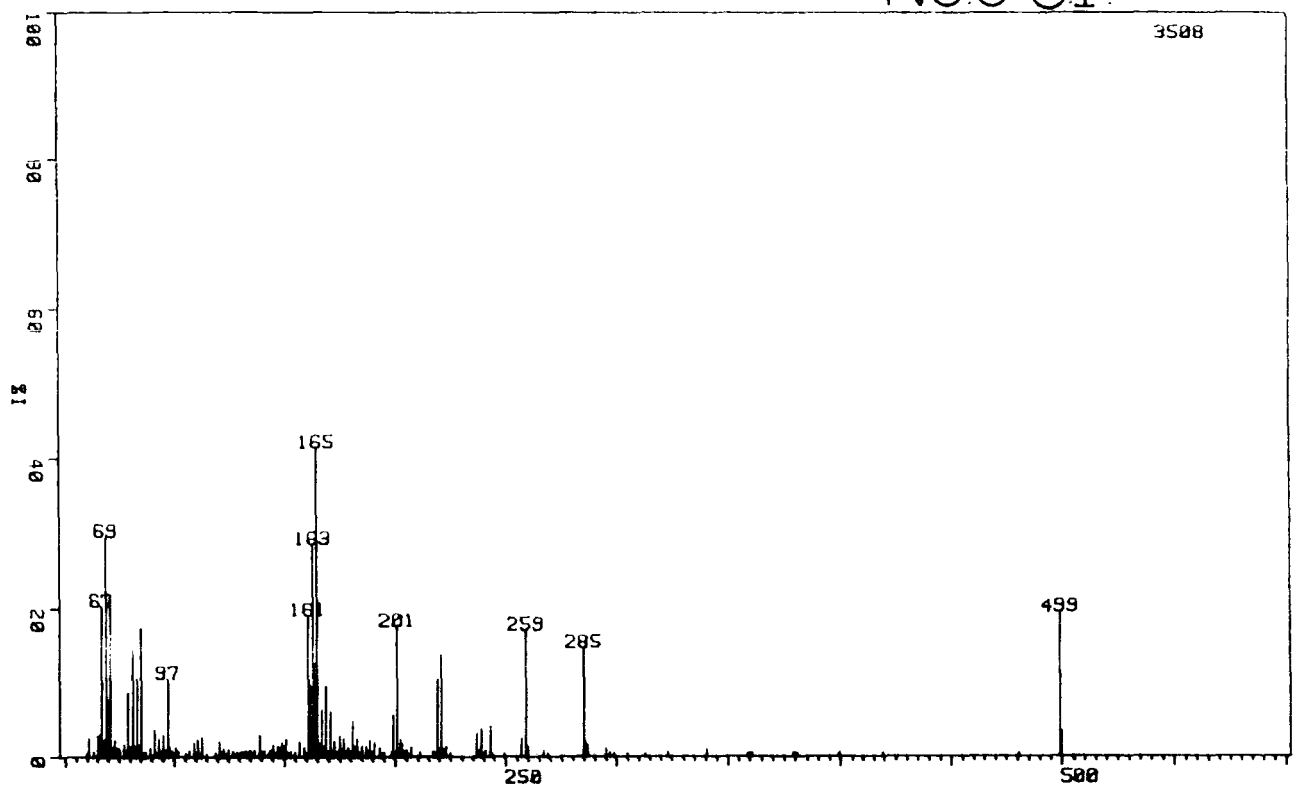
04-DEC-85
1:4



MASS	%HT. BASE	MASS	%HT. BASE
26.00	1.45	89.90	0.87
27.23	15.60	90.98	1.10
28.11	4.70	94.01	0.96
28.13	4.09	95.05	3.17
28.97	7.66	99.91	1.70
29.00	44.22	100.98	1.88
29.81	0.87	104.04	0.75
29.83	0.95	109.01	1.24
30.88	37.43	113.04	0.61
31.97	1.47	119.01	0.83
33.08	1.01	121.03	1.97
38.97	2.48	122.07	0.64
42.01	1.19	125.08	0.64
43.08	16.65	127.08	0.60
43.12	0.60	131.01	1.97
44.12	2.25	133.09	0.69
45.14	100.00	139.04	1.15
46.14	2.43	144.08	1.79
47.11	3.11	145.09	1.01
48.97	1.06	151.05	1.38
50.93	4.34	157.09	0.96
54.09	3.14	163.09	1.06
59.02	3.48	171.07	2.71
65.13	2.52	175.10	1.61
68.96	5.92	195.12	0.60
71.00	0.96	201.05	2.16
73.11	52.11	221.10	1.10
74.11	2.43	243.10	6.42
75.03	3.76	259.10	0.83
77.01	2.06	271.12	0.50
81.96	1.15	287.15	0.78
88.94	1.28		

P93FSX 11 P.T.TELFORD CI I-BU 26-FEB-85
CAL:CALT31 STR: 1:43

No.6 CI

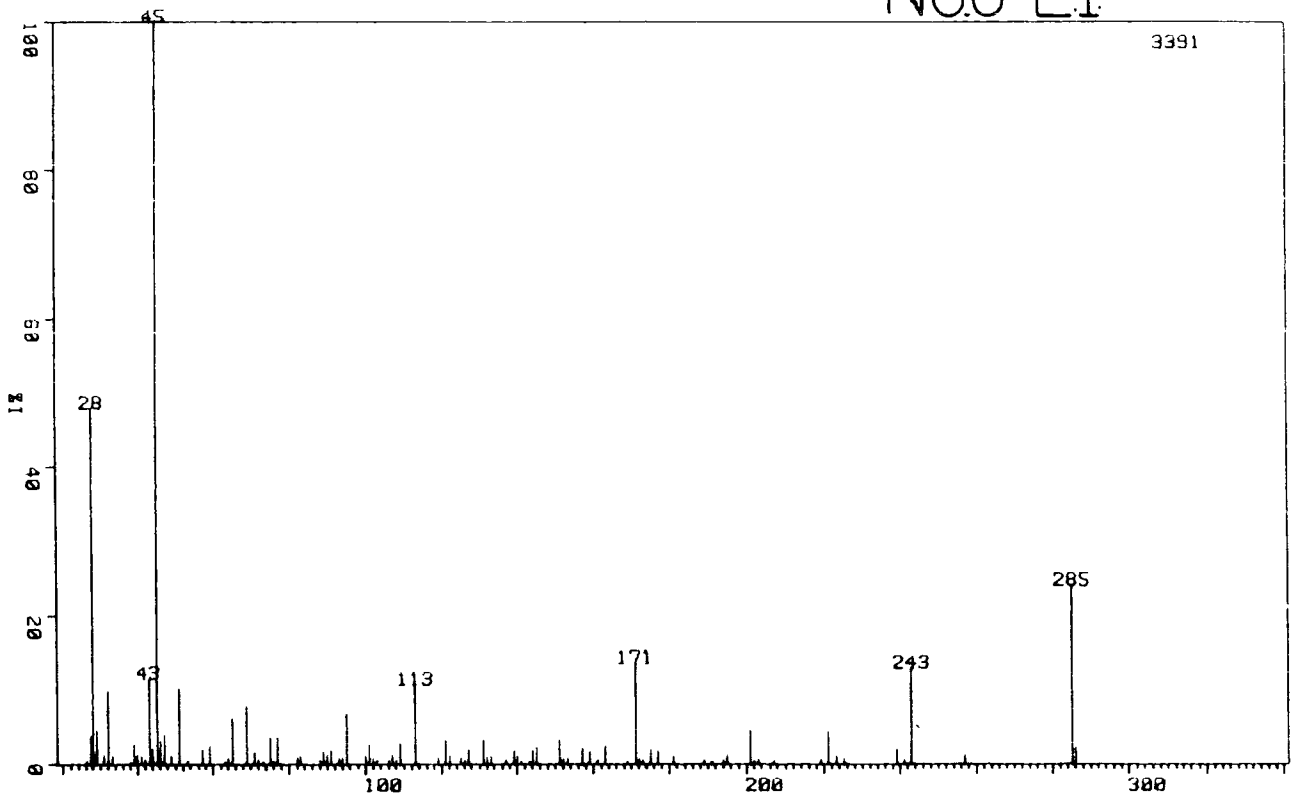


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE		
61.01	2.51	101.01	1.20	143.07	0.37	179.95	0.74	241.05	0.91
63.07	0.77	101.96	0.88	144.02	0.97	180.97	4.79	243.02	4.10
65.11	2.96	105.06	0.48	145.08	1.80	181.98	1.34	244.05	0.40
66.10	3.11	107.02	0.88	145.97	0.51	183.00	2.59	249.10	0.37
67.09	20.30	108.98	2.00	147.00	1.57	184.01	0.66	257.08	2.42
68.05	2.54	109.97	0.66	147.95	1.40	185.00	1.68	259.06	17.16
69.01	29.65	111.00	2.39	148.93	1.94	186.97	1.45	260.05	1.45
69.96	7.73	112.06	0.48	149.05	0.60	187.97	0.83	267.13	0.94
71.03	21.09	112.99	2.65	149.90	1.65	188.95	2.25	269.05	0.43
72.07	1.34	113.11	0.63	150.96	2.51	189.94	0.77	285.08	14.74
73.07	2.48	115.05	0.40	151.10	0.80	190.95	2.02	286.09	2.14
74.10	1.40	118.92	0.57	152.00	0.43	192.99	1.23	287.08	1.68
75.04	0.40	118.96	0.48	152.97	0.40	194.01	0.37	295.12	1.17
75.10	1.08	120.97	2.14	153.09	0.77	195.00	0.66	297.04	0.51
77.03	1.85	121.99	0.68	154.99	0.63	198.00	0.74	299.04	0.48
78.01	0.88	123.04	1.20	157.01	2.05	198.98	5.84	305.07	0.37
78.97	8.72	124.06	0.37	158.99	1.25	199.96	0.54	313.12	0.40
79.92	1.62	125.05	1.14	159.93	0.48	200.98	17.67	323.10	0.60
80.98	14.60	126.98	0.71	160.95	19.16	201.99	2.54	341.13	1.05
82.02	1.51	127.07	0.77	161.98	9.78	203.01	1.85	359.03	0.37
83.06	10.58	128.97	0.57	163.00	28.71	204.00	0.74	360.02	0.37
84.09	1.77	129.03	0.43	164.01	12.60	205.03	1.05	361.07	0.57
85.11	17.47	130.92	0.66	165.01	41.51	205.99	0.43	379.10	0.51
86.08	0.77	131.97	0.66	166.00	1.91	207.00	1.31	380.03	0.54
86.98	0.34	132.90	0.80	166.98	6.36	211.06	0.54	381.10	0.37
87.04	0.74	133.01	0.74	167.13	0.60	217.06	0.77	399.14	0.43
88.92	1.23	133.12	0.31	167.92	1.31	218.03	0.57	400.05	0.66
90.94	3.65	133.92	0.63	168.93	9.58	219.01	10.60	419.10	0.46
91.98	0.37	134.94	0.94	169.93	0.83	220.01	1.08	481.21	0.54
93.03	2.37	135.12	0.71	170.98	6.16	221.02	13.88	499.11	19.61
94.03	0.66	136.85	0.68	172.01	0.77	222.03	1.17	500.08	3.39
95.04	2.94	136.99	0.63	172.97	2.02	223.07	1.45		
96.05	1.05	137.11	1.05	173.98	0.68	225.04	0.57		
97.04	10.63	138.86	0.60	174.97	2.88	225.15	0.40		
98.02	1.28	138.99	1.51	175.97	1.08	237.04	3.16		
99.00	0.91	139.08	3.02	176.98	2.71	238.03	0.88		
99.94	0.34	139.96	0.77	177.97	0.66	239.02	3.65		
100.93	1.23	141.01	0.91	178.94	1.17	240.02	0.37		

P93FSX 4 P.T.TELFORD EI
CAL:CALT31 STA:

No6 EI

26-FEB-85
0:43



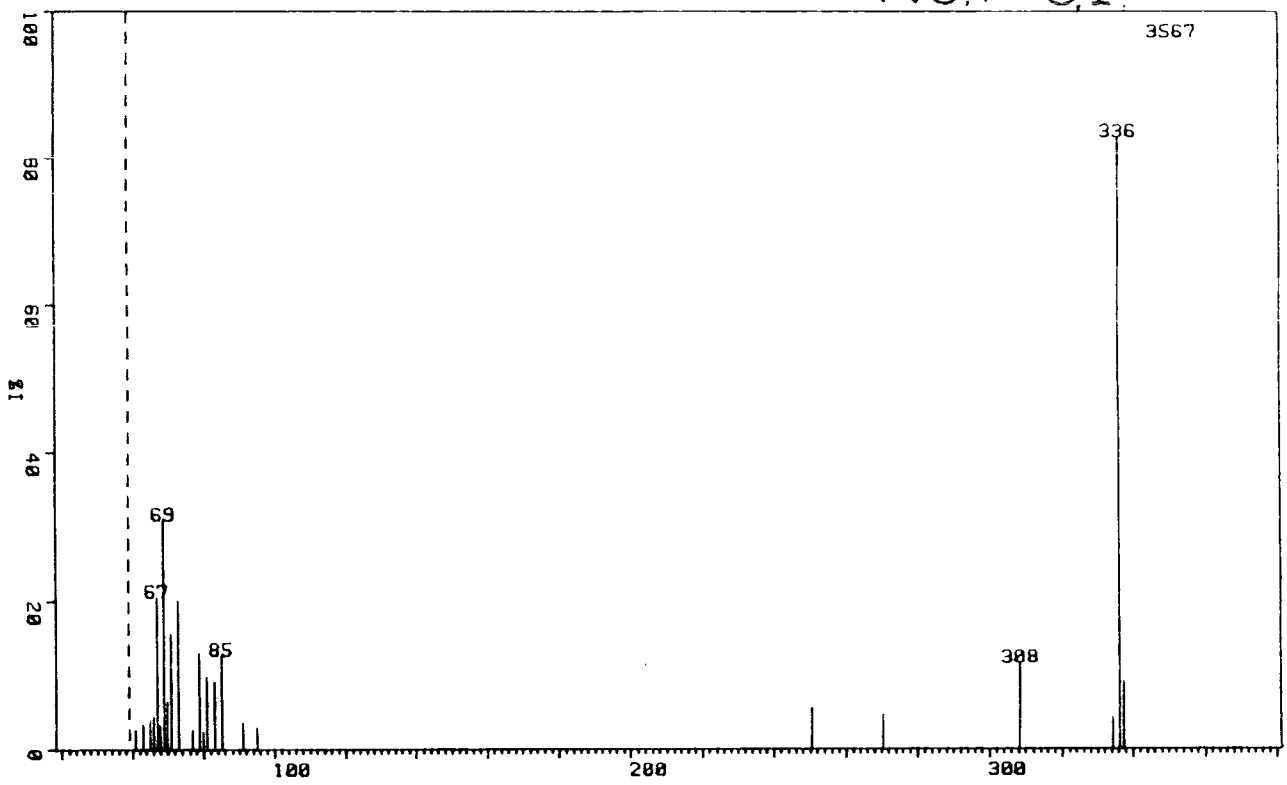
MASS	%HT. BASE	MASS	%HT. BASE				
26.30	0.47	68.96	7.90	131.02	3.30	207.11	0.41
27.23	3.83	70.99	1.62	132.07	1.09	219.11	0.74
28.11	47.86	72.05	0.68	133.08	1.18	221.10	4.48
28.13	1.24	73.11	0.41	137.07	0.56	223.08	1.21
28.97	4.63	75.08	3.66	139.05	1.89	225.09	0.80
29.00	1.09	76.08	0.53	140.02	1.21	239.08	2.03
30.86	1.33	77.06	3.57	141.06	0.38	241.10	0.50
30.89	0.62	82.02	1.00	143.07	0.35	243.09	13.06
31.97	9.97	83.07	1.15	144.09	1.92	257.13	1.24
33.08	1.21	88.03	0.50	145.10	2.33	285.16	24.15
38.05	0.35	89.00	1.77	151.04	3.21	286.13	2.27
38.97	2.74	89.95	1.33	152.07	0.83		
39.81	1.42	91.02	1.89	153.09	0.83		
40.96	1.09	93.05	0.97	157.07	2.09		
42.02	0.68	94.06	0.91	159.05	1.74		
42.06	0.47	95.08	6.81	161.05	0.62		
43.09	11.68	99.95	1.36	163.07	2.48		
43.12	1.56	101.02	2.65	169.05	0.38		
44.10	1.03	102.06	0.88	171.07	13.68		
44.13	2.21	103.10	0.50	172.10	0.86		
45.16	100.00	106.06	0.71	173.09	0.56		
46.15	3.18	107.06	1.33	175.08	2.06		
47.12	4.10	108.05	0.62	177.08	1.89		
48.98	1.12	109.02	2.83	181.04	1.09		
50.96	10.29	113.07	10.85	189.05	0.59		
53.12	0.47	119.03	0.91	191.07	0.38		
57.11	1.95	121.05	3.21	194.09	0.62		
59.03	2.45	122.09	1.39	195.09	1.30		
63.11	0.41	125.10	0.94	201.07	4.54		
64.13	0.88	126.10	0.50	202.10	0.47		
65.12	6.28	127.07	2.03	203.09	0.77		

PT211X S P.T.TELFORD 121/1 CI I-BU
CAL:CALT1 STA:

No.7 CI

02-JUL-85
8:50

X 8

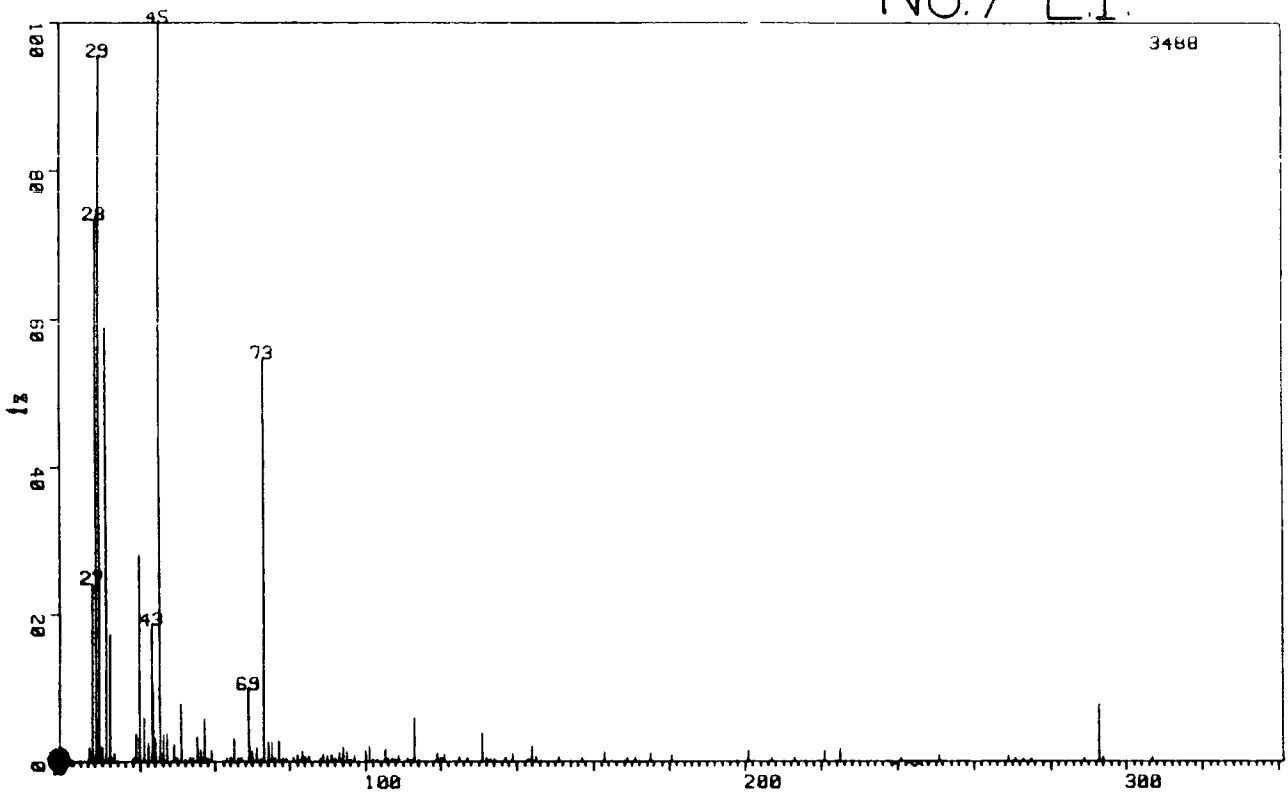


MASS	%HT. BASE
60.91	0.34
62.98	0.42
65.02	0.53
66.02	0.59
67.01	2.58
67.98	0.42
68.94	3.87
69.88	0.81
70.96	1.96
73.03	2.52
77.01	0.34
78.95	1.63
79.90	0.31
80.95	1.23
83.04	1.15
85.08	1.60
90.93	0.45
95.03	0.39
250.54	0.70
270.50	0.59
308.46	1.46
334.42	0.53
336.44	10.37
337.43	1.15

PT211X S P.T.TELFORD 121/1
CAL:CALT1 STA:

No.7 E.I.

02-JUL-85
0:50

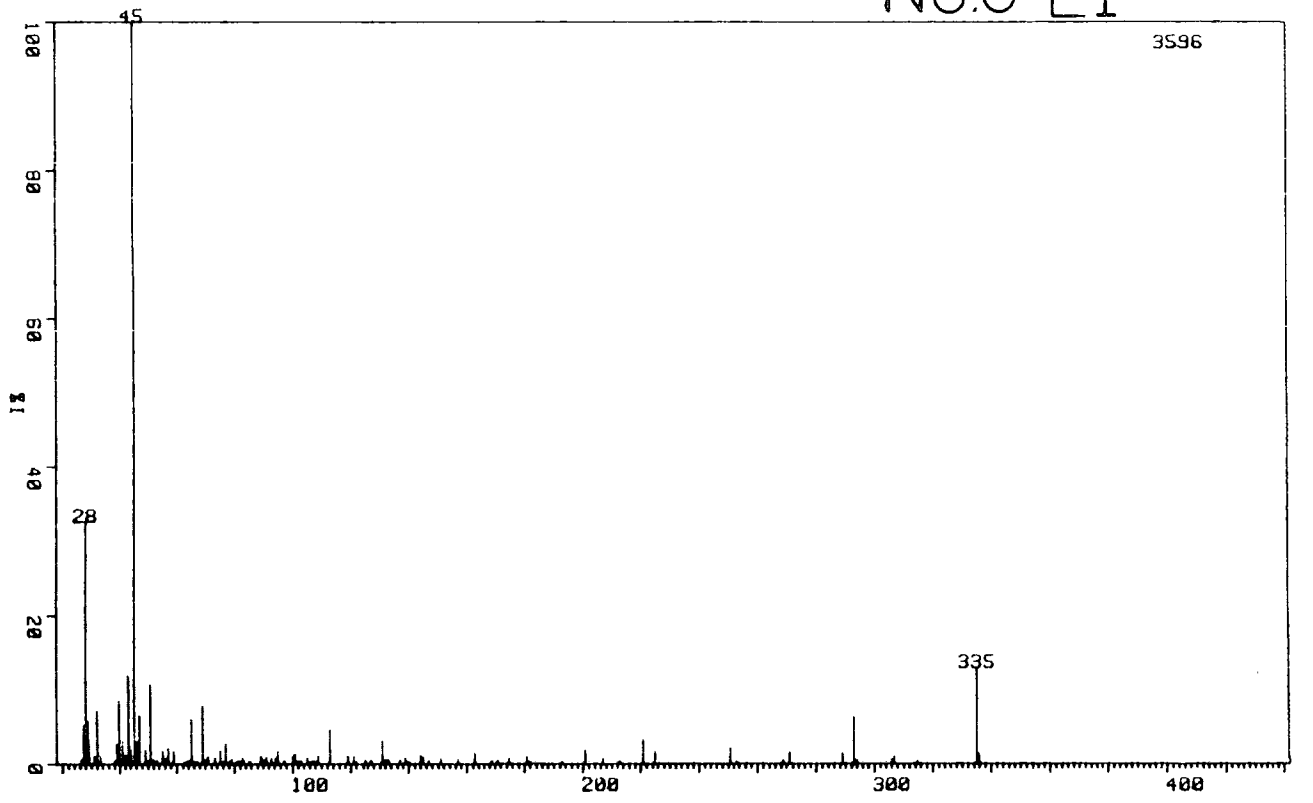


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.37	1.98	55.14	3.50	89.87	0.83	138.95	1.12
27.29	24.23	56.14	1.78	90.96	1.06	142.97	0.29
28.17	73.37	57.07	1.46	92.02	0.43	143.98	2.15
28.19	5.59	57.12	5.82	92.98	1.32	144.99	0.83
29.02	11.01	58.05	0.49	94.03	2.04	150.94	0.72
29.05	95.41	58.99	1.66	95.02	1.43	156.98	0.57
29.86	0.60	63.06	0.60	95.09	0.66	162.95	1.35
29.88	2.12	64.08	0.66	96.09	0.32	168.91	0.43
30.95	58.94	65.09	3.24	97.09	0.92	170.92	0.54
32.03	17.35	66.11	0.52	99.88	1.58	174.94	1.20
32.06	0.72	67.07	0.60	100.97	2.15	180.90	0.97
33.13	1.12	68.93	9.83	102.01	0.40	200.90	1.55
38.07	0.52	69.00	2.55	103.05	0.29	206.95	0.60
38.99	3.81	69.88	0.34	105.09	1.69	212.92	0.54
39.82	28.12	69.94	1.46	106.01	0.43	220.90	1.55
39.89	0.60	70.95	1.06	107.01	0.40	224.95	1.78
40.97	6.14	71.01	2.04	107.99	0.49	240.88	0.54
42.03	1.12	72.02	0.37	108.96	0.89	250.92	0.86
42.06	2.58	73.07	54.73	111.05	0.43	268.92	0.89
43.09	18.61	74.09	2.67	111.96	0.34	270.91	0.60
43.13	9.63	75.04	2.75	112.98	6.02	272.91	0.34
44.10	1.26	76.05	0.54	114.01	0.26	274.94	0.34
44.13	3.24	77.04	2.87	118.91	1.18	288.91	0.43
45.15	100.00	78.02	0.40	119.00	1.18	292.91	7.83
46.14	3.81	78.99	0.46	119.97	0.60	293.93	0.66
47.11	3.93	81.00	0.66	120.93	1.06	306.88	0.66
48.97	2.38	82.01	1.00	124.97	0.72		
49.00	0.46	83.04	0.40	126.97	0.54		
49.88	0.52	83.10	1.43	130.90	3.84		
50.94	7.88	84.12	0.77	131.97	0.57		
52.03	0.34	85.10	0.92	133.00	0.40		
53.09	0.66	87.94	0.40	134.09	0.29		
54.13	0.49	88.90	1.00	136.98	0.57		

PT212X 4 P.T.TELFORD 121/2
CAL:CALT1 STA:

No.8 EI

02-JUL-85
0:42

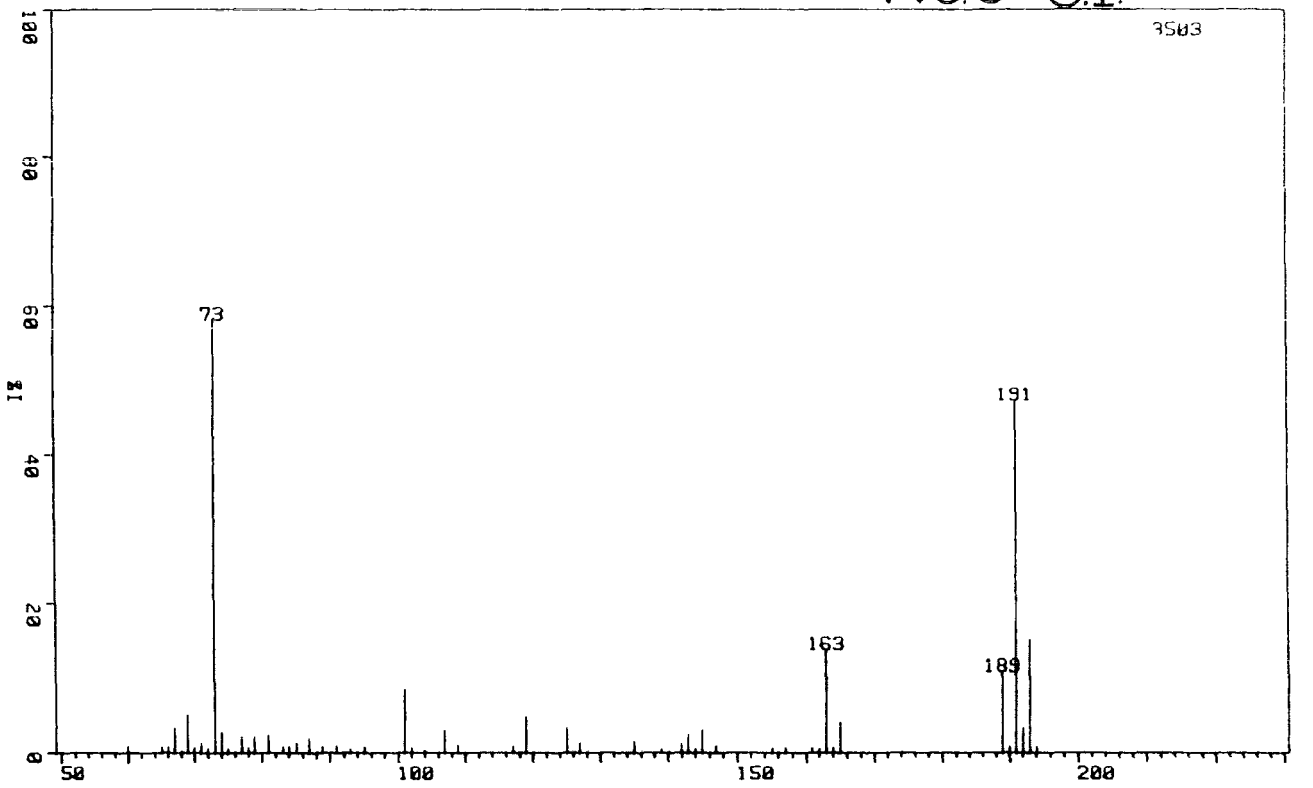


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE		
26.37	0.67	57.06	1.06	95.04	1.75	170.89	0.47
27.30	5.34	57.12	2.14	97.12	0.36	174.93	0.70
28.17	32.68	58.98	1.70	99.91	1.17	180.87	1.03
28.19	1.61	63.06	0.33	100.96	1.47	181.94	0.31
29.02	5.81	64.06	0.36	102.01	0.47	192.92	0.31
29.05	3.25	65.08	0.09	103.04	0.39	200.87	1.89
30.93	0.72	66.09	0.31	105.08	0.86	206.93	0.81
30.95	1.20	67.09	0.33	106.02	0.31	212.93	0.36
32.03	7.20	68.94	7.79	107.01	0.42	220.90	3.31
33.13	1.25	69.01	0.97	107.99	0.39	224.93	1.70
38.07	0.39	69.90	0.25	108.96	1.25	250.86	2.17
38.99	2.75	69.96	0.58	112.96	4.59	252.93	0.33
39.82	8.54	70.97	1.00	118.91	1.20	268.91	0.64
39.88	0.42	71.02	0.95	118.98	0.47	270.87	1.67
40.97	3.17	73.08	0.89	120.92	1.17	288.91	1.53
42.02	0.72	75.05	1.89	121.95	0.28	292.87	6.37
42.06	1.31	76.06	0.33	124.96	0.47	293.95	0.53
43.09	11.99	77.04	2.73	126.97	0.56	305.91	0.61
43.12	5.42	78.03	0.31	130.88	3.11	306.90	1.20
44.09	0.53	79.00	0 58	131.97	0.70	314.96	0.47
44.13	2.14	81.02	0.36	132.99	0.64	334.93	12.99
45.15	100.00	81.99	0.42	136.97	0.56	335.92	1.45
46.14	3.09	82.03	0.42	138.94	0.92		
47.10	6.51	83.05	0.83	139.91	0.33		
48.96	1.95	83.11	0.47	143.96	1.28		
49.88	0.39	85.15	0.42	144.97	0.97		
50.93	10.73	88.97	1.08	146.98	0.36		
52.02	0.53	89.92	0.70	150.93	0.83		
53.08	0.42	90.98	0.97	156.96	0.81		
55.13	1.78	93.01	0.83	162.93	1.45		
56.14	0.83	94.06	0.81	168.90	0.36		

PT1121 4 P.T.TELFORD 112/1 I-BU CI
CAL:CALT31 STA:

No.9 C.I.

04-DEC-85
0:40

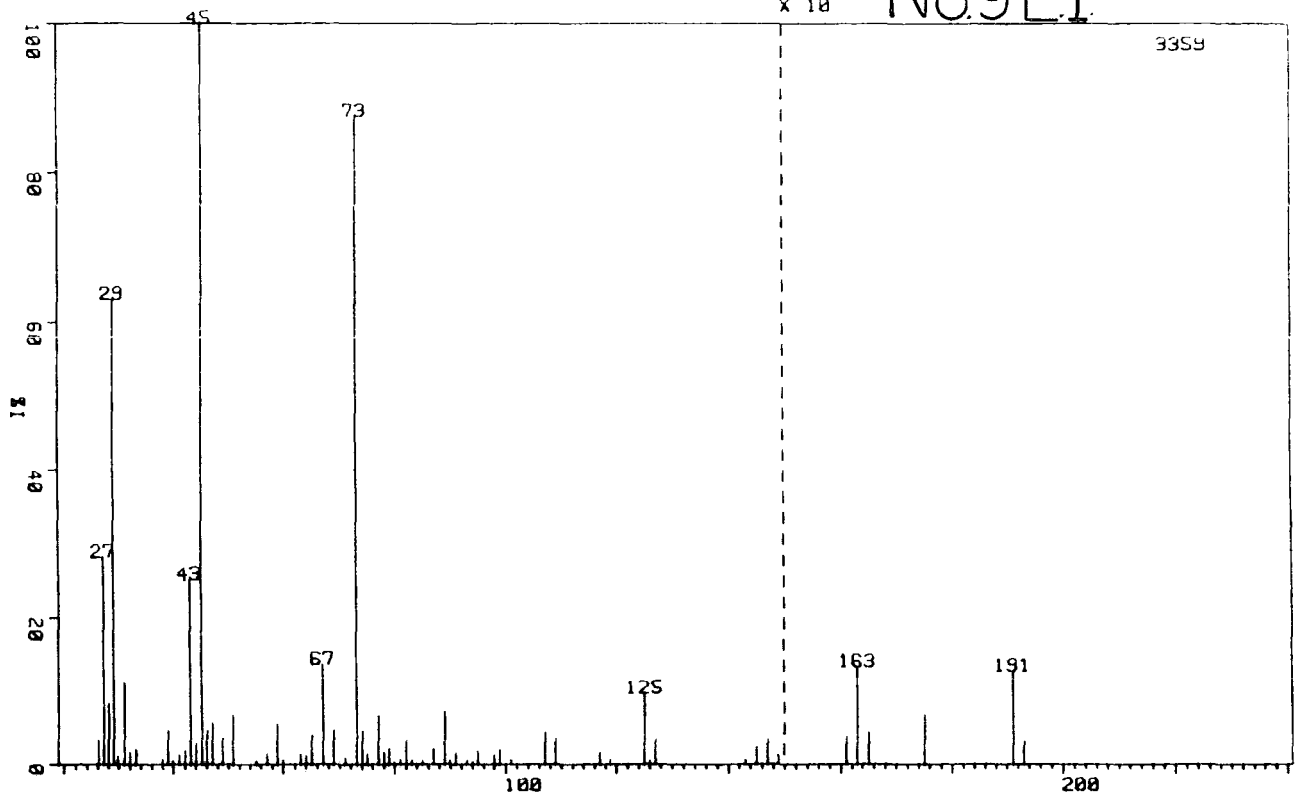


MASS	%HT. BASE	MASS	%HT. BASE
65.03	0.83	108.91	1.11
66.04	0.91	117.02	0.97
66.95	0.94	118.98	4.88
67.02	3.34	124.94	3.45
68.00	0.29	126.93	1.23
68.95	5.17	134.98	1.54
69.90	0.88	138.97	0.54
70.95	1.43	141.91	1.26
72.01	0.54	142.90	2.63
73.01	58.21	143.93	0.51
74.04	2.83	144.91	3.11
74.98	0.63	146.90	0.91
75.05	0.37	147.07	0.94
76.97	2.14	154.99	0.63
77.95	0.69	157.00	0.74
78.91	2.26	160.86	0.63
80.92	2.37	161.95	0.49
83.01	0.91	190.92	47.47
83.99	0.94	191.95	3.37
85.05	1.43	192.97	15.16
86.95	2.06	193.98	0.91
88.89	0.97	238.92	0.43
90.91	0.94		
92.93	0.34		
93.00	0.49		
94.96	0.94		
95.05	0.54		
100.96	8.51		
102.00	0.71		
104.01	0.43		
106.96	3.14		

PT1121 4 P.T.TELFORD 112/1 EI
CAL:CALT31 STA:

No.9EI

04-DEC-85
0:44

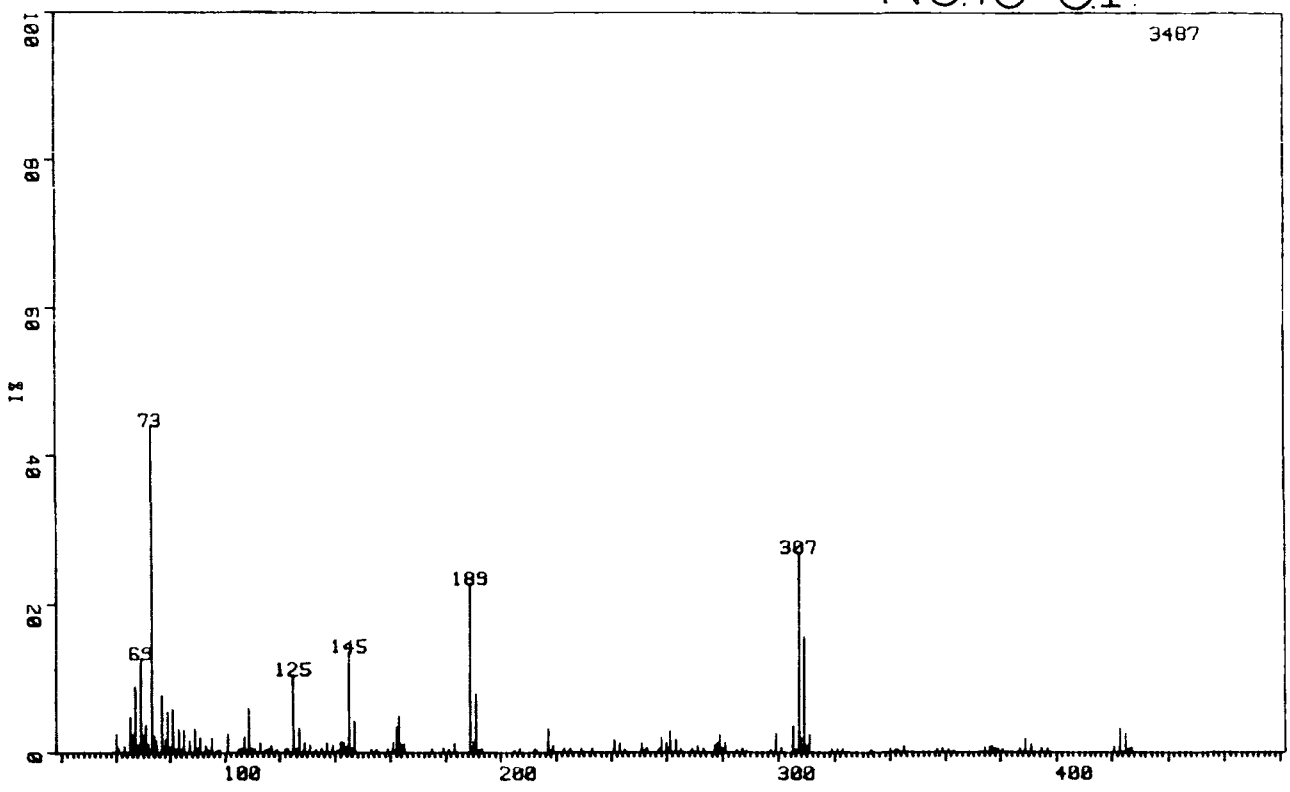


MASS	%HT. BASE	MASS	%HT. BASE		
26.29	3.39	65.09	4.08	126.02	0.45
27.22	28.19	67.02	13.72	127.01	3.36
28.11	8.37	68.94	4.76	143.01	0.60
28.96	10.09	70.98	0.95	145.02	2.44
28.99	63.11	73.09	87.62	146.99	3.42
29.80	0.68	74.12	4.61	148.94	1.40
29.82	1.19	75.03	1.55	160.97	0.39
30.87	11.34	77.02	6.73	163.01	1.34
31.96	1.82	77.99	1.82	165.03	0.45
33.06	2.20	78.90	0.39	175.00	0.68
38.02	0.80	78.95	2.26	190.99	1.28
38.95	4.88	79.87	0.39	193.03	0.33
39.79	0.48	80.91	0.77		
39.85	0.51	81.95	3.36		
40.93	1.49	82.99	0.54		
41.98	1.94	84.97	0.60		
43.05	25.22	86.99	2.23		
43.09	1.10	88.93	7.35		
44.10	3.01	89.90	0.51		
45.12	100.00	90.96	1.73		
46.12	4.85	93.01	0.54		
47.08	5.72	94.03	0.36		
48.94	3.57	95.03	1.88		
48.98	0.45	97.95	1.37		
50.92	6.79	98.92	2.11		
55.13	0.48	100.92	0.63		
57.06	1.55	107.03	4.53		
58.97	5.69	108.97	[illegible]		
59.91	0.60	116.98	1.70		
63.04	1.46	118.94	0.74		
64.07	1.25	125.01	9.79		

P1122X 5 P.T.TELFORD 112/2 I-BU CI
CAL:CALT31 STR:

No.10 CI

04-DEC-85
8:51

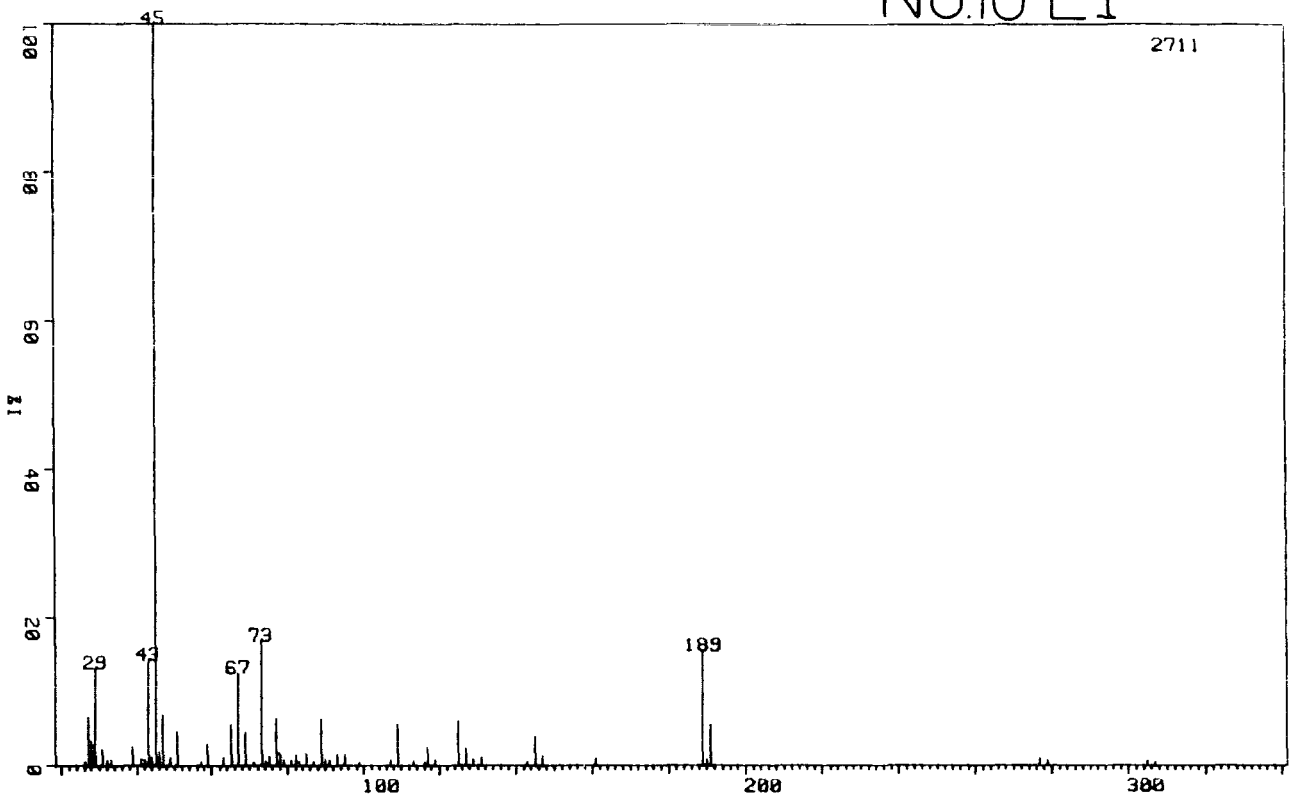


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
60.91	0.60	100.99	2.44	161.98	3.50	268.96	0.49	380.92	0.36
62.99	0.89	104.05	0.46	162.97	5.05	270.96	0.94	382.03	0.63
65.03	4.28	106.03	0.60	163.10	0.54	272.99	0.54	388.99	1.92
66.04	2.55	107.60	2.15	164.00	1.29	276.94	1.06	390.98	1.12
66.94	3.67	107.98	0.32	164.99	1.18	277.94	1.35	394.94	0.26
67.03	8.86	108.95	5.97	174.96	0.54	278.91	2.38	396.94	0.63
68.00	1.00	109.02	0.32	178.99	0.57	279.91	0.25	420.94	0.83
68.87	1.23	109.92	0.52	181.01	0.37	280.88	1.35	422.92	0.32
69.00	12.62	110.90	0.54	183.03	1.23	284.98	0.32	424.94	0.41
69.94	2.47	112.97	1.38	188.92	22.77	287.00	0.57	426.00	0.46
70.93	3.29	115.06	0.34	189.91	1.55	288.97	0.43	434.98	0.25
72.03	1.23	115.95	0.46	190.91	7.94	297.03	0.32		
73.06	44.02	116.95	0.95	191.94	0.32	299.01	2.58		
74.05	2.38	117.05	0.49	192.95	0.43	301.01	0.69		
75.03	1.52	119.92	0.32	204.93	0.29	304.96	3.61		
77.01	7.80	121.97	0.54	206.90	0.52	305.98	0.43		
77.99	1.92	122.96	0.49	211.96	0.43	306.98	24.99		
78.96	5.59	124.97	10.50	212.91	0.34	307.97	1.98		
79.91	0.80	125.98	0.54	216.97	3.24	308.97	15.66		
80.89	0.66	126.96	3.30	217.94	0.34	309.96	1.09		
80.99	5.94	128.89	1.29	218.94	1.00	310.94	2.38		
81.97	0.52	130.91	1.06	222.88	0.52	318.90	0.57		
82.04	0.92	133.06	0.34	224.94	0.37	320.96	0.40		
83.08	3.15	135.05	0.49	225.03	0.26	322.96	0.46		
84.10	0.46	137.05	1.29	229.02	0.57	333.02	0.29		
84.99	0.66	138.95	0.49	232.96	0.54	339.96	0.43		
85.11	3.13	139.04	1.06	240.81	1.69	341.96	0.34		
86.99	1.75	140.96	0.29	242.90	1.26	342.98	0.32		
88.92	3.27	141.97	1.49	244.92	0.34	345.09	0.86		
89.83	0.66	142.97	1.49	250.93	1.35	356.92	0.43		
90.95	2.12	143.99	0.80	252.04	0.32	358.88	0.60		
92.93	0.63	144.98	13.51	252.92	0.57	360.93	0.52		
93.05	0.98	145.98	0.60	256.94	0.43	362.99	0.26		
94.00	0.32	146.96	4.30	257.92	1.98	373.98	0.25		
94.04	0.37	152.99	0.43	259.90	1.35	375.98	0.77		
95.03	1.98	154.96	0.40	260.88	2.90	376.94	1.00		
97.01	0.32	158.94	0.46	262.97	1.81	377.94	0.43		
97.94	0.40	160.89	1.46	264.95	0.32	378.91	0.52		

P1122X 5 P.T.TELFORD 112/2 EI
CAL:CALT31 STA:

No.10 EI

04-DEC-85
0:52

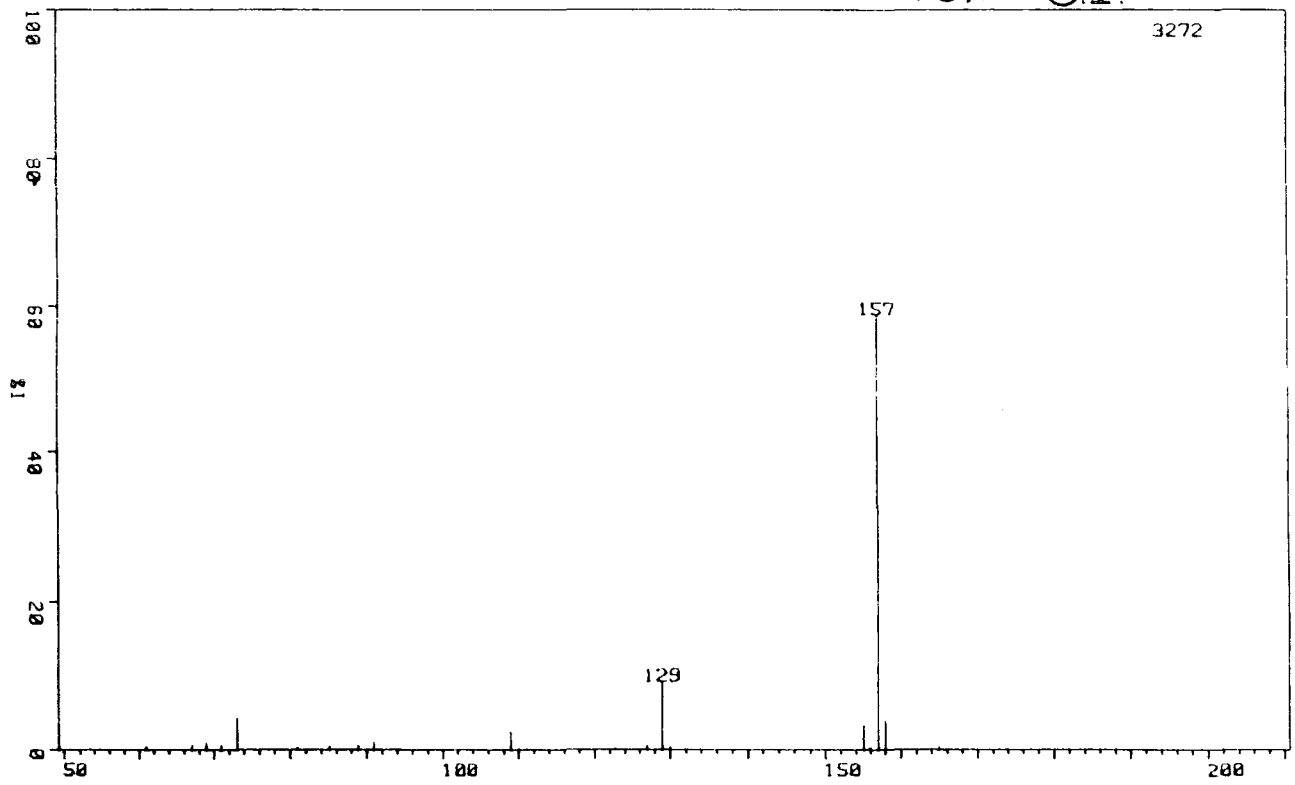


MASS	%HT. BASE	MASS	%HT. BASE		
24.50	0.63	77.01	6.46	276.99	1.07
27.23	6.64	77.99	1.81	278.97	0.81
28.11	3.47	78.95	0.85	305.05	0.77
29.13	1.25	80.90	0.77	307.07	0.55
28.96	2.95	81.98	1.44		
39.00	13.71	83.03	0.52		
40.88	2.29	85.00	1.66		
31.97	0.85	86.98	0.63		
33.07	1.00	88.97	6.46		
38.96	2.62	89.92	0.96		
40.94	0.94	90.98	0.85		
42.00	0.89	93.01	1.70		
43.07	14.31	95.04	1.51		
43.11	0.89	98.94	0.52		
44.11	1.33	107.04	0.85		
45.13	100.00	109.99	5.64		
46.14	2.07	113.03	0.77		
47.10	0.90	116.00	0.55		
48.94	1.11	117.00	2.51		
48.96	0.94	118.95	0.85		
50.94	4.45	125.05	6.12		
57.08	0.63	127.03	2.47		
59.00	3.06	128.96	0.89		
63.06	1.14	130.98	1.14		
65.11	5.61	143.03	0.63		
67.02	12.50	145.05	4.06		
68.94	4.54	147.02	1.40		
70.99	0.48	160.99	1.07		
73.09	15.86	189.02	15.53		
74.12	0.70	190.01	0.89		
75.03	1.29	191.02	5.57		

P1131X 2 P.T.TELFORD CI I-BU
CAL:CALT31 STA:

No.11 C.I.

26-FEB-85
8:27

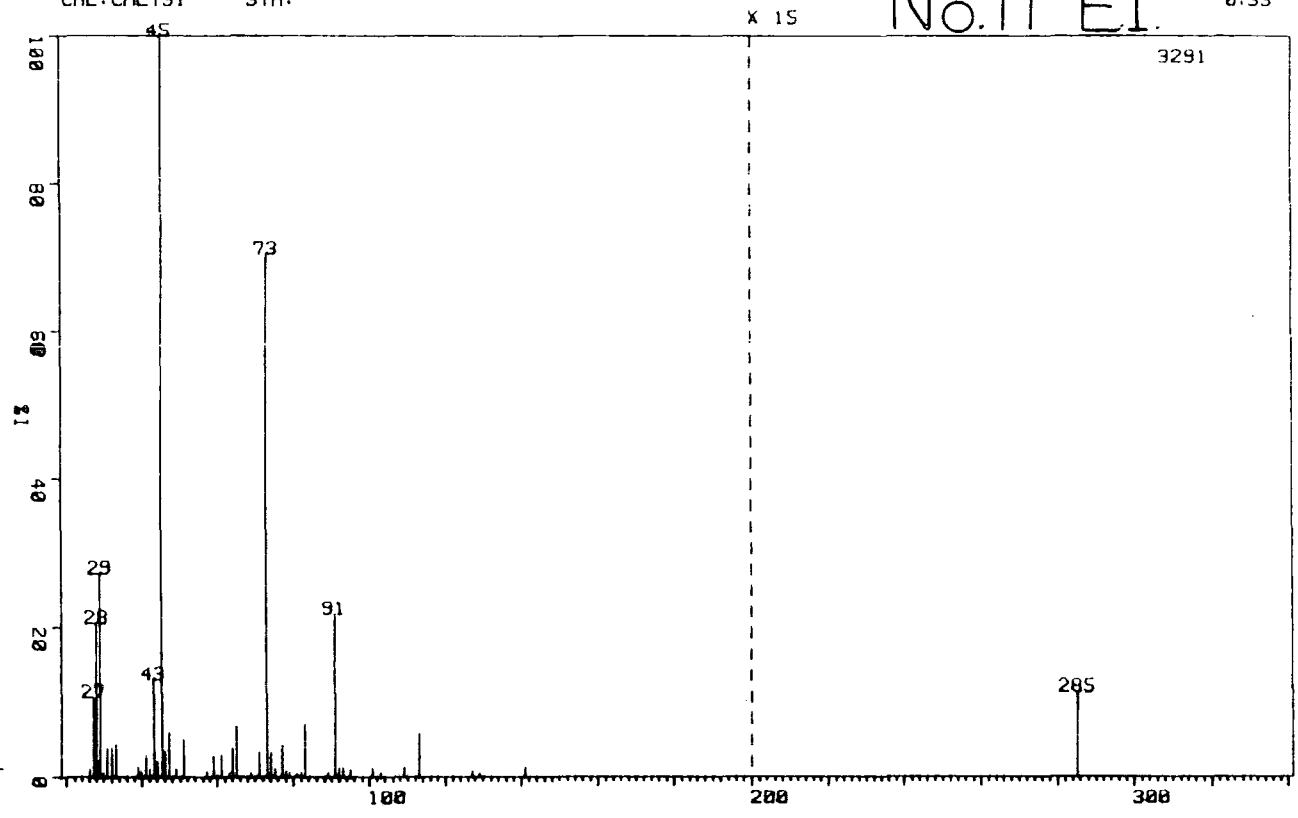


MASS	%HT. BASE
60.90	0.31
67.02	0.58
68.95	1.01
70.94	0.58
73.00	4.43
80.91	0.34
85.03	0.49
88.90	0.55
90.89	1.13
108.94	2.54
126.97	0.55
128.94	9.38
129.91	0.40
154.98	3.39
155.98	0.31
156.98	58.89
157.97	4.00
164.88	0.40

P1131X 3 P.T.TELFORD EI
CAL:CALT31 STA:

No.11 EI

26-FEB-85
0:35

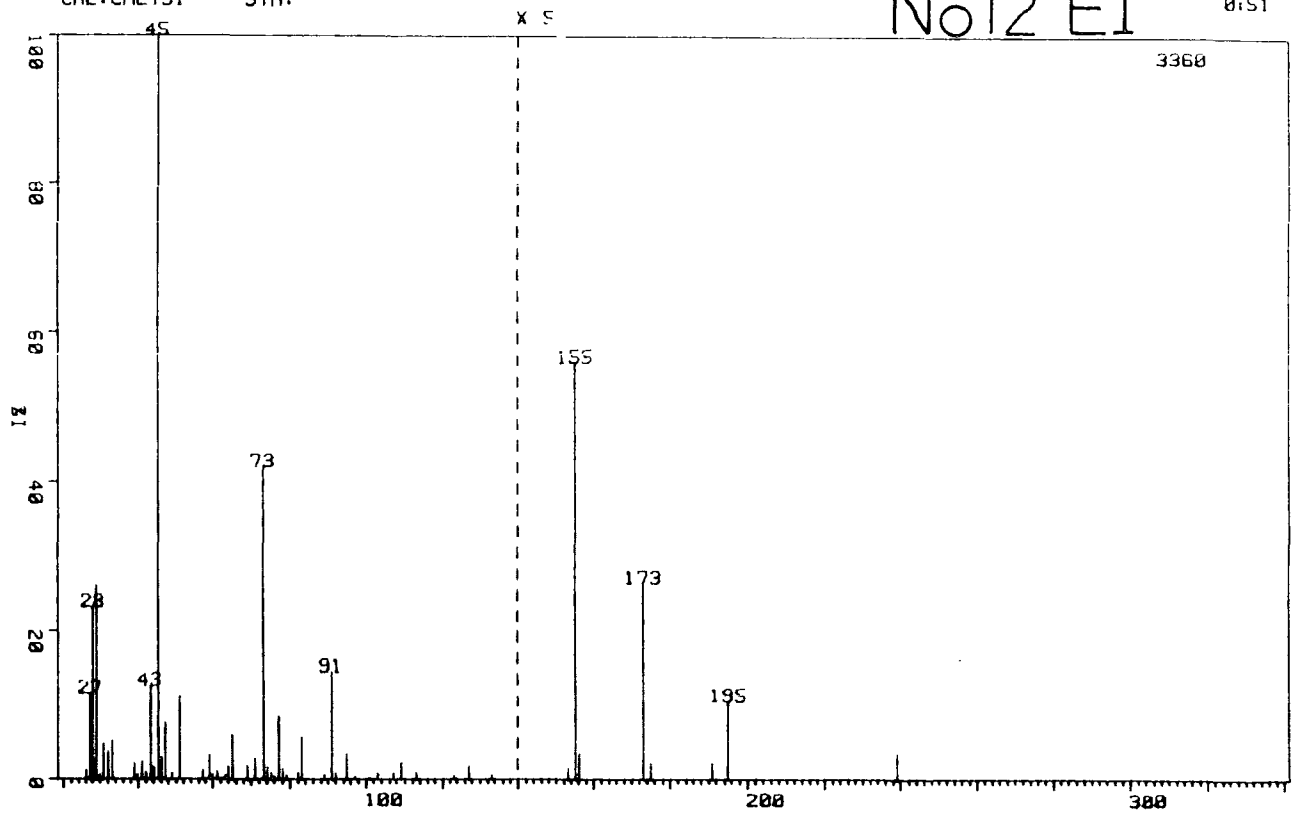


MASS	%HT. BASE	MASS	%HT. BASE
26.30	1.15	68.96	0.49
27.23	10.67	71.00	3.22
28.11	20.63	73.11	70.50
28.13	2.10	74.10	3.31
28.97	3.89	75.03	1.19
29.00	27.35	77.01	4.22
29.83	0.64	77.98	0.82
30.86	0.70	78.95	0.70
30.88	3.86	80.93	0.40
31.97	3.89	81.96	0.70
33.08	4.41	83.00	7.14
38.97	1.37	88.96	0.61
39.81	0.76	90.96	21.85
40.96	3.04	92.00	1.28
42.01	1.19	93.00	1.28
43.08	13.10	95.03	1.06
43.12	0.64	100.87	1.34
44.12	2.16	102.96	0.70
45.15	100.00	109.04	1.37
46.15	3.52	113.08	5.80
47.11	6.05	127.12	0.82
48.98	1.19	129.05	0.58
50.96	5.07	141.08	1.46
57.10	0.79	285.23	0.76
59.02	2.80		
59.96	0.30		
60.99	1.31		
61.03	3.01		
63.10	0.70		
64.10	3.98		
65.09	6.75		

P1132X 5 P.T.TELFORD EI
CAL:CALT31 STA:

No12 EI

26-FEB-85
0:51

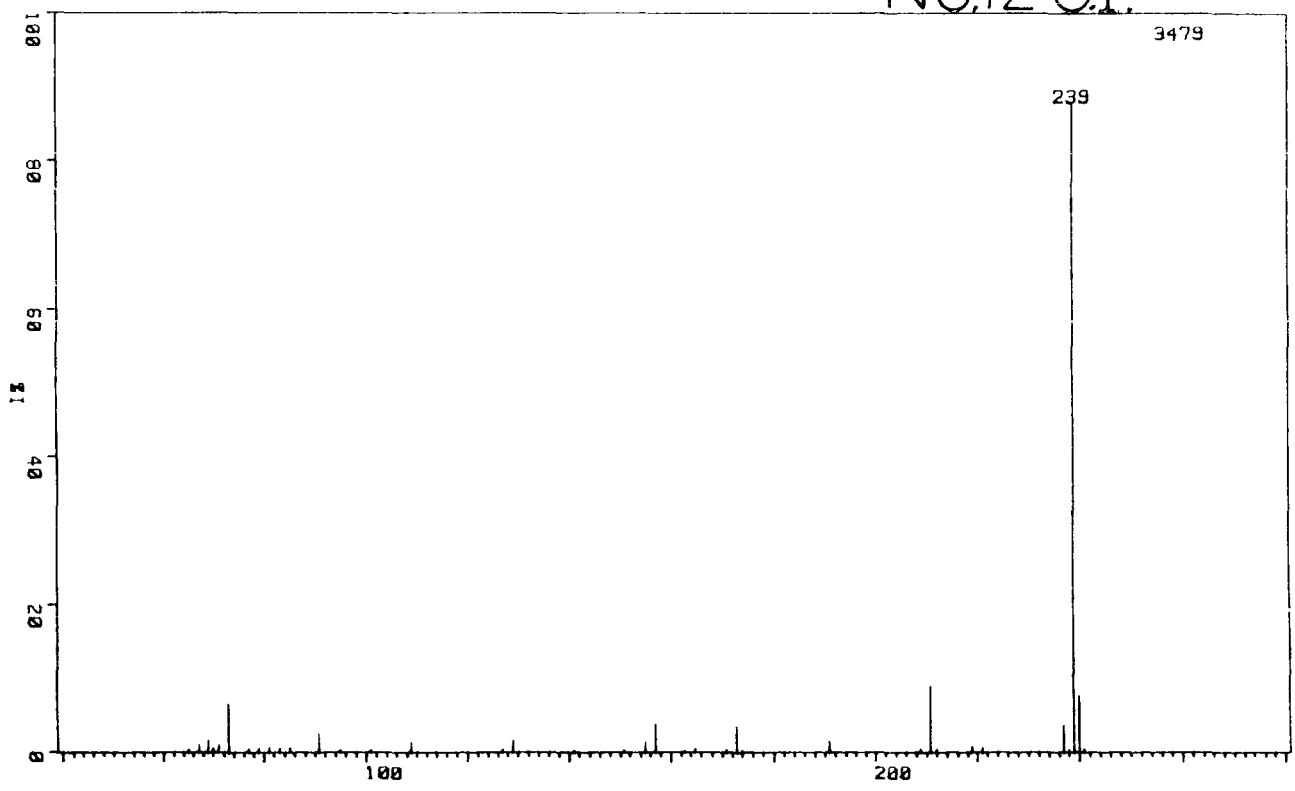


MASS	%HT. BASE	MASS	%HT. BASE
26.30	1.37	70.98	2.80
27.23	11.70	73.10	42.14
28.11	23.30	74.12	1.73
28.13	2.71	75.05	0.95
28.97	5.33	76.04	0.42
29.00	26.19	77.02	8.54
29.83	0.62	78.00	1.49
30.86	1.04	78.96	0.62
30.89	4.79	81.97	1.04
31.97	3.81	83.01	5.83
33.08	5.27	88.96	0.68
38.97	2.17	90.97	14.52
39.81	0.57	92.01	0.89
40.96	2.38	95.04	3.48
42.01	1.04	97.04	0.39
43.08	12.65	100.96	0.30
43.12	1.01	103.05	0.86
44.12	1.85	107.05	0.89
45.15	100.00	109.00	2.32
46.15	3.07	113.04	1.04
47.11	7.59	123.10	0.45
48.98	0.86	127.07	1.90
50.96	11.43	133.09	0.51
57.10	1.22	153.11	0.33
59.02	3.27	155.15	11.22
59.96	0.65	156.11	0.71
60.99	0.57	173.07	5.33
61.03	1.13	175.04	0.45
63.10	0.48	191.04	0.45
64.12	1.82	195.06	2.14
65.11	6.13	239.12	0.71
68.96	1.96		

P1132X 4 P.T. TELFORD CI I-BU
CAL: CALT31 STA:

No.12 C.I.

26-FEB-85
8:44

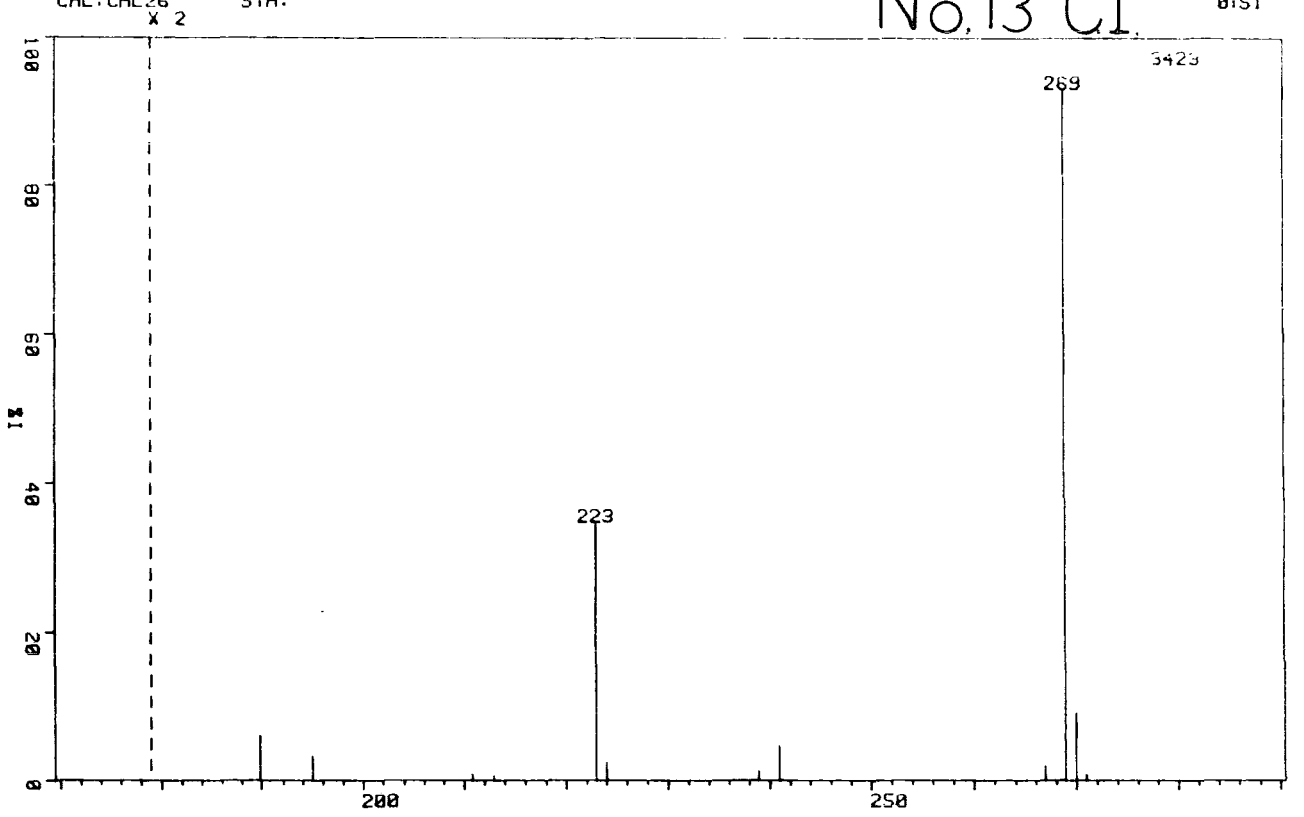


MASS	%HT. BASE		
65.01	0.37	220.96	0.75
67.01	1.12	236.94	3.77
68.95	1.70	237.90	0.37
69.89	0.46	238.92	87.96
70.94	1.09	239.91	7.79
73.00	6.64	240.91	0.52
76.95	0.43		
78.91	0.55		
80.90	0.69		
82.99	0.63		
85.03	0.75		
90.86	2.62		
94.96	0.32		
100.94	0.34		
108.92	1.44		
126.94	0.40		
128.92	1.67		
140.89	0.26		
150.86	0.29		
154.96	1.55		
156.95	3.88		
162.84	0.34		
164.84	0.46		
170.86	0.40		
172.88	3.45		
173.92	0.32		
190.85	1.61		
208.88	0.46		
210.87	9.08		
211.93	0.60		
218.95	0.80		

PT131X S P.T.TELFORD 1.6U C.I.
CAL:CAL26 STA:

No.13 CI

09-MAY-85
8:51

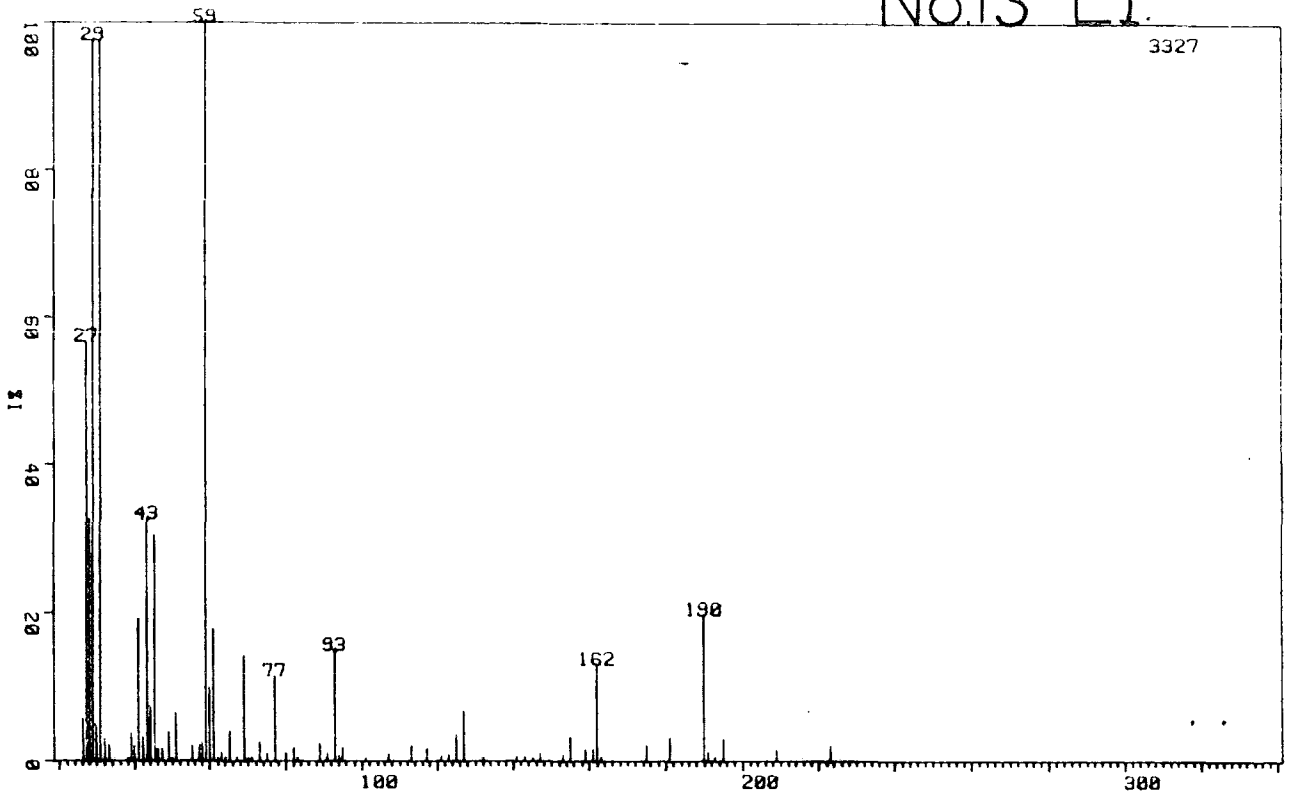


MASS	%HT. BASE	MASS	%HT. BASE
26.24	0.56	67.02	3.33
27.18	65.41	68.94	5.64
28.07	2.72	69.88	1.08
28.94	49.05	70.96	2.69
29.78	1.14	73.01	1.20
30.81	0.58	78.89	1.64
37.02	0.41	80.91	1.75
37.97	2.25	83.01	1.58
38.90	95.35	85.05	2.54
39.80	31.52	86.99	0.82
40.86	94.39	90.94	0.76
41.96	100.00	95.05	0.35
43.02	98.33	118.98	0.47
44.07	89.75	161.83	0.44
45.06	2.48	174.83	0.44
45.09	1.02	189.76	3.83
47.04	0.88	194.86	2.07
50.86	5.61	210.82	0.56
51.94	3.01	212.89	0.38
53.00	21.09	222.91	21.65
54.04	3.07	223.93	1.55
55.06	57.96	238.87	0.82
56.05	99.21	240.91	2.92
57.04	94.36	266.91	1.26
58.00	98.60	268.89	57.93
58.93	11.22	269.91	5.70
59.85	0.41	270.92	0.58
60.88	0.58		
60.95	0.53		
65.04	0.44		
66.03	0.56		

PT131X S P.T.TELFORD
CAL:CAL26 STA:

No.13 EI.

09-MAY-85
0:50

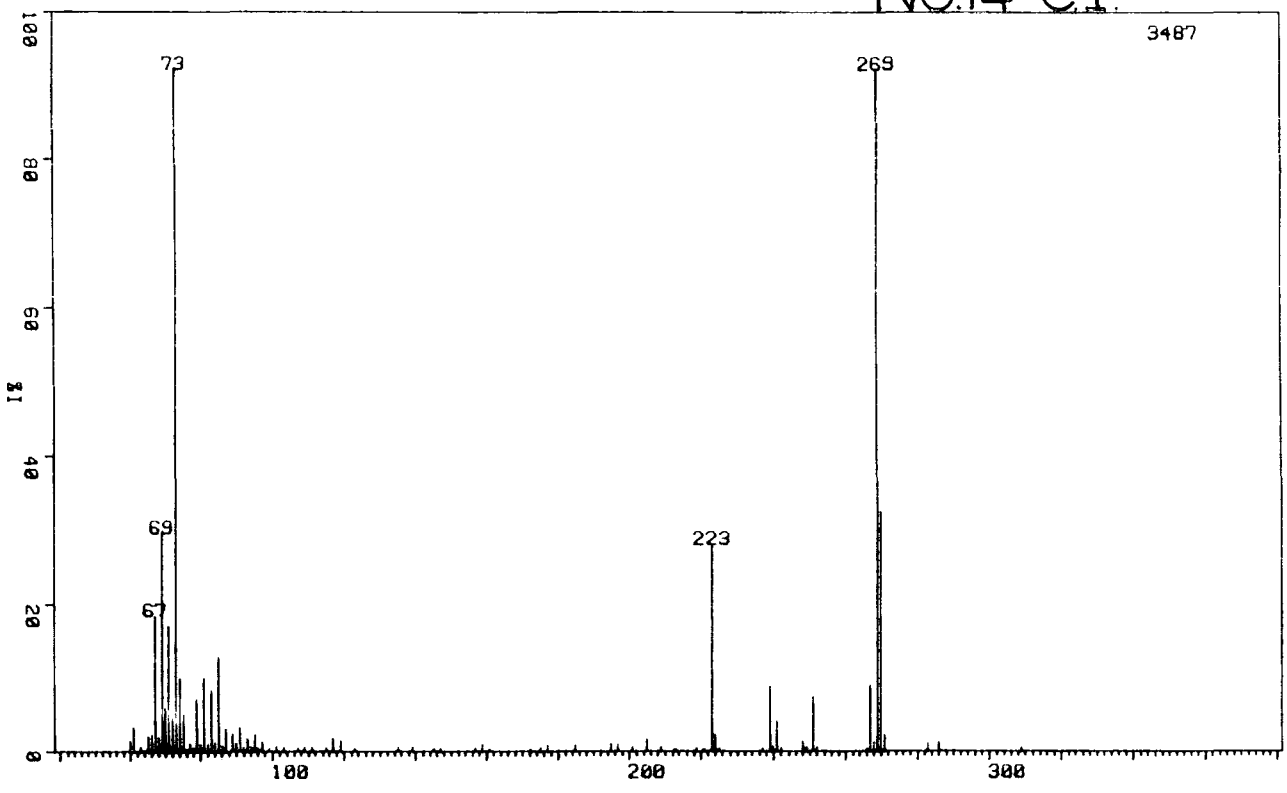


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.28	5.74	55.13	2.07	117.12	1.83
27.21	56.72	57.08	1.11	121.01	0.72
28.09	32.73	57.12	2.28	123.00	0.87
28.11	12.71	58.05	2.61	125.03	3.64
28.95	27.89	59.00	100.00	127.00	6.82
28.98	97.60	59.93	9.86	131.96	0.54
29.79	2.89	60.97	17.88	140.93	0.78
29.82	4.96	62.02	0.39	142.99	0.51
30.86	97.29	63.05	1.20	145.01	0.45
31.95	3.01	64.06	0.66	146.98	1.05
31.97	0.36	65.08	4.09	152.97	0.96
31.98	2.37	67.03	0.51	154.98	3.31
33.06	2.22	68.93	14.22	158.94	1.74
38.02	0.39	69.00	0.63	160.92	1.65
38.95	3.82	69.95	0.36	161.96	13.10
39.79	2.13	70.93	0.57	162.98	0.69
39.85	0.48	73.04	2.58	174.99	2.19
40.93	19.24	75.02	1.14	180.94	3.16
41.99	3.34	76.99	11.54	189.94	19.84
42.02	1.98	79.83	1.11	190.95	1.23
43.06	32.70	81.95	1.92	192.98	0.51
43.09	5.86	83.00	0.60	194.97	3.04
44.06	2.43	89.01	2.46	208.94	1.71
44.10	7.48	90.95	1.14	222.98	2.13
45.12	30.45	91.00	0.69		
46.12	1.65	93.04	15.03		
47.08	1.71	94.06	0.72		
47.10	0.96	95.05	1.92		
48.95	4.03	100.98	0.36		
49.87	0.39	107.05	0.99		
50.92	6.49	113.03	2.10		

PT132X S P.T.TELFORD I.BU C.I.
CAL:CAL26 STA:

No.14 CI

09-MAY-85
0:50

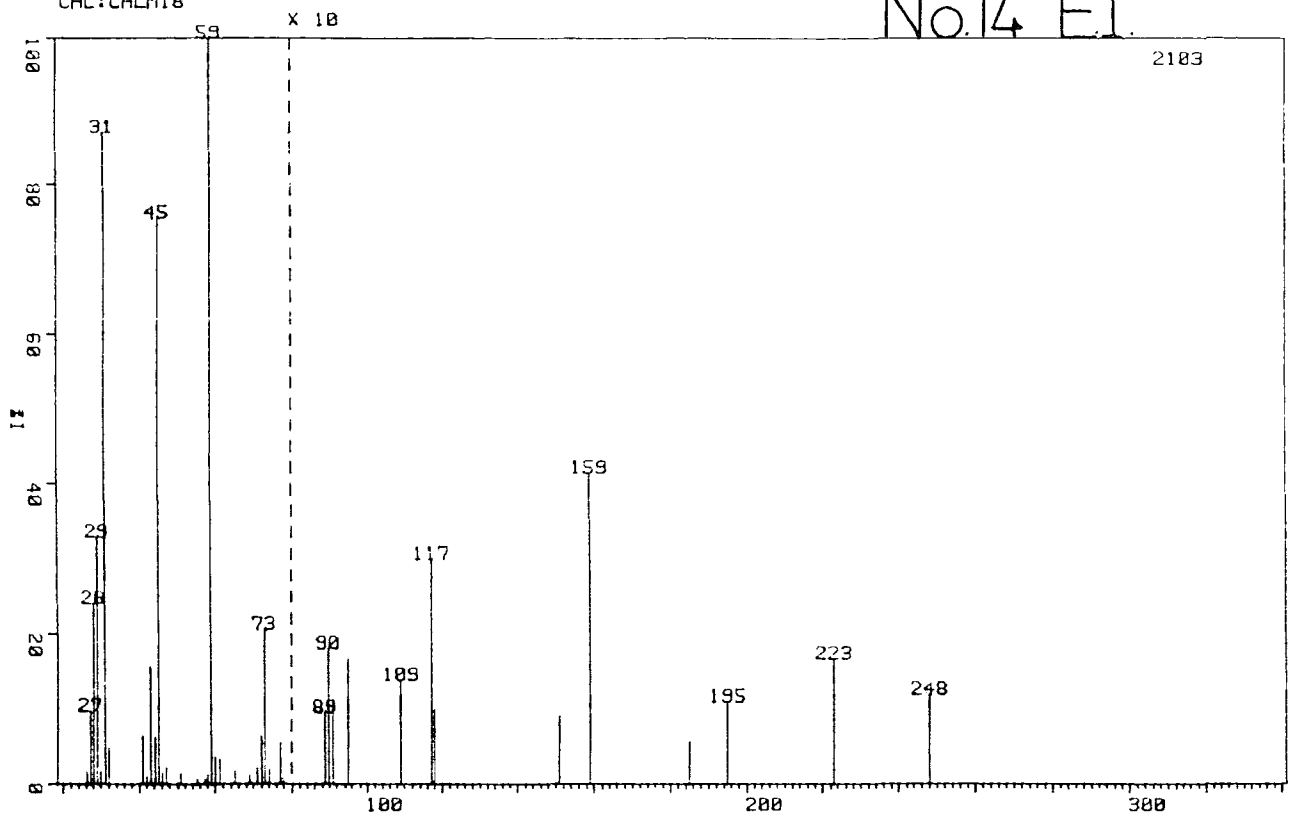


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
60.92	3.33	95.01	0.43	212.92	0.34
62.98	0.63	95.08	2.32	218.91	0.43
65.03	2.04	96.10	0.37	220.91	0.32
66.03	2.35	97.09	1.32	222.94	28.19
67.01	18.55	99.04	0.32	223.96	2.32
67.97	2.06	101.00	0.83	224.95	0.40
68.94	29.71	103.06	0.63	236.92	0.46
69.87	6.11	107.06	0.46	238.91	9.00
70.95	17.18	108.96	0.32	239.88	0.77
71.97	4.82	109.03	0.52	240.93	4.27
73.00	92.23	111.03	0.54	241.97	0.54
74.03	10.09	115.08	0.52	247.97	1.43
75.03	5.25	117.06	1.81	248.96	0.69
76.03	0.32	119.02	1.49	250.96	7.60
76.95	1.15	123.07	0.37	251.99	0.69
77.93	0.54	135.05	0.57	265.94	0.40
78.89	7.34	139.01	0.63	266.93	9.15
79.86	1.06	145.05	0.37	267.92	1.32
80.94	10.12	147.02	0.43	268.91	92.23
82.00	1.09	156.94	0.54	269.90	32.64
83.04	8.46	158.91	1.00	270.92	2.35
84.07	1.35	160.98	0.32	282.91	1.18
85.08	12.99	171.93	0.32	285.97	1.26
86.09	0.92	174.92	0.60	308.90	0.60
87.03	3.18	177.03	0.92		
88.98	2.47	184.94	0.83		
89.93	1.23	194.91	1.06		
90.97	3.27	196.90	0.95		
92.02	0.52	200.91	0.69		
93.05	1.81	204.95	1.69		
94.07	0.57	208.88	0.60		

PT132 S P.T.TELFORD 13/2
CAL:CALM18

No.14 EI.

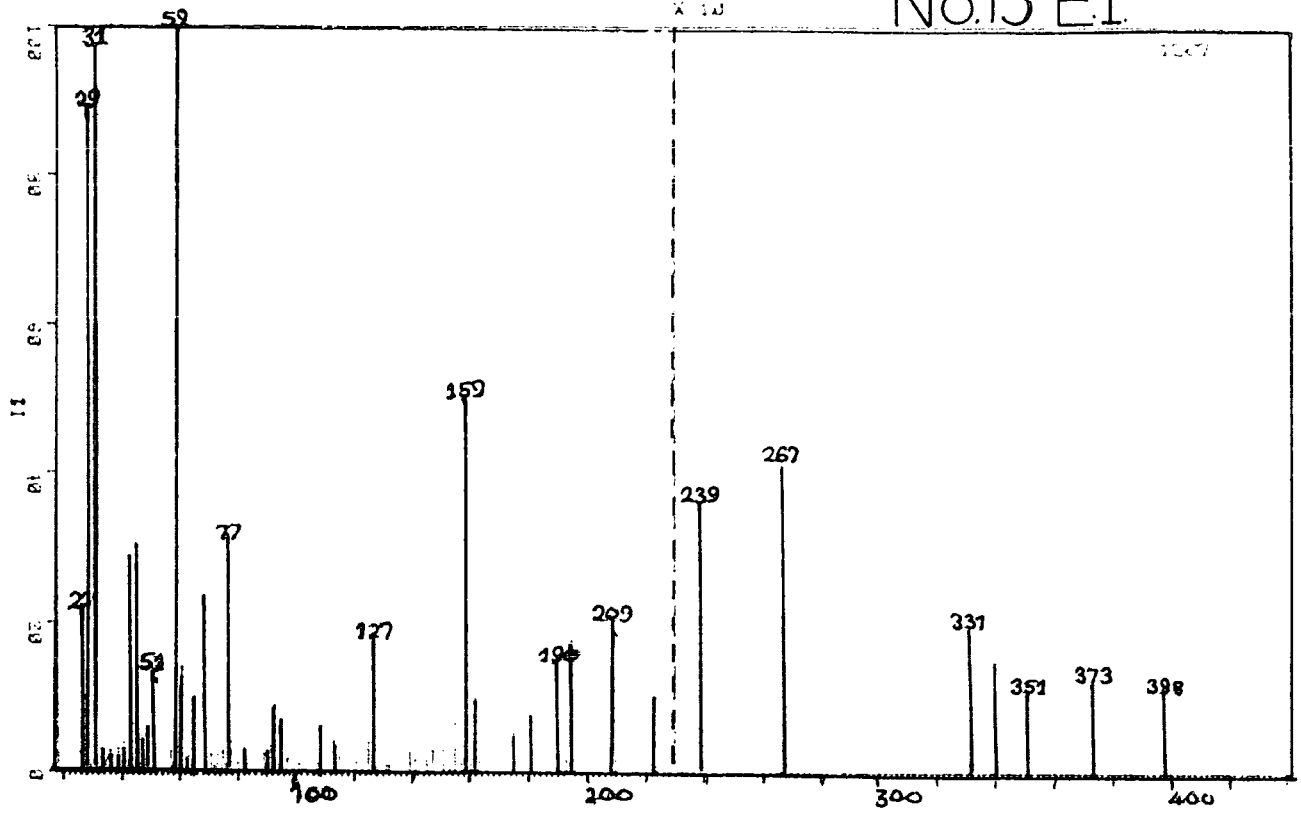
23-MAY-83



MASS	%HT. BASE	MASS	%HT. BASE
26.71	1.71	90.95	1.09
27.25	9.75	95.04	1.66
28.13	24.11	108.98	1.38
29.02	32.91	117.08	3.00
29.84	1.66	118.00	1.00
30.95	87.21	150.91	0.90
32.02	4.80	158.92	4.14
40.98	6.37	185.02	0.57
42.07	1.00	194.99	1.09
43.10	15.60	222.95	1.66
44.14	6.28	248.00	1.19
45.16	75.46		
46.16	1.66		
47.12	2.28		
50.94	1.43		
55.14	0.76		
57.10	0.62		
58.10	1.33		
59.02	100.00		
59.94	3.66		
61.00	3.38		
65.11	1.85		
68.93	1.24		
70.94	2.09		
72.01	6.32		
73.05	20.59		
74.06	2.00		
76.98	5.52		
77.94	0.76		
88.92	0.95		
89.84	1.81		

PT133R 1 P.T.TELFORD
CHL:CHL1

No.15 E.I.

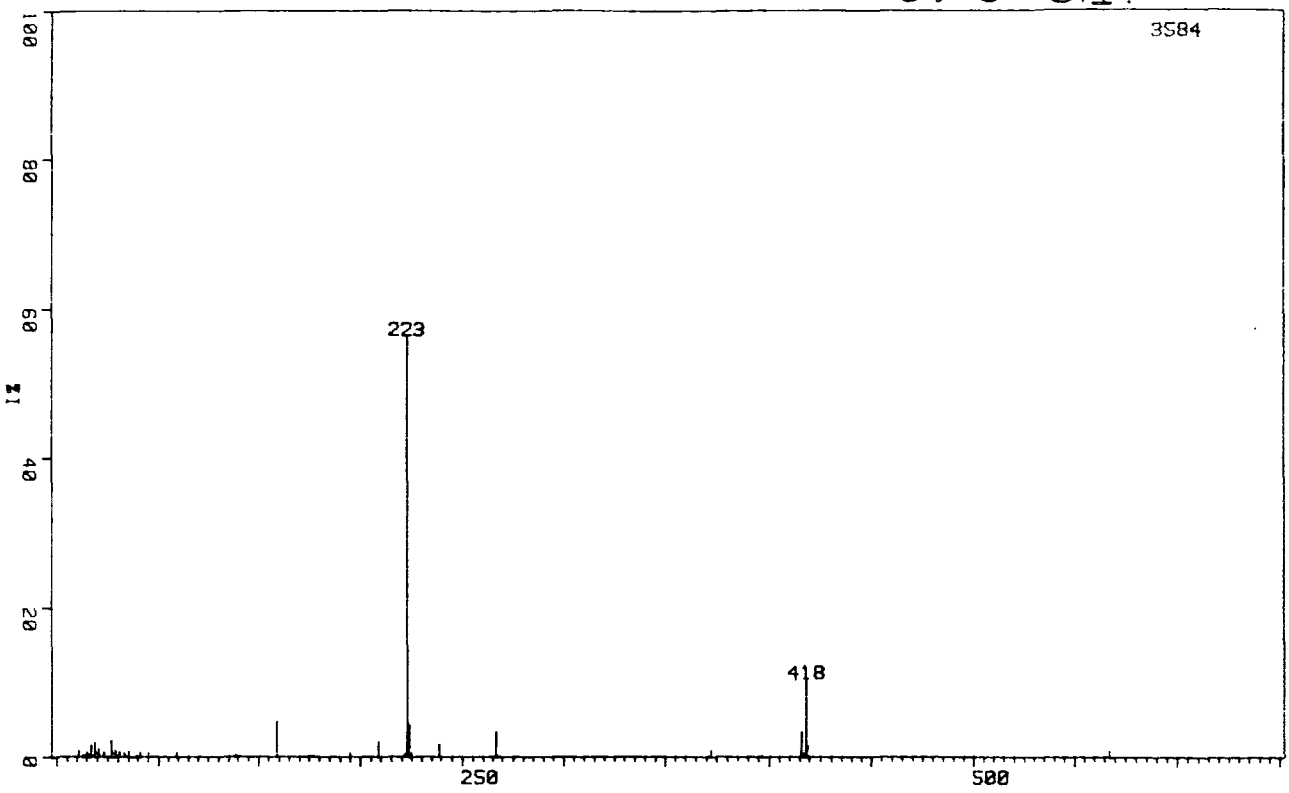


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.30	2.60	74.10	0.87	147.07	2.92
27.23	22.10	75.05	2.92	150.99	3.08
28.12	10.26	76.06	1.10	153.07	1.89
29.01	89.42	77.03	31.25	155.04	6.71
29.85	2.13	78.01	4.18	157.11	1.18
30.91	97.71	79.88	1.26	158.94	50.36
32.04	1.89	82.02	3.24	159.99	3.55
33.13	3.08	83.09	1.18	160.98	1.82
36.16	2.84	88.99	2.53	161.97	9.87
39.01	3.08	89.98	1.18	163.08	1.50
41.00	3.95	91.01	3.63	175.02	5.21
42.07	2.37	93.04	9.00	181.03	7.34
43.13	28.89	94.09	0.95	190.02	15.00
44.16	6.47	95.07	7.10	191.12	1.34
45.19	30.54	97.08	1.82	193.09	1.66
46.18	1.18	101.00	1.18	195.02	17.76
47.14	4.97	107.06	1.50	196.13	1.42
49.00	6.16	108.06	1.18	208.95	20.44
50.98	13.97	109.00	6.24	210.05	1.74
57.15	2.76	113.04	4.03	223.07	10.10
58.13	1.18	115.11	1.97	224.14	0.95
59.06	100.00	121.02	1.42	239.00	3.63
59.98	4.18	123.07	0.79	267.05	4.18
61.04	14.13	125.07	4.03	331.08	1.97
63.14	2.05	127.04	18.15	340.02	1.50
64.12	1.18	128.06	1.03	351.09	1.10
65.10	9.87	131.02	1.03	373.06	1.26
68.94	23.36	132.06	1.03	397.89	1.10
70.99	2.29	139.03	2.76		
72.07	1.10	141.05	1.74		
73.10	2.45	145.14	1.66		

PT134X 4 P.T.TELFORD 13/4 C.I. I-BU
CAL:CALT31 STA:

No.16 C.I.

26-MAR-85
0:44

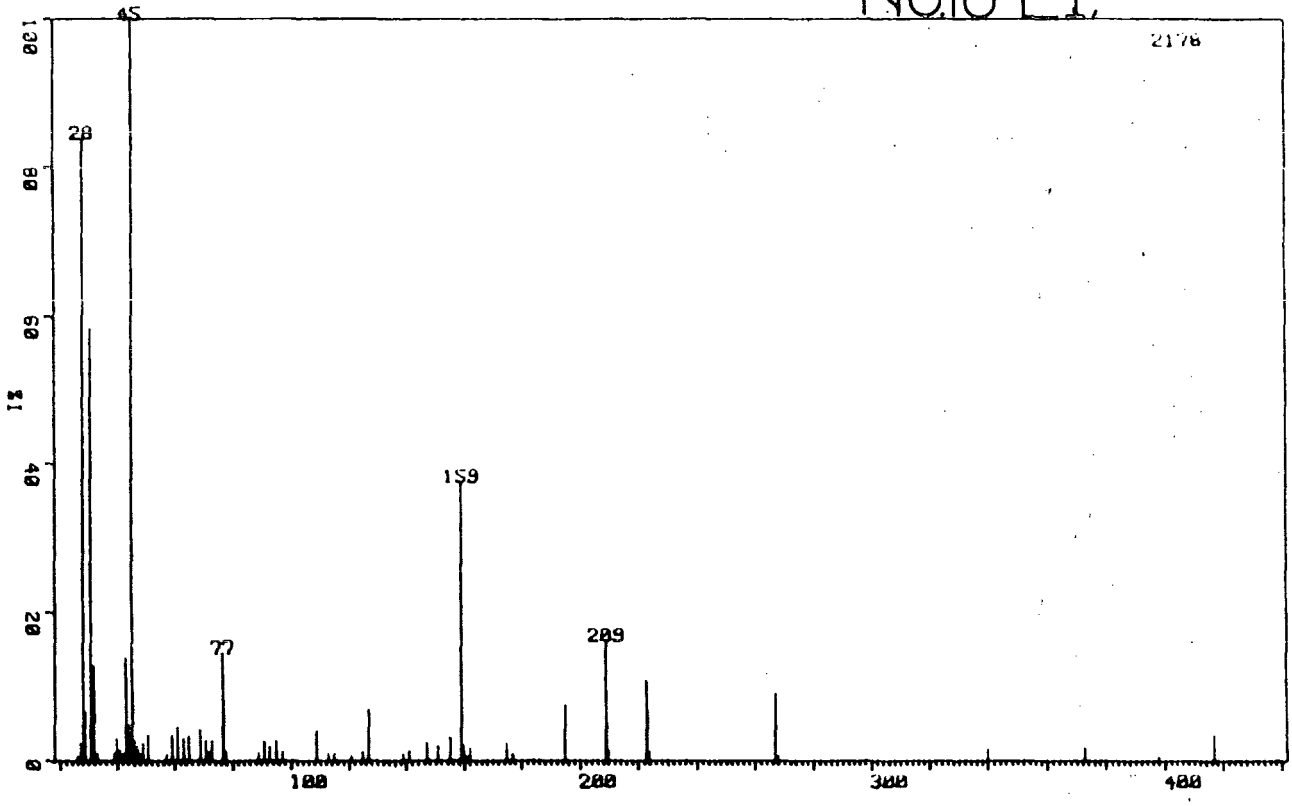


MASS	%HT. BASE		
60.87	0.89	266.65	3.26
62.99	0.28	267.64	0.33
65.04	0.59	372.27	0.99
66.05	0.28	397.08	0.28
67.03	1.65	416.04	3.38
68.89	0.31	416.99	0.47
68.96	1.95	419.03	10.63
69.90	0.47	419.02	1.51
70.94	1.09		
73.00	0.64		
76.96	2.26		
77.94	0.36		
78.91	0.89		
80.90	0.73		
82.99	0.50		
85.02	0.75		
88.85	0.25		
90.85	0.59		
94.93	0.61		
108.85	0.61		
138.81	0.31		
158.76	4.77		
174.79	0.22		
176.78	0.31		
194.71	0.61		
208.72	2.01		
221.78	0.42		
222.79	56.45		
223.82	4.21		
224.80	0.36		
238.71	1.73		

PT134 6 P.T.TELFORD
CAL:CALM22

24-MAR-83

No.16 EI.

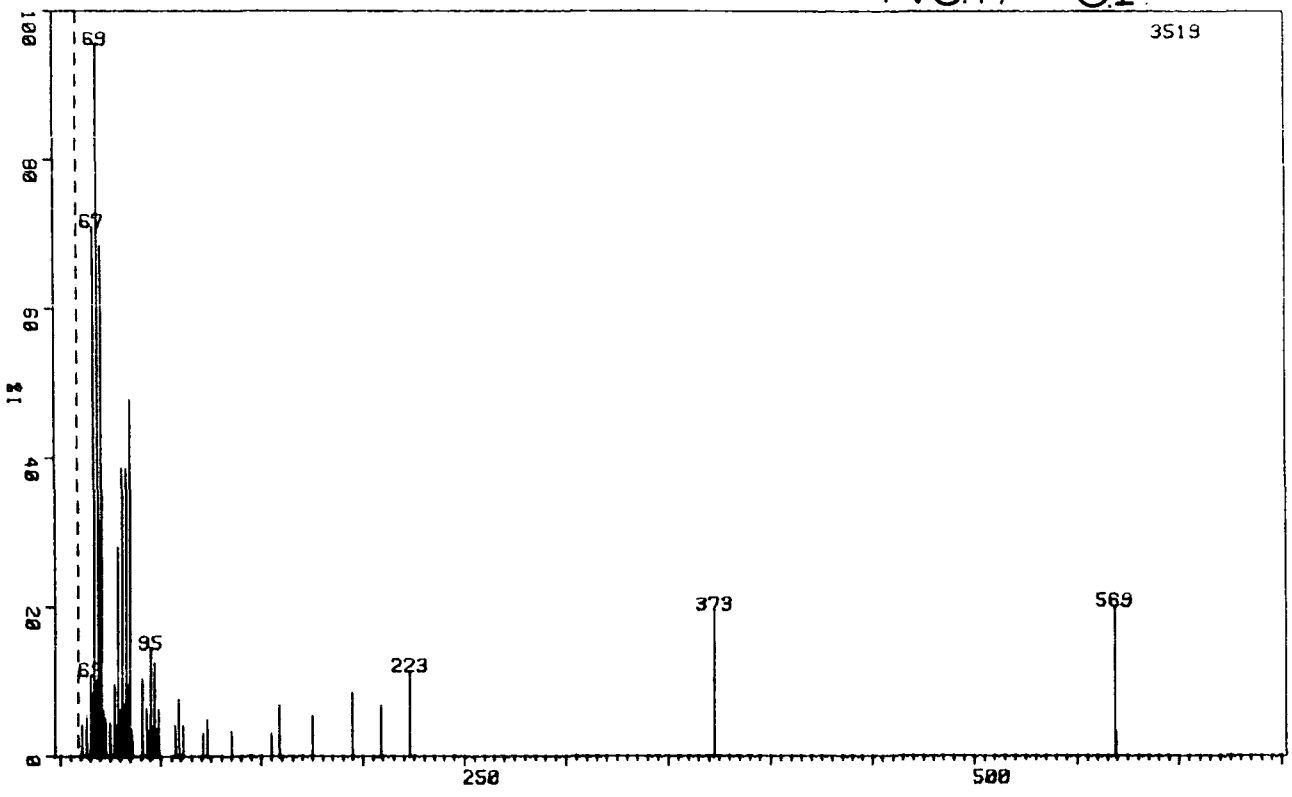


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE		
26.32	1.09	73.01	37.40	139.86	0.62	339.29	0.89
27.25	6.25	74.05	4.43	140.89	7.14	354.24	0.68
28.13	63.12	75.03	1.30	143.00	0.89	371.95	1.82
29.01	17.19	76.96	13.44	144.00	1.41	397.90	0.73
29.85	1.04	77.95	0.83	145.05	1.25	415.66	2.34
30.92	69.48	82.96	0.52	146.96	5.21	416.89	0.57
32.00	12.60	85.00	2.55	150.88	0.94		
33.11	0.89	85.99	0.68	152.97	0.89		
38.98	0.99	86.96	1.98	154.95	4.43		
39.83	1.30	88.89	3.70	156.93	2.76		
40.96	4.43	90.88	2.14	158.86	42.97		
42.03	1.20	92.95	1.98	159.86	3.02		
43.07	19.43	94.97	3.44	160.97	1.09		
44.11	5.83	96.99	0.99	161.92	1.98		
45.13	100.00	98.94	0.83	162.99	0.83		
46.13	2.76	100.89	2.34	168.99	1.15		
47.09	3.70	102.96	1.30	174.93	3.85		
48.94	3.23	108.86	5.10	176.94	3.07		
50.90	2.92	112.94	1.35	180.91	0.99		
55.10	2.45	114.96	2.45	188.86	1.20		
56.12	0.83	115.93	0.68	190.85	1.82		
57.05	3.49	117.00	12.97	194.88	6.41		
58.01	1.41	118.05	1.20	204.99	0.83		
58.96	21.61	120.84	1.15	208.86	10.57		
59.88	1.25	122.90	0.78	209.90	0.89		
60.92	12.40	124.96	0.83	210.95	0.89		
63.01	2.86	126.94	9.01	222.83	5.83		
65.03	4.37	128.92	4.01	238.77	1.30		
68.90	2.55	132.94	0.99	248.83	0.57		
70.92	2.60	136.91	2.29	266.76	2.55		
71.97	4.95	138.84	2.08	321.45	0.99		

PT38SX S PT1385 I-BU C.I. +
CAL:CALTS STA:
X 10

No.17 C.I.

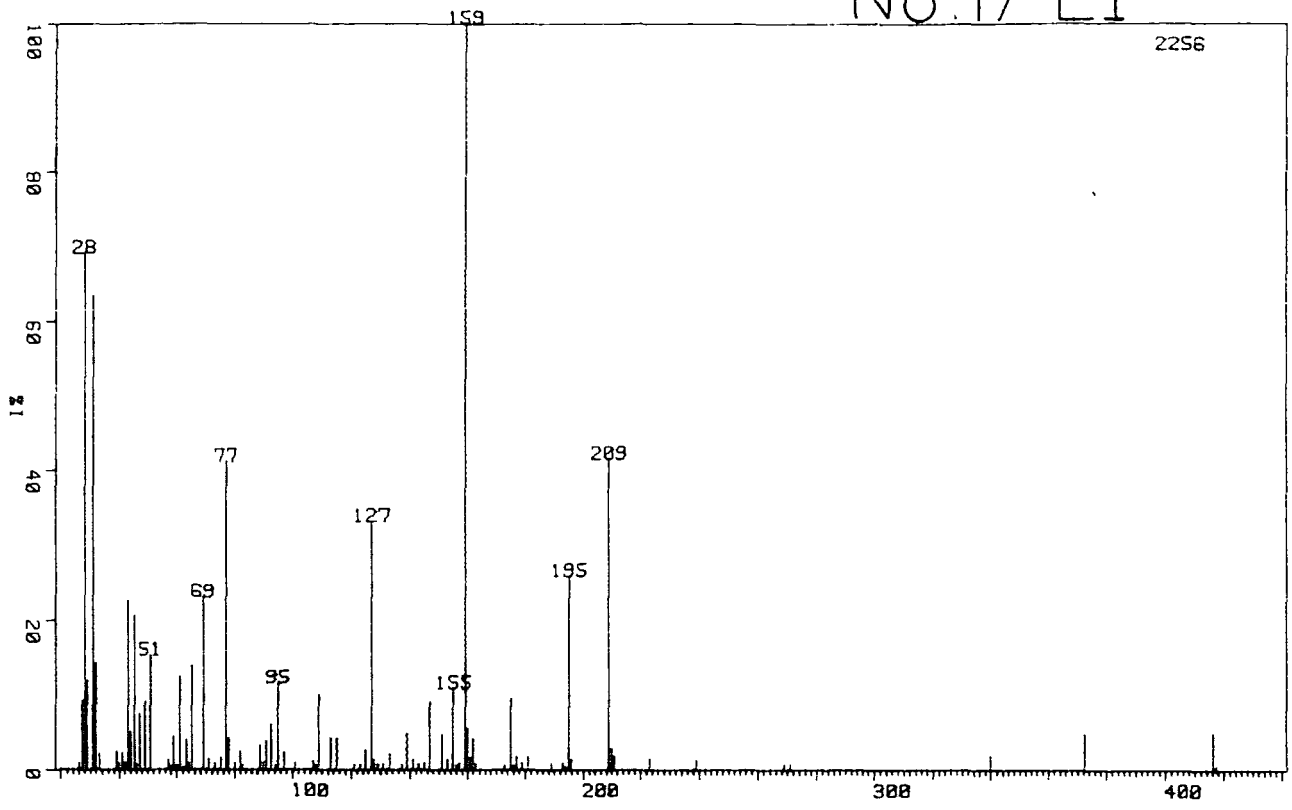
26-SEP-84
0:50



MASS	%HT. BASE	MASS	%HT. BASE
60.91	0.28	107.02	0.43
60.94	0.43	108.96	0.77
63.02	0.40	110.97	0.43
65.06	1.08	120.92	0.31
66.06	0.85	120.98	0.26
67.05	7.10	123.00	0.48
68.02	1.02	154.98	0.34
68.98	9.55	154.91	0.31
69.92	3.15	158.83	0.68
70.98	6.85	174.94	0.54
72.03	0.63	194.91	0.85
73.03	0.51	208.86	0.68
75.07	0.45	222.90	1.14
77.01	0.97	372.89	1.96
77.99	0.43	568.51	2.02
78.96	2.31	569.50	0.31
79.90	0.63		
80.95	3.86		
81.99	0.71		
83.04	3.86		
84.06	0.92		
85.03	4.77		
86.09	0.57		
90.94	1.05		
93.01	0.65		
94.03	0.34		
95.04	1.45		
96.04	0.40		
97.03	1.25		
98.01	0.37		
98.99	0.63		

PT135 3 P.T.TELFORD 13/S E.I. 25-MAR-85
CAL:CALT31 STA: 0:34

No.17 EI

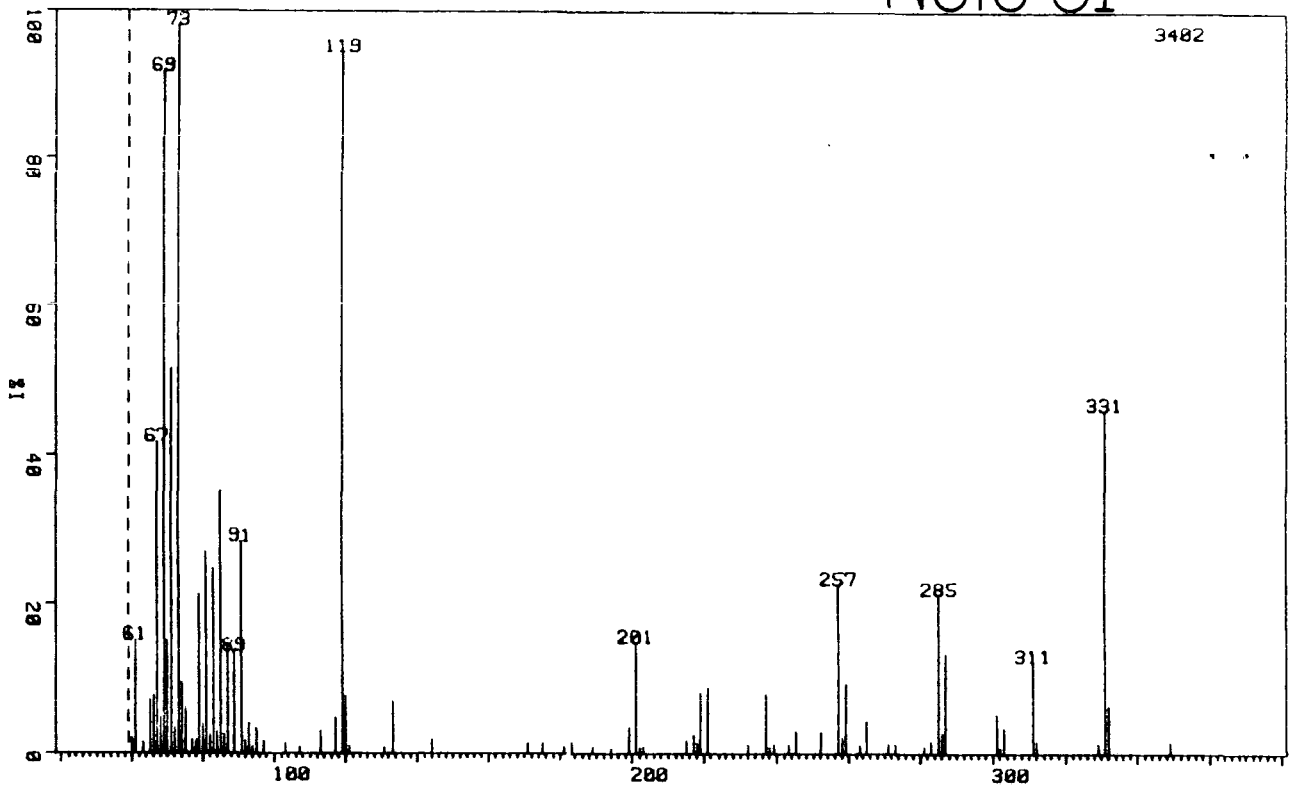


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.30	0.89	70.94	1.51	138.93	4.83	268.82	0.80
27.23	9.18	73.00	0.58	140.90	1.42	270.83	0.84
28.11	69.19	73.04	0.98	142.94	0.84	339.68	1.99
28.96	11.88	75.01	1.60	144.96	0.98	372.62	4.88
28.99	4.17	76.99	41.36	146.95	9.13	416.51	5.05
30.88	63.43	77.96	4.34	150.88	4.74	417.50	0.58
31.96	14.23	79.84	0.93	152.96	1.46		
33.07	2.17	81.96	2.48	154.97	10.95		
38.95	2.53	82.98	0.62	155.95	0.66		
39.78	0.93	88.93	3.28	156.94	0.98		
40.93	2.17	89.88	1.02	158.92	100.00		
41.98	1.02	90.95	3.90	159.89	5.54		
42.01	0.71	93.00	6.07	160.91	1.77		
43.05	22.65	94.00	0.66	161.92	4.21		
44.05	0.66	95.01	11.70	162.93	0.89		
44.09	5.14	97.00	2.48	172.92	0.62		
45.11	20.74	100.91	1.06	174.93	9.53		
46.11	0.84	106.98	1.20	175.91	0.58		
47.07	7.49	107.95	0.66	176.92	1.82		
48.93	9.09	108.94	10.20	178.87	0.93		
50.90	15.38	112.95	4.34	180.88	1.86		
57.05	1.24	114.98	4.21	188.91	0.93		
58.02	0.53	120.91	0.66	192.90	0.93		
58.96	4.52	122.93	0.66	193.92	0.44		
59.87	0.58	124.95	2.70	194.95	26.02		
60.93	12.54	126.94	33.33	195.94	1.46		
61.98	0.40	127.92	1.42	208.90	41.67		
63.02	3.95	128.88	0.75	209.89	2.79		
64.04	0.93	130.87	0.84	210.89	1.91		
65.05	13.96	132.99	2.08	222.97	1.55		
68.91	23.18	136.98	0.66	238.87	1.42		

PT8SBX 4 P.T.TELFORD I.BU C.I.
CAL:CAL26 STA:
X 2

No18 CI

09-MAY-85
0:42

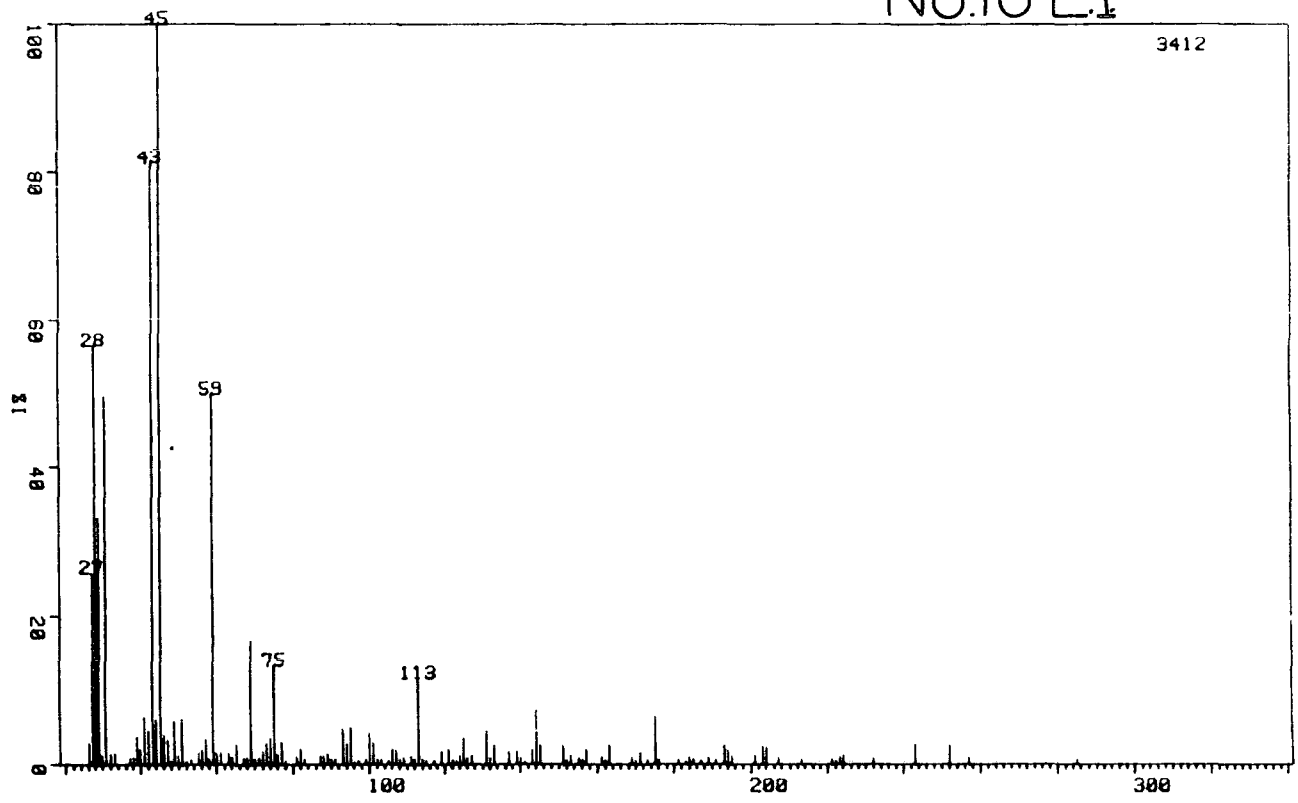


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
61.04	7.93	94.09	0.55	239.07	0.69
63.10	0.84	95.11	1.79	243.09	0.67
65.14	3.82	97.09	0.93	245.11	1.62
66.11	4.17	103.07	0.75	252.08	1.59
67.06	21.74	107.07	0.55	257.07	11.81
68.03	2.60	113.00	1.62	258.07	1.19
68.99	47.70	117.09	2.52	259.05	4.92
69.92	7.87	119.06	49.09	263.11	0.61
70.99	26.86	120.03	4.08	265.06	2.32
72.03	1.82	121.06	0.58	271.05	0.72
73.04	50.91	130.95	0.46	273.05	0.69
74.06	4.95	133.09	3.68	281.06	0.58
75.00	0.78	144.01	1.01	283.08	0.93
75.04	1.94	171.03	0.72	285.10	11.11
75.07	3.27	175.05	0.75	286.09	1.48
77.00	0.98	181.05	0.46	287.07	7.03
77.97	0.98	183.07	0.81	301.06	2.75
78.93	11.09	189.02	0.49	302.08	0.46
79.87	2.11	194.07	0.38	303.07	1.82
80.97	14.10	199.05	1.88	311.07	6.48
82.02	1.39	201.04	7.79	312.10	0.90
83.07	12.91	202.06	0.46	329.10	0.72
84.09	1.53	203.07	0.49	331.12	24.05
85.12	18.26	215.09	0.96	332.08	3.39
86.09	1.36	217.08	1.30	349. 6	0.84
87.03	7.76	218.09	0.75		
88.98	7.18	219.06	4.31		
91.00	14.82	221.06	4.66		
92.05	0.96	232.10	0.64		
92.99	0.35	237.09	4.20		
93.07	2.14	238.08	0.49		

PT8SBX 4 P.T.TELFORD
CAL:CAL26 STA:

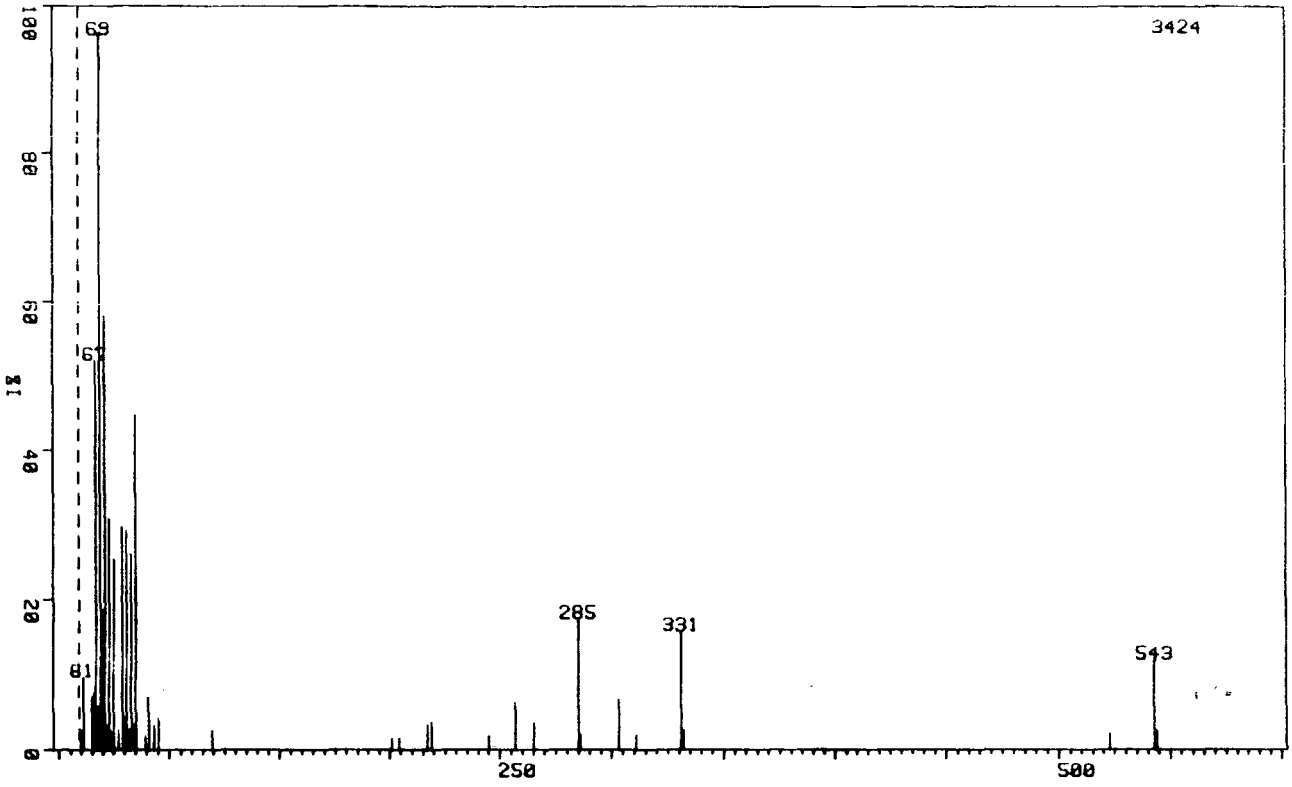
No.18 E.I

09-MAY-85
8:42



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.29	3.05	55.16	1.70	89.96	0.73	139.03	1.91	213.10	0.75
27.22	25.91	56.11	2.05	91.00	0.79	140.00	1.00	221.05	0.73
28.09	56.54	56.16	0.50	93.05	4.89	141.01	0.32	222.09	0.50
28.10	34.67	57.09	3.43	94.07	2.87	143.04	2.05	223.07	1.08
28.12	6.54	57.15	1.99	95.09	5.10	144.06	7.47	224.08	1.35
28.96	27.14	58.07	0.79	96.10	0.38	145.07	2.64	232.09	0.79
28.99	33.26	59.03	49.91	97.06	0.50	151.03	2.55	243.10	2.78
29.80	1.32	59.97	1.64	99.01	0.73	152.05	0.70	252.10	2.67
29.82	1.00	61.00	1.64	99.95	4.31	153.07	1.23	257.06	1.06
30.87	49.71	63.08	1.55	101.02	3.05	155.05	0.91	285.09	0.76
31.96	1.47	64.10	1.03	102.07	0.76	156.05	0.67		
31.98	0.38	65.09	2.78	103.10	0.64	157.06	2.14		
32.00	0.62	67.04	1.00	105.06	0.47	161.03	1.06		
33.07	1.55	68.01	1.03	106.06	2.08	162.03	0.59		
37.09	0.91	68.94	16.76	107.05	1.96	163.07	2.67		
38.04	0.94	69.02	0.70	108.03	0.79	169.03	1.06		
38.96	3.84	69.90	0.79	109.00	1.03	170.02	0.53		
39.80	2.17	69.96	0.47	110.99	1.17	171.05	1.64		
39.86	0.29	70.95	0.91	112.01	0.79	173.07	0.67		
40.95	6.45	71.02	0.88	113.04	11.75	175.08	6.62		
42.00	4.66	72.03	1.91	114.07	0.73	176.09	0.64		
42.05	1.96	73.06	2.93	115.09	0.59	181.06	0.67		
43.08	81.36	74.02	1.26	117.06	0.56	183.09	0.35		
43.12	5.66	74.09	3.66	119.01	1.79	184.09	1.06		
44.10	6.24	75.03	13.45	121.03	2.05	185.09	0.79		
45.14	100.00	76.03	1.38	122.07	0.59	187.07	0.47		
46.14	4.22	77.02	3.14	123.05	0.56	189.05	0.94		
47.10	3.49	77.99	0.44	124.06	1.26	191.04	0.70		
48.04	0.56	80.89	1.08	125.07	3.60	193.08	2.52		
48.97	5.95	81.97	2.14	126.07	1.00	194.07	2.05		
49.88	1.17	83.03	0.64	127.07	1.23	195.09	1.20		
50.95	6.27	83.10	0.41	131.00	4.63	201.06	1.23		
52.04	0.41	87.05	1.14	132.06	1.00	203.07	2.43		
53.10	0.70	88.02	1.26	133.08	2.58	204.08	2.34		
55.11	0.41	88.99	1.61	137.06	1.76	207.07	0.97		

PT8SCX 5 P.T.TELFORD I.BU C.I. No.19 CI 09-MAY-85
CAL:CAL26 STA: 0:50
X 4

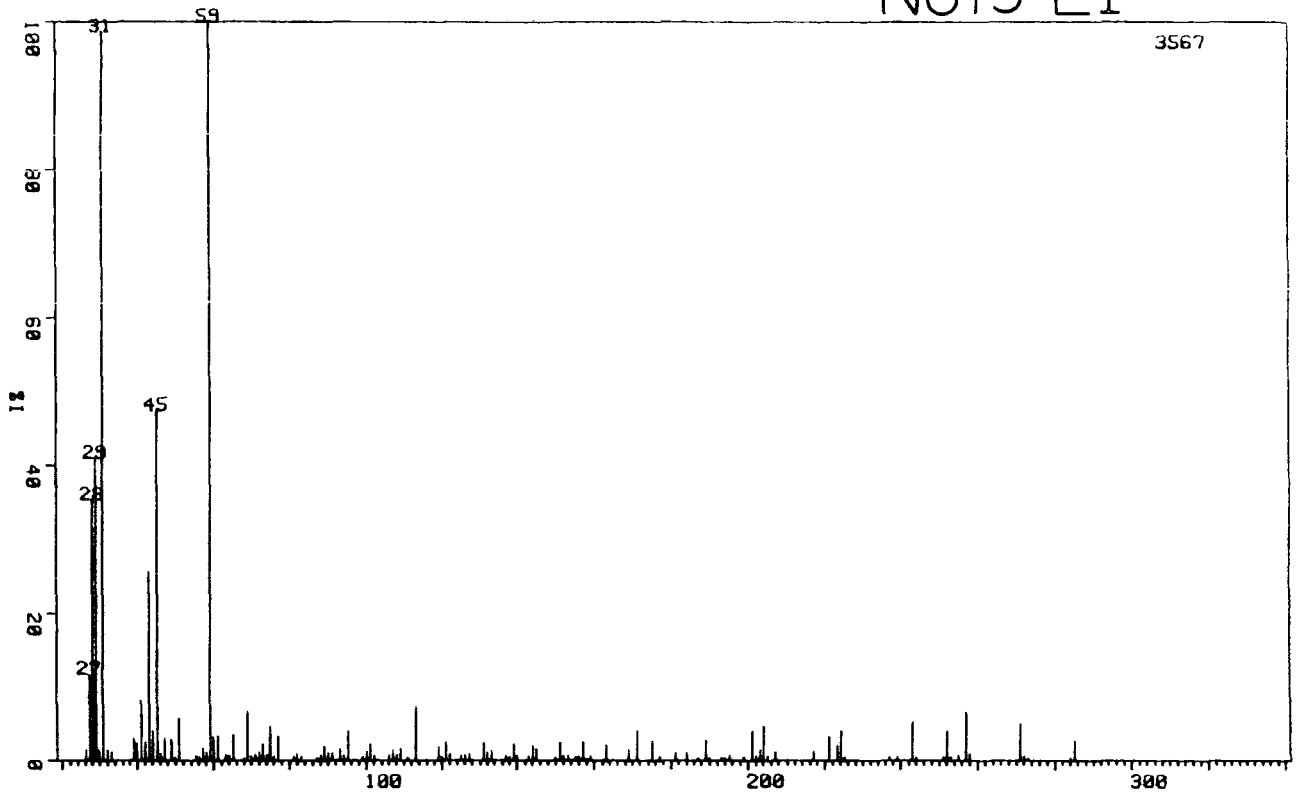


MASS	%HT. BASE	MASS	%HT. BASE
60.90	1.20	244.97	0.44
60.94	2.28	256.92	1.46
65.03	1.75	264.94	0.85
66.03	1.96	284.93	4.09
67.01	12.18	285.91	0.50
67.98	1.37	302.92	1.58
68.94	22.43	310.91	0.47
69.88	4.41	330.93	3.71
70.96	13.55	331.95	0.64
71.98	0.35	522.76	0.53
72.01	0.82	542.85	2.83
73.02	7.24	543.93	0.61
74.03	0.61		
75.05	5.93		
76.97	0.61		
78.91	6.98		
79.85	1.02		
80.93	6.86		
81.99	0.64		
83.03	6.13		
84.06	0.85		
85.08	10.46		
88.98	0.44		
90.97	1.64		
93.04	0.76		
95.08	0.99		
119.03	0.61		
200.88	0.38		
203.91	0.38		
216.90	0.79		
218.89	0.88		

PT85CX 4 P.T.TELFORD
CAL:CAL26 STA:

No19 EI

09-MAY-85
0:41



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.28	1.51	59.96	3.31	108.05	0.93	181.06	1.09
27.22	11.80	61.00	3.48	109.03	1.68	184.07	1.09
28.09	35.41	63.09	0.76	111.01	0.36	187.08	0.31
28.10	31.60	64.10	0.78	113.05	7.40	189.06	2.80
28.12	3.87	65.09	3.56	119.03	1.93	190.05	0.31
28.96	11.10	68.01	0.31	120.00	0.59	193.05	0.39
28.99	41.01	68.95	6.67	121.04	2.52	194.09	0.42
29.80	0.87	69.91	0.53	122.07	1.07	195.10	0.76
29.82	1.49	70.97	0.93	125.09	0.64	199.04	0.53
30.87	98.68	71.02	0.34	126.09	0.84	201.05	4.01
31.96	1.46	71.98	0.42	127.08	1.07	202.08	0.64
32.00	1.21	72.04	1.26	131.01	2.50	203.06	1.54
33.07	1.18	73.07	2.35	132.06	1.18	204.07	4.77
38.96	3.11	74.02	0.42	133.09	1.43	205.07	0.70
39.81	2.47	74.10	0.87	137.07	0.67	207.07	1.21
40.95	8.21	75.01	4.65	138.05	0.50	217.07	1.37
42.00	1.07	76.00	0.62	139.05	2.27	221.07	3.22
42.05	2.75	76.99	3.34	140.02	0.73	223.09	2.16
43.08	25.71	80.88	0.56	143.06	0.64	224.11	4.12
43.12	7.20	81.96	1.01	144.08	2.05	225.07	0.48
44.09	4.01	83.02	0.67	145.09	1.68	237.10	0.48
44.12	4.18	87.06	0.42	150.01	0.36	239.06	0.59
45.14	47.55	88.00	0.87	151.03	2.50	243.08	5.33
46.14	1.04	88.98	1.93	152.06	0.76	244.09	0.36
47.10	3.17	89.94	1.21	153.10	0.76	251.10	0.45
48.97	2.92	90.99	1.09	155.06	0.45	252.13	4.04
49.89	0.39	93.03	1.60	156.06	0.62	253.10	0.45
50.95	5.83	94.05	0.78	157.06	2.55	255.08	0.84
55.16	0.73	95.07	4.01	158.06	0.25	257.06	6.67
56.11	0.39	98.99	0.45	159.04	0.70	258.06	1.01
56.17	0.50	99.94	1.29	163.06	2.13	271.06	5.07
57.10	1.77	101.01	2.33	169.04	1.54	272.08	0.62
57.15	0.87	102.05	0.76	171.05	4.18	273.06	0.31
58.08	1.23	106.07	0.90	175.09	2.64	284.13	0.42
59.03	100.00	107.07	1.54	177.08	0.56	285.11	2.72

PT85DX 2 P.T.TELFORD I.BU C.I. 09-MAY-85
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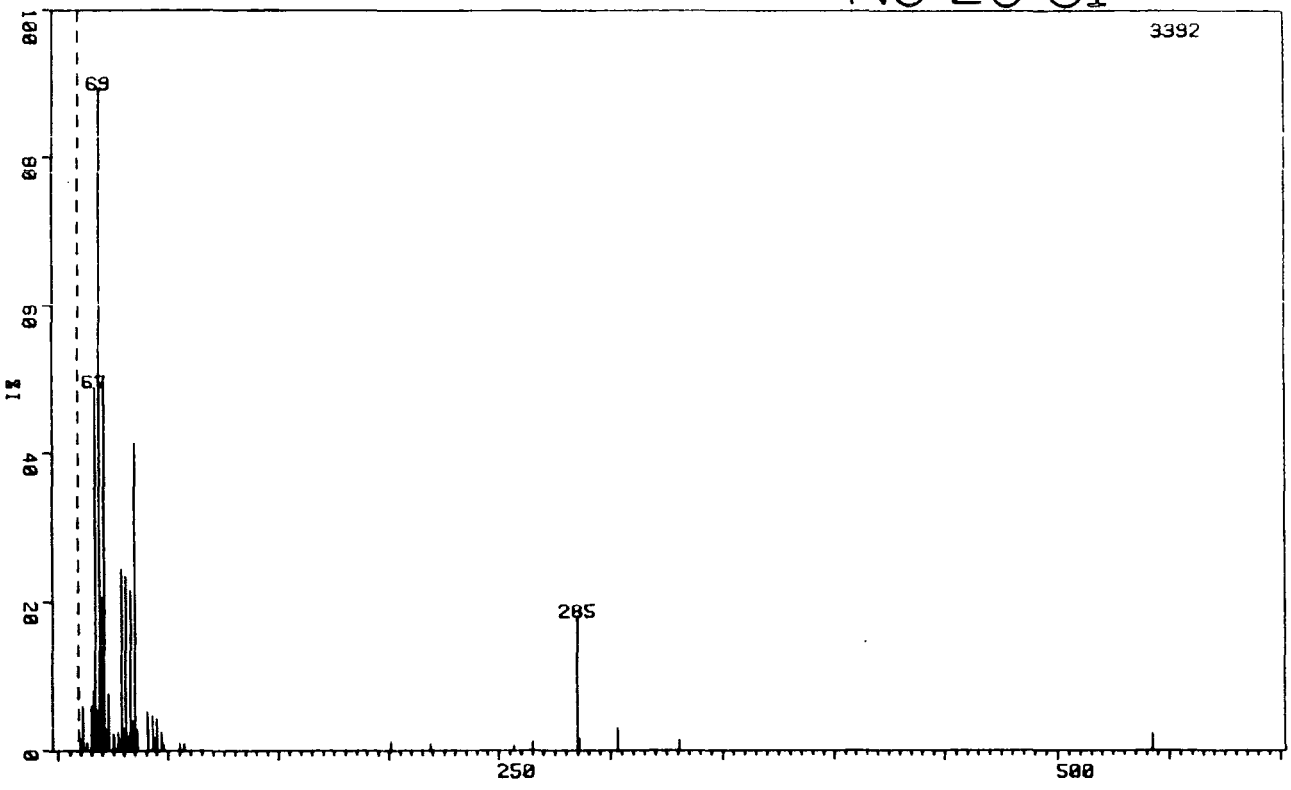
X 2

No 20 CI

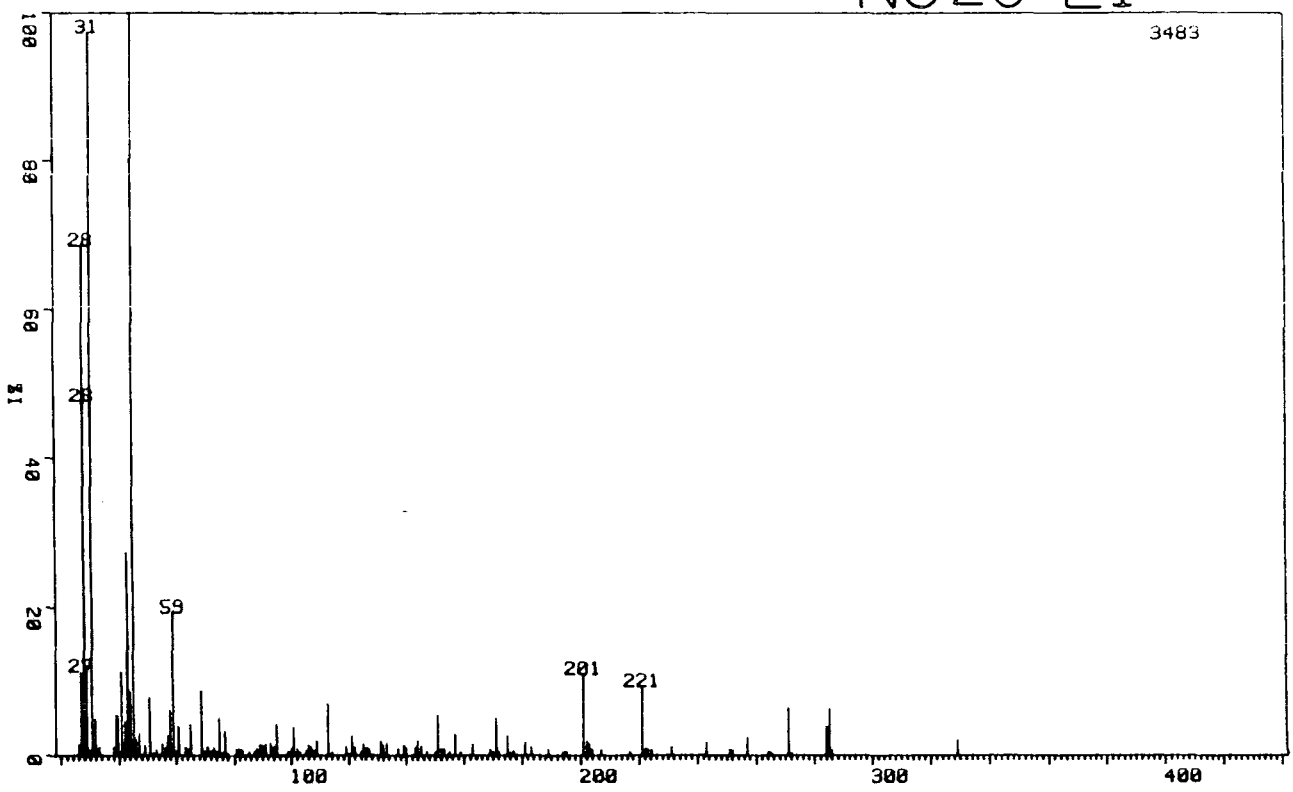


MASS	%HT. BASE	MASS	%HT. BASE
60.92	1.30	200.93	0.68
60.95	3.04	218.94	0.53
63.01	0.56	256.93	0.38
65.05	3.10	264.96	0.65
66.04	4.10	284.95	9.02
67.03	24.50	285.96	0.85
67.99	2.77	302.95	1.56
68.96	44.58	330.96	0.74
69.89	10.38	542.86	1.21
70.97	25.12		
72.02	1.53		
73.02	3.86		
75.06	1.15		
76.98	1.36		
77.95	0.80		
78.91	12.23		
79.86	1.53		
80.94	11.76		
81.99	1.00		
83.04	10.85		
84.07	2.06		
85.09	20.73		
86.10	1.44		
90.97	2.65		
93.06	2.36		
94.08	0.83		
95.09	2.15		
97.10	1.27		
98.08	0.41		
105.08	0.50		
107.08	0.50		

PT8SDX 3 P.T.TELFORD
CAL:CAL26 STA:

No 20 EI

09-MAY-85
0:33

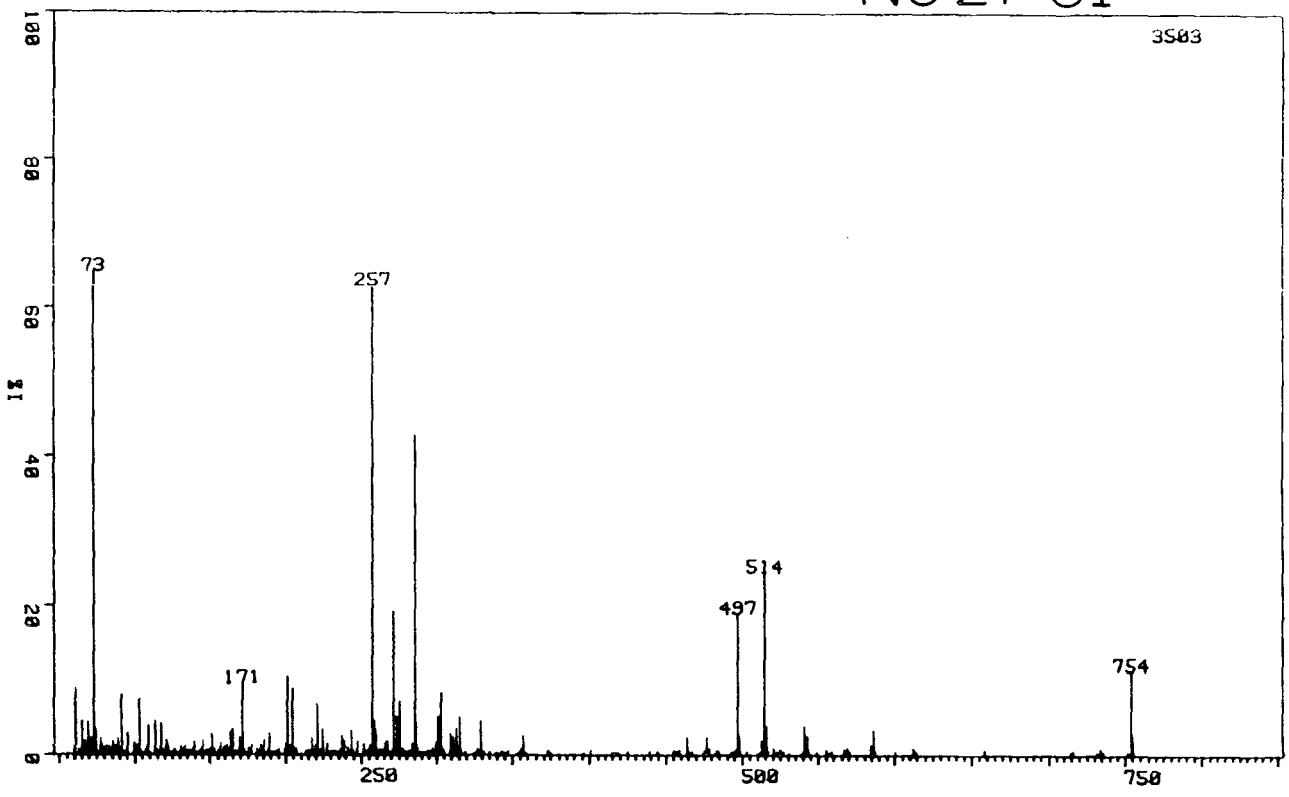


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.27	1.64	57.13	2.78	93.00	1.81	150.97	5.51	265.07	0.40
27.21	11.43	58.07	6.26	94.03	1.29	152.00	0.95	271.05	6.55
28.08	47.77	59.02	19.35	94.07	0.72	153.04	1.06	272.05	0.32
28.09	68.68	59.94	0.60	95.04	4.31	155.02	0.43	284.12	3.93
28.11	6.66	60.99	3.93	98.97	0.57	157.02	2.96	285.08	6.40
28.95	10.34	63.07	1.23	99.92	1.18	159.00	0.49	286.09	0.80
28.98	12.20	64.09	0.89	100.98	3.90	163.02	1.58	329.14	2.15
29.79	0.72	65.10	4.28	102.01	1.03	169.00	0.89		
30.86	97.39	68.93	8.76	103.07	0.49	169.99	0.43		
31.95	5.08	69.00	1.38	105.11	0.78	171.01	5.14		
31.98	1.46	69.89	0.55	106.01	1.46	172.04	0.46		
33.06	1.21	69.97	0.57	107.00	1.35	175.05	2.67		
38.03	1.21	70.98	1.32	107.99	0.80	176.04	0.32		
38.95	5.68	71.03	1.15	108.96	2.01	177.04	0.63		
39.79	5.60	72.03	0.66	113.00	7.09	181.01	1.84		
39.85	0.63	73.05	0.72	114.04	0.46	183.05	1.18		
40.94	11.34	73.08	1.18	118.96	1.35	189.00	0.92		
41.99	1.29	74.02	0.60	119.94	0.23	194.04	0.55		
42.03	4.79	74.11	0.63	120.99	2.67	195.06	0.57		
43.06	27.36	75.01	5.20	122.02	1.26	201.03	11.02		
43.10	14.76	76.01	0.43	124.01	0.57	202.05	2.18		
44.07	8.73	76.99	3.42	125.02	1.58	203.04	1.75		
44.10	8.24	77.97	0.37	126.03	1.18	204.05	1.06		
44.14	0.66	80.88	0.95	127.02	0.89	207.04	0.80		
45.13	100.00	81.96	1.03	130.95	2.07	217.07	0.55		
46.13	2.44	81.99	0.26	132.00	1.52	221.05	9.39		
47.09	3.13	82.04	0.37	133.03	1.89	222.06	1.00		
48.96	1.46	83.02	0.83	137.01	1.06	223.06	1.00		
50.94	7.98	83.08	0.60	138.99	1.49	224.08	0.83		
52.03	0.32	85.13	0.60	139.97	1.21	231.05	1.23		
53.09	0.83	87.00	0.55	143.00	1.21	243.07	1.92		
55.15	1.81	87.98	1.06	144.02	2.12	251.09	0.92		
56.09	0.75	88.95	1.64	145.03	1.35	252.10	0.83		
56.15	1.09	89.91	1.49	147.03	0.63	257.11	2.56		
57.08	1.69	90.97	1.69	149.93	0.49	264.08	0.49		

PT8SER 1S P.T.TELFORD CI 1.8U
CAL:CALT1 STA:

No 21 CI

04-JUN-85
2:16

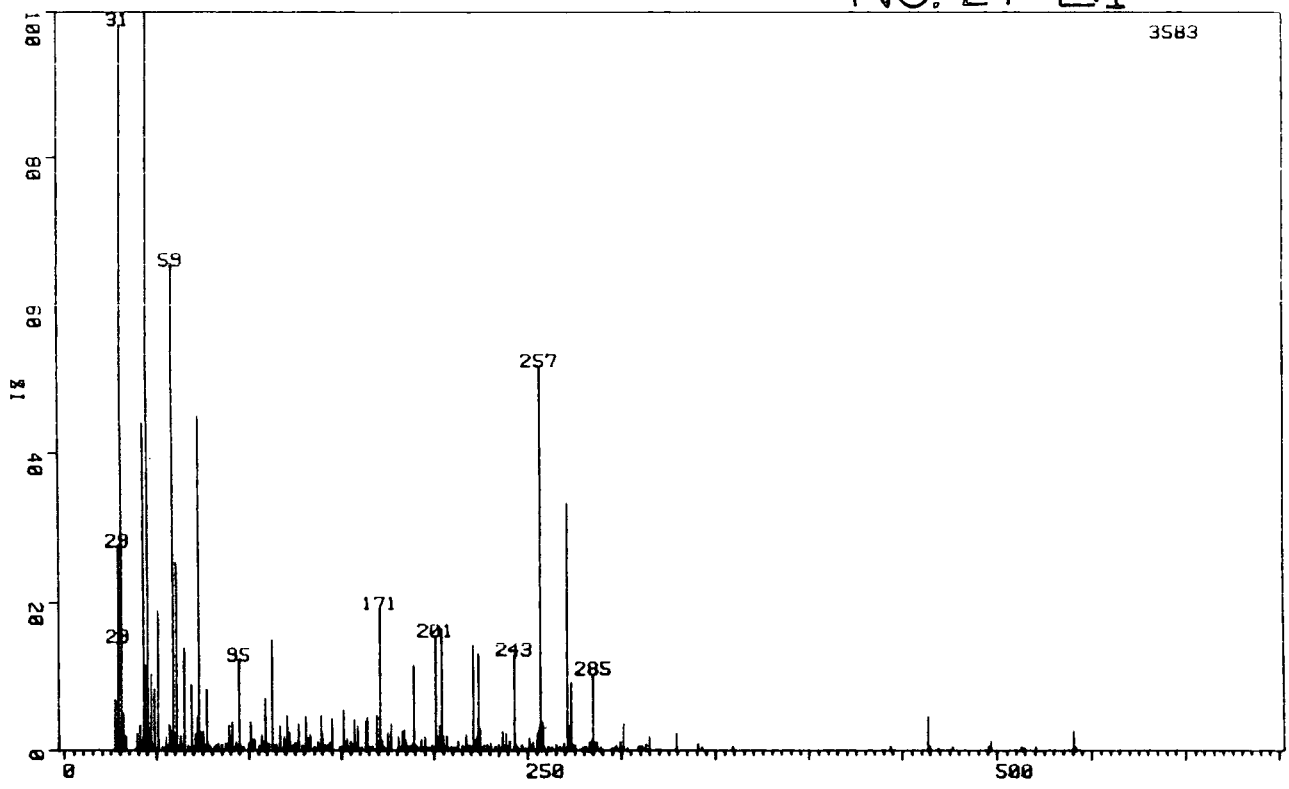


MASS	%HT. BASE	MASS	%HT. BASE				
60.88	8.98	145.08	2.05	246.95	1.90	512.44	2.02
65.03	4.55	150.91	2.90	250.90	1.62	514.45	24.52
67.04	2.13	156.93	1.65	254.95	1.45	515.43	3.95
68.99	4.52	158.91	1.28	255.92	1.28	540.36	3.95
70.97	2.41	160.84	1.53	256.93	62.70	542.38	2.67
72.01	2.10	162.94	3.10	257.93	4.69	568.20	1.11
73.05	64.55	163.94	1.16	258.92	3.38	584.04	1.51
74.07	3.61	164.92	3.49	264.95	1.90	586.04	3.44
77.01	2.24	168.89	2.44	266.96	2.02	753.53	11.39
78.97	1.34	170.93	9.60	270.88	19.09	754.53	2.67
80.97	1.22	174.95	1.05	271.94	1.85		
83.04	1.16	176.94	1.42	272.92	5.26		
85.08	1.85	182.98	1.56	274.95	7.27		
87.02	1.28	183.94	1.11	282.94	1.73		
88.94	2.19	184.94	2.13	283.95	1.08		
90.98	8.15	188.92	2.93	284.97	42.70		
95.02	3.04	198.89	1.53	285.98	4.46		
99.00	1.73	200.88	10.48	286.96	1.02		
100.95	1.39	201.94	1.08	298.90	1.79		
103.02	7.59	202.94	1.36	300.89	5.20		
107.96	1.42	203.93	8.92	302.93	0.38		
108.93	3.98	204.96	1.14	308.90	3.04		
112.91	4.52	216.90	2.41	310.90	2.56		
116.99	4.23	218.89	1.56	312.95	3.64		
120.89	2.10	220.90	6.93	314.94	5.23		
121.93	1.25	223.91	3.55	328.91	4.69		
130.86	1.28	226.94	1.62	356.91	2.59		
132.97	1.39	236.91	2.70	463.60	2.47		
138.92	1.85	238.90	2.05	476.56	2.44		
139.89	1.16	240.91	1.16	496.53	18.92		
144.98	1.11	242.91	3.30	497.52	2.73		

PT8SER 6 P.T. TELFORD
CAL:CALT1 STA:

No. 21 E.I.

04-JUN-85
0:59

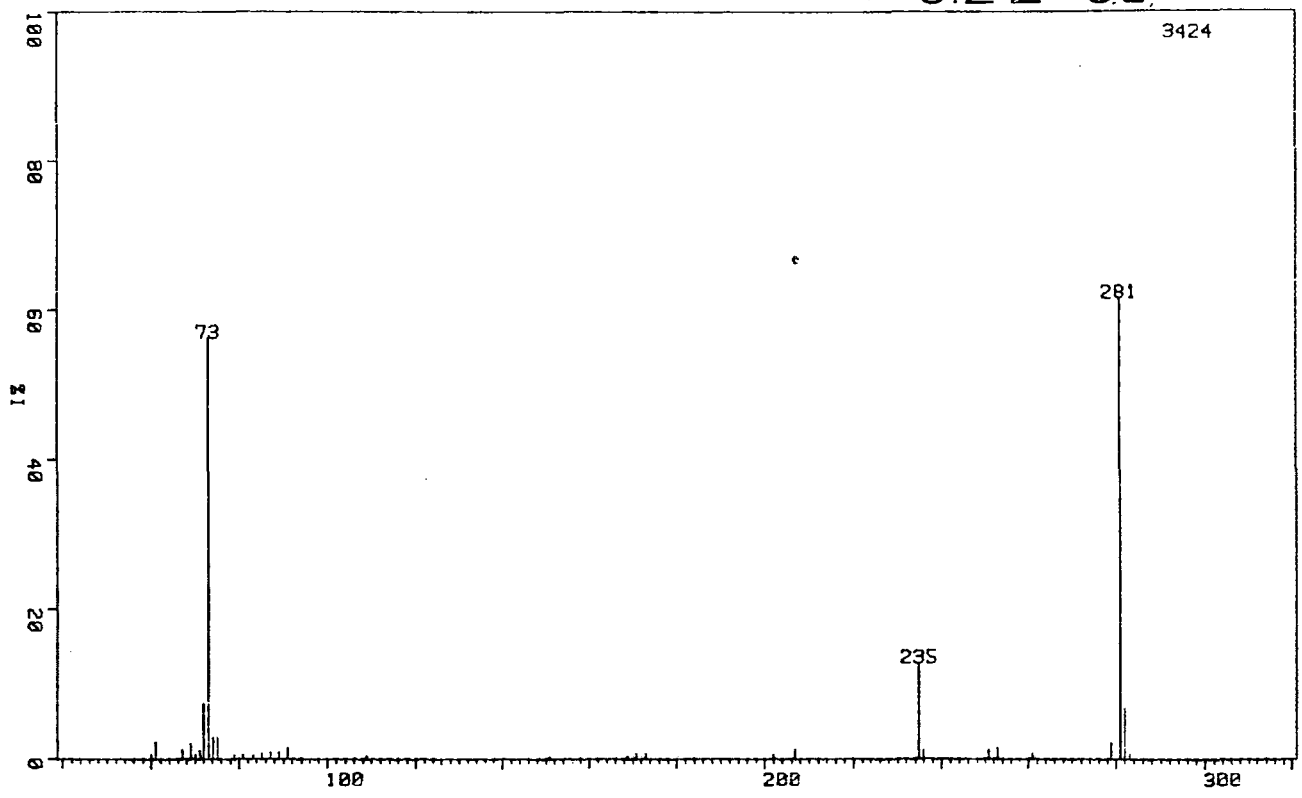


MASS	%INT. BASE	MASS	%INT. BASE	MASS	%INT. BASE	MASS	%INT. BASE	MASS	%INT. BASE	MASS	%INT. BASE
27.27	7.01	69.88	0.33	117.05	3.43	165.95	0.42	221.93	1.37	283.94	1.48
28.14	2.51	70.94	2.29	118.92	1.95	166.94	0.53	222.93	2.04	284.95	10.29
28.17	4.13	71.95	1.14	119.88	0.70	168.90	4.83	223.93	13.15	285.96	1.02
29.00	14.91	72.00	4.56	120.95	4.69	169.91	1.00	224.94	3.04	286.94	1.23
29.03	22.59	73.05	45.10	121.98	2.51	170.92	19.17	226.96	0.78	288.91	0.34
29.83	0.64	74.08	2.51	122.99	0.42	171.95	1.54	228.93	0.92	294.94	0.42
29.86	0.64	75.03	2.60	123.98	0.73	172.93	0.45	230.90	1.09	296.94	0.78
30.92	98.21	76.03	0.78	124.99	1.09	174.95	2.51	232.93	0.61	298.92	1.29
32.00	0.56	77.02	8.29	125.98	0.92	175.96	0.73	234.92	0.92	300.88	3.71
32.03	5.02	77.99	0.73	126.99	3.71	176.95	3.68	236.90	2.57	302.95	0.36
33.10	2.12	78.96	0.61	129.01	0.73	180.88	1.90	237.90	0.47	308.93	0.67
38.96	2.46	80.92	0.36	130.90	4.66	182.96	2.54	238.89	2.32	310.90	0.75
39.79	0.78	81.93	0.78	131.98	1.76	183.96	2.75	239.91	0.45	312.93	0.87
40.93	3.54	83.01	0.98	133.00	2.34	184.96	1.45	240.91	1.37	314.93	1.93
41.98	1.40	85.06	0.87	135.01	0.53	185.96	0.59	242.91	12.92	328.90	2.43
42.02	0.61	87.03	1.06	136.98	1.20	186.96	0.64	243.92	0.48	340.85	0.98
43.05	44.18	87.97	0.64	137.98	0.53	187.94	0.81	244.93	0.53	342.94	0.39
43.08	1.59	88.95	3.43	138.96	4.72	188.93	11.53	246.95	0.31	358.87	0.61
44.09	11.50	89.89	1.87	139.93	2.40	189.91	0.78	248.91	0.31	443.73	0.56
45.11	100.00	90.96	3.91	140.95	0.75	190.93	0.47	250.91	1.81	463.73	4.63
46.10	2.82	92.00	0.28	141.96	0.59	192.92	1.56	251.91	0.87	464.31	0.70
47.06	10.49	93.00	1.20	142.96	0.78	194.94	1.84	252.92	1.20	468.31	0.33
48.92	8.40	94.02	0.59	143.97	1.12	196.94	0.39	254.93	2.28	476.77	0.45
50.89	18.98	95.03	12.17	144.98	4.30	198.90	0.75	255.91	8.32	495.76	0.47
53.04	0.70	96.03	0.47	148.96	0.53	200.91	15.49	256.91	51.75	496.75	1.42
55.05	0.67	97.02	0.53	149.91	0.59	201.94	1.93	257.92	3.12	513.71	0.42
55.09	1.98	99.89	1.03	150.93	5.44	202.95	3.38	258.90	0.64	514.72	0.42
56.09	0.53	100.98	3.99	151.97	1.20	203.93	16.49	260.91	0.42	520.20	0.53
57.03	3.54	102.01	1.42	152.99	1.76	204.94	2.04	262.94	0.42	540.66	2.65
57.07	0.64	103.07	1.70	153.98	0.33	205.95	0.47	264.92	0.92	541.70	0.47
58.00	2.65	106.03	0.64	154.98	1.40	206.94	2.09	266.95	0.53		
58.95	65.42	107.01	2.20	155.97	0.81	208.93	0.36	268.90	1.03		
59.87	2.29	108.00	1.20	156.96	4.27	210.92	0.36	270.90	35.27		
60.91	25.48	108.97	7.13	157.95	0.47	212.93	1.31	271.91	3.32		
61.97	0.59	109.93	0.33	158.94	3.52	214.95	0.75	272.91	9.01		
63.00	2.12	110.93	1.06	160.90	0.36	216.91	2.20	273.91	0.73		
64.01	0.23	112.92	15.07	162.94	3.96	217.91	0.47	274.92	0.81		
65.02	14.04	113.99	0.64	163.97	4.55	218.90	0.81	278.90	0.36		
66.96	0.70	115.01	0.92	164.48	0.64	219.89	0.42	280.87	0.50		
68.89	8.93	116.98	0.64	164.96	0.36	220.92	14.29	282.95	1.14		

PT1071 0 P.T.TELFORD C.I. I-BU 107/1
CAL:CALT31 STA:

No.22 CI

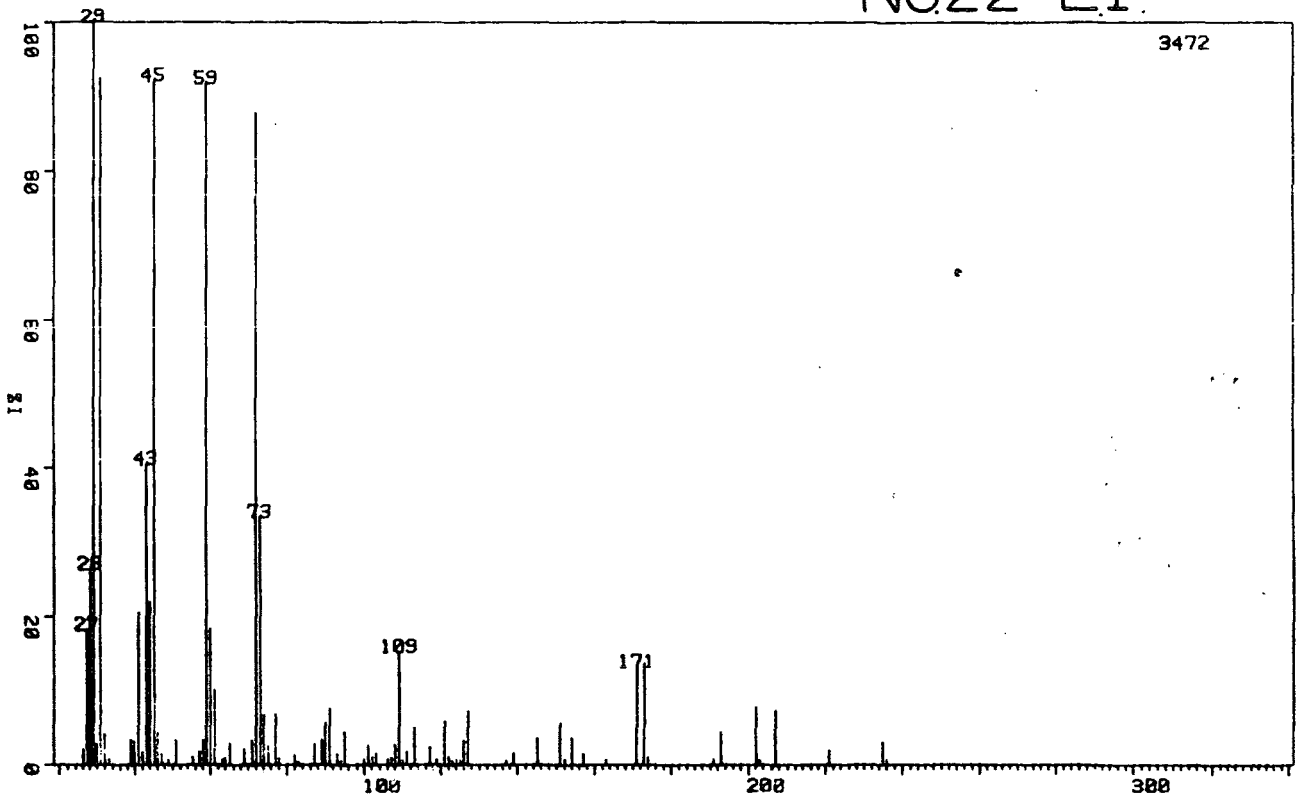
16-APR-85
1:43



MASS	%RT BASE
40.93	2.31
67.06	1.79
68.99	2.10
69.93	6.53
71.00	1.20
72.01	7.36
73.05	56.31
74.07	3.04
75.03	3.01
76.96	0.67
80.95	0.64
83.04	0.55
85.08	0.79
87.00	1.02
88.95	0.96
90.94	1.55
108.90	0.38
150.85	0.38
168.85	0.32
170.84	0.73
172.89	0.76
201.88	0.55
206.90	1.29
234.89	12.91
235.93	1.17
250.86	1.29
252.93	1.55
260.92	0.79
278.89	2.25
280.92	51.68
281.93	6.78
282.94	0.61

PT1071 0 P.T.TELFORD 107/1 E.I. 16-APR-85
CAL:CALT31 STA: 0:26

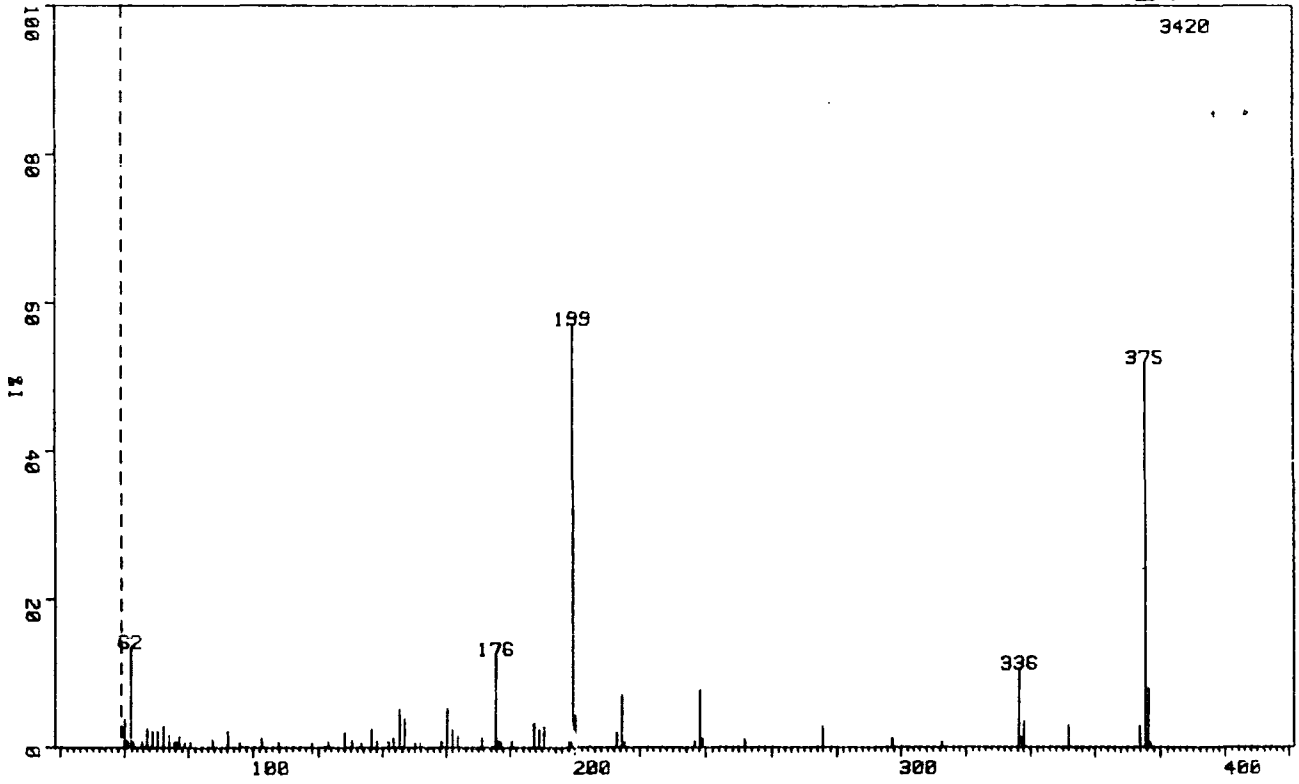
No.22 EI



MASS	%HT. BASE	MASS	%HT. BASE		
26.30	2.07	59.01	91.73	109.98	0.72
27.23	18.15	59.94	18.40	110.99	1.81
28.11	26.41	60.99	10.08	113.03	5.04
28.13	17.45	63.08	0.81	117.12	2.39
28.56	0.26	64.09	1.07	118.97	0.78
28.97	11.72	65.11	3.00	120.98	5.99
29.00	100.00	68.95	2.07	122.02	1.15
29.81	2.53	70.98	3.28	123.01	0.66
29.83	2.76	72.05	87.79	124.03	0.72
30.88	92.48	73.09	33.38	125.02	0.78
31.97	3.89	74.11	6.77	126.03	3.23
32.00	4.12	75.03	2.62	127.02	7.23
33.08	0.78	77.01	6.91	137.01	0.52
38.96	3.40	77.99	0.95	138.97	1.67
39.80	3.20	81.95	1.41	145.02	3.60
40.94	20.71	82.99	0.46	150.97	5.76
42.00	1.38	87.03	2.74	152.00	0.78
42.04	1.81	88.95	3.43	153.99	3.66
43.07	40.55	89.89	5.65	157.00	1.56
43.11	6.48	90.97	7.69	162.97	0.75
44.11	21.98	93.02	1.61	170.96	13.22
44.15	0.32	94.02	0.52	172.97	13.68
45.14	92.17	95.04	4.49	173.98	1.01
46.13	4.29	99.90	0.75	190.96	0.89
47.11	1.53	100.99	2.65	192.97	4.52
48.96	0.78	102.03	1.12	201.98	7.72
50.94	3.31	103.06	1.58	203.00	0.69
55.15	1.12	106.06	0.84	206.97	7.37
57.09	1.81	107.05	1.04	220.96	2.02
57.13	1.18	108.03	2.71	234.99	3.08
58.06	3.25	109.00	15.24	236.00	0.84

PT1072 0 P.T.TELFORD C.I. I-BU 107/2 16-APR-85
CAL:CALT31 STA: 1:26

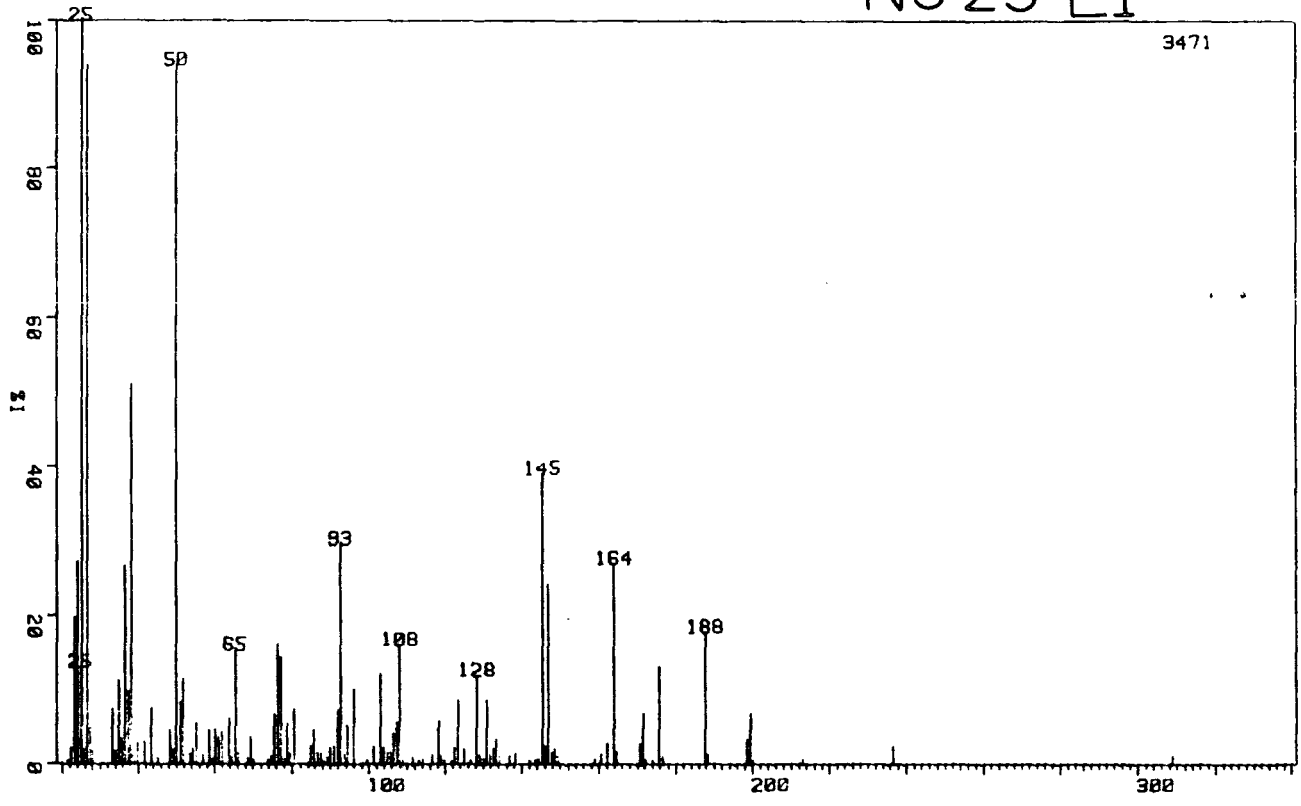
No.23 CI



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
61.06	0.53	151.75	0.29	373.78	1.40
61.96	6.73	158.53	0.44	375.50	25.94
62.85	0.44	160.21	2.63	376.32	4.04
65.40	0.44	161.94	1.23	377.18	0.38
67.09	1.29	163.66	0.79		
68.74	1.11	171.26	0.67		
70.39	1.08	175.51	6.26		
72.18	1.46	176.36	0.47		
73.87	0.88	177.20	0.41		
75.58	0.38	180.55	0.44		
76.39	0.41	187.36	1.61		
77.24	0.76	189.02	1.20		
78.83	0.32	190.71	1.37		
80.56	0.38	198.35	0.35		
87.42	0.56	199.19	28.51		
92.44	1.11	200.04	2.16		
95.84	0.32	200.91	0.29		
102.63	0.61	212.77	0.96		
107.70	0.32	214.49	3.57		
117.88	0.35	215.36	0.32		
122.96	0.41	236.53	0.44		
128.05	1.02	238.22	3.92		
130.53	0.53	239.05	0.58		
133.15	0.29	251.74	0.58		
136.52	1.26	275.52	1.49		
138.20	0.50	297.46	0.64		
141.58	0.38	312.71	0.32		
143.32	0.67	336.48	5.29		
145.02	2.60	337.31	0.64		
146.69	1.93	338.14	1.75		
150.00	0.29	351.73	1.52		

PT1072 0 P.T.TRLFORD 107/2 E.I. 16-APR-85
CAL:CRLT31 STR: 0:44

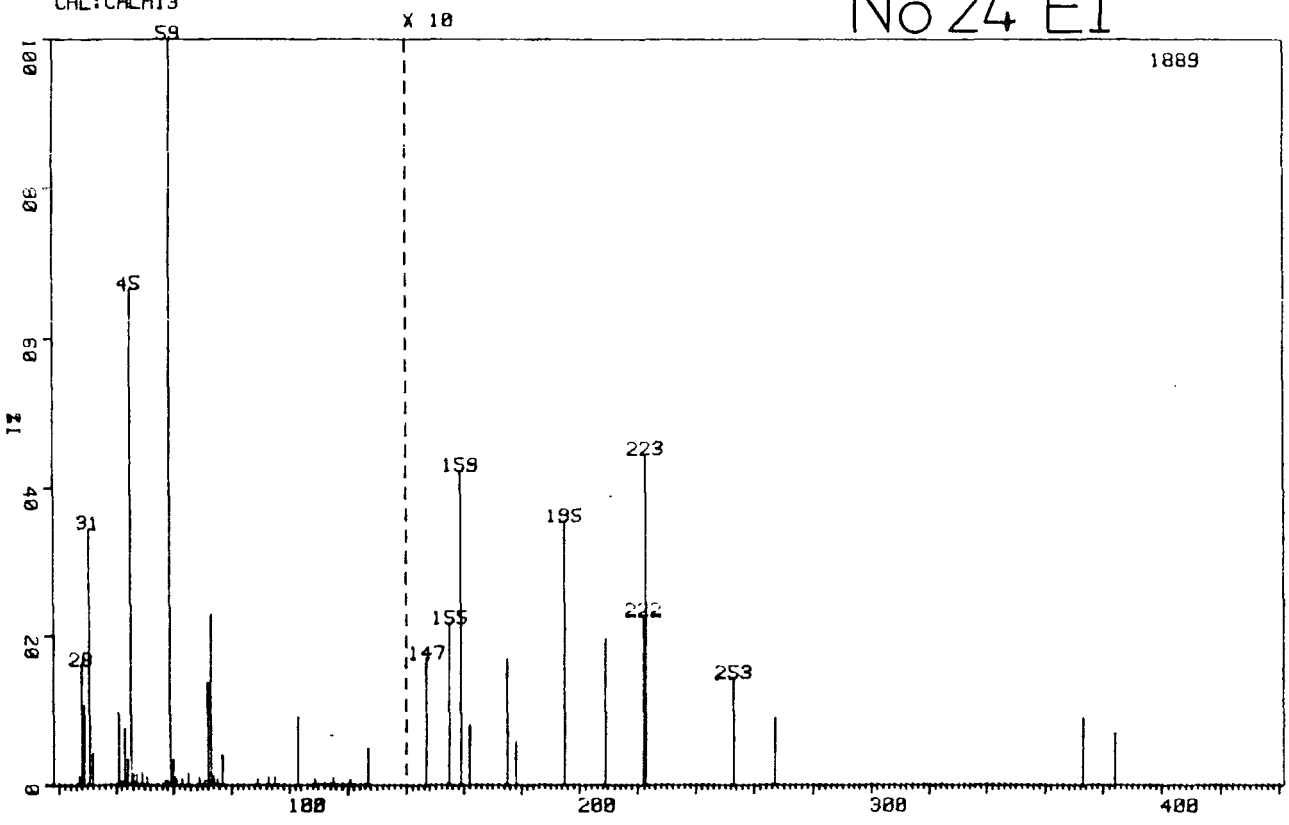
No 23 EI



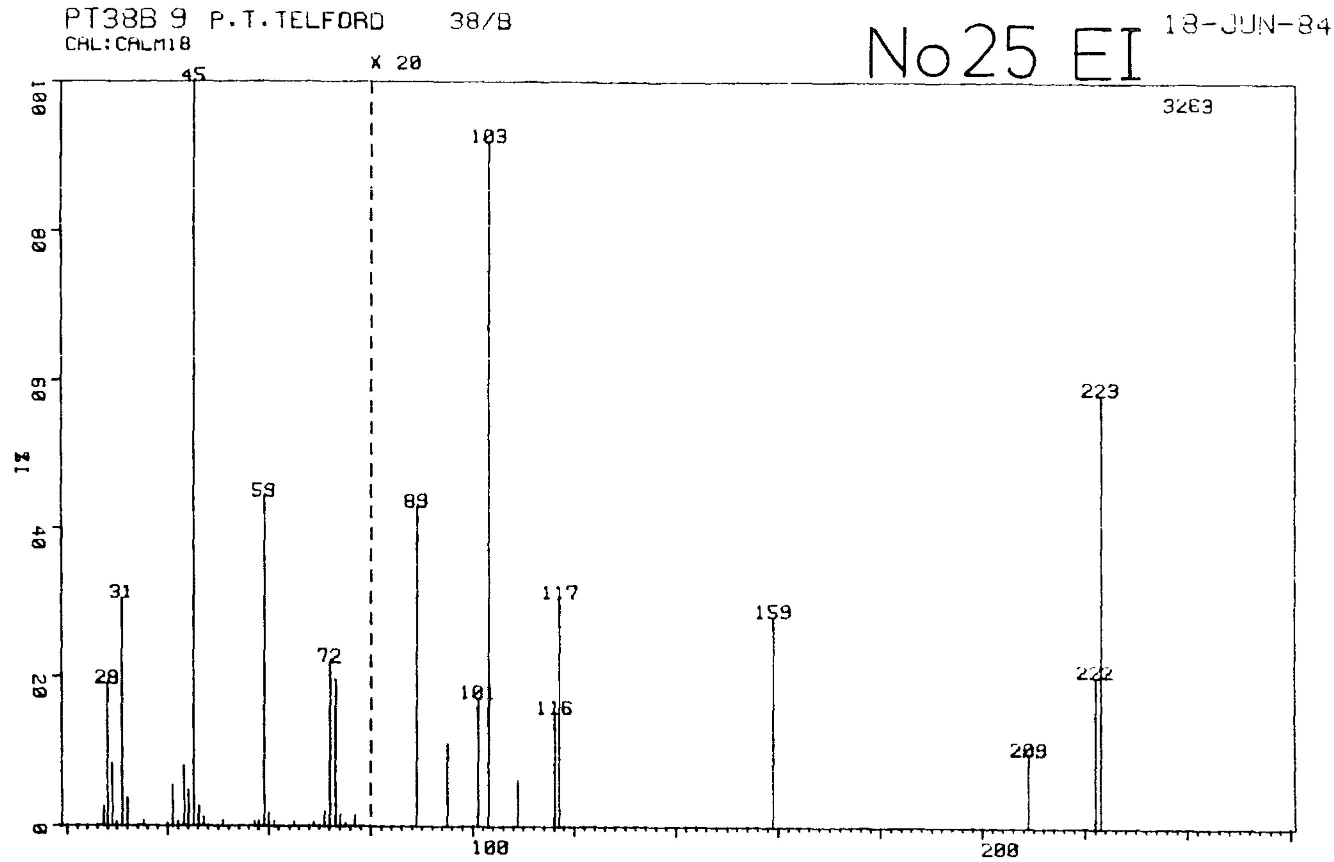
MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE		
21.30	0.46	50.85	8.38	87.48	1.61	128.29	11.99
22.27	2.22	51.74	11.61	88.27	0.37	129.05	1.24
23.20	19.79	51.77	0.63	89.09	1.04	129.86	0.72
24.07	27.20	53.51	1.41	89.89	2.25	130.74	8.76
24.10	7.72	54.38	2.13	90.80	2.42	131.68	1.24
24.93	13.14	55.24	5.59	91.73	7.35	132.55	2.07
24.96	100.00	56.87	1.33	92.67	29.59	133.40	3.43
25.76	1.90	58.51	4.61	93.55	1.24	134.27	1.04
25.79	2.05	59.33	0.81	94.39	5.21	136.74	1.12
26.57	94.04	60.14	4.75	96.08	10.29	138.46	1.50
27.33	4.96	61.04	3.60	99.40	0.55	145.29	39.07
27.36	2.28	61.93	4.35	101.09	2.42	146.01	2.56
28.11	1.76	63.65	6.19	102.86	12.19	146.82	24.17
33.17	7.43	64.52	1.04	103.76	2.22	147.71	1.61
34.00	1.84	65.38	15.44	104.66	1.64	148.62	2.07
34.06	0.81	66.22	1.61	105.51	1.61	149.45	1.12
34.94	11.29	68.60	0.89	106.35	4.21	158.79	0.66
35.76	1.07	69.41	3.66	107.20	5.76	160.50	1.38
35.79	3.46	70.26	0.78	107.98	16.13	162.25	2.85
36.59	26.59	73.72	0.63	108.81	0.78	163.89	26.97
36.63	9.45	74.63	1.12	109.66	0.26	164.72	1.79
37.41	9.82	75.49	6.77	111.37	1.04	170.61	2.82
38.21	51.14	76.33	16.34	113.14	0.58	171.47	7.00
38.98	1.30	77.16	14.49	113.99	0.66	175.74	13.22
39.73	2.85	77.94	0.78	116.50	1.33	176.59	1.12
41.52	3.03	78.73	5.56	118.17	5.96	187.60	17.83
43.33	7.69	79.60	1.53	118.95	1.15	188.44	1.33
45.09	0.89	80.46	7.38	119.78	0.61	198.61	3.37
48.36	4.70	84.79	2.51	121.53	0.35	199.43	7.03
49.16	1.93	85.72	4.70	122.40	2.25	200.28	0.58
49.94	94.01	86.63	1.53	123.28	8.73	213.01	0.75
						236.77	2.36
						308.79	1.15

PT384 4 P.T.TELFORD 38 FRACTION 4 13-MAR-84
CAL:CALM13

No 24 EI



m/z	Rel. Abund.	m/z	Rel. Abund.
27.10	1.22	103.00	5.11
28.07	16.04	108.95	3.77
29.06	10.59	115.06	0.90
30.05	34.37	120.78	0.56
31.05	4.34	127.00	4.82
40.93	9.69	140.98	1.69
42.03	0.59	155.00	2.17
43.09	7.46	158.95	4.24
44.13	3.39	161.96	0.79
45.14	66.60	173.00	1.69
46.15	1.48	177.99	0.58
47.11	1.22	194.97	3.55
48.96	1.59	206.93	1.96
50.93	1.01	221.94	2.28
57.10	0.69	222.96	4.45
58.06	0.64	252.99	1.43
59.00	100.00	266.98	0.90
59.93	3.44	372.91	0.90
60.96	0.95	383.95	0.69
63.06	0.90		
65.09	1.59		
68.96	1.06		
71.00	0.74		
72.04	13.76		
73.08	22.92		
74.10	1.22		
75.07	0.58		
76.99	3.92		
88.94	0.85		
93.00	1.01		
95.01	1.01		

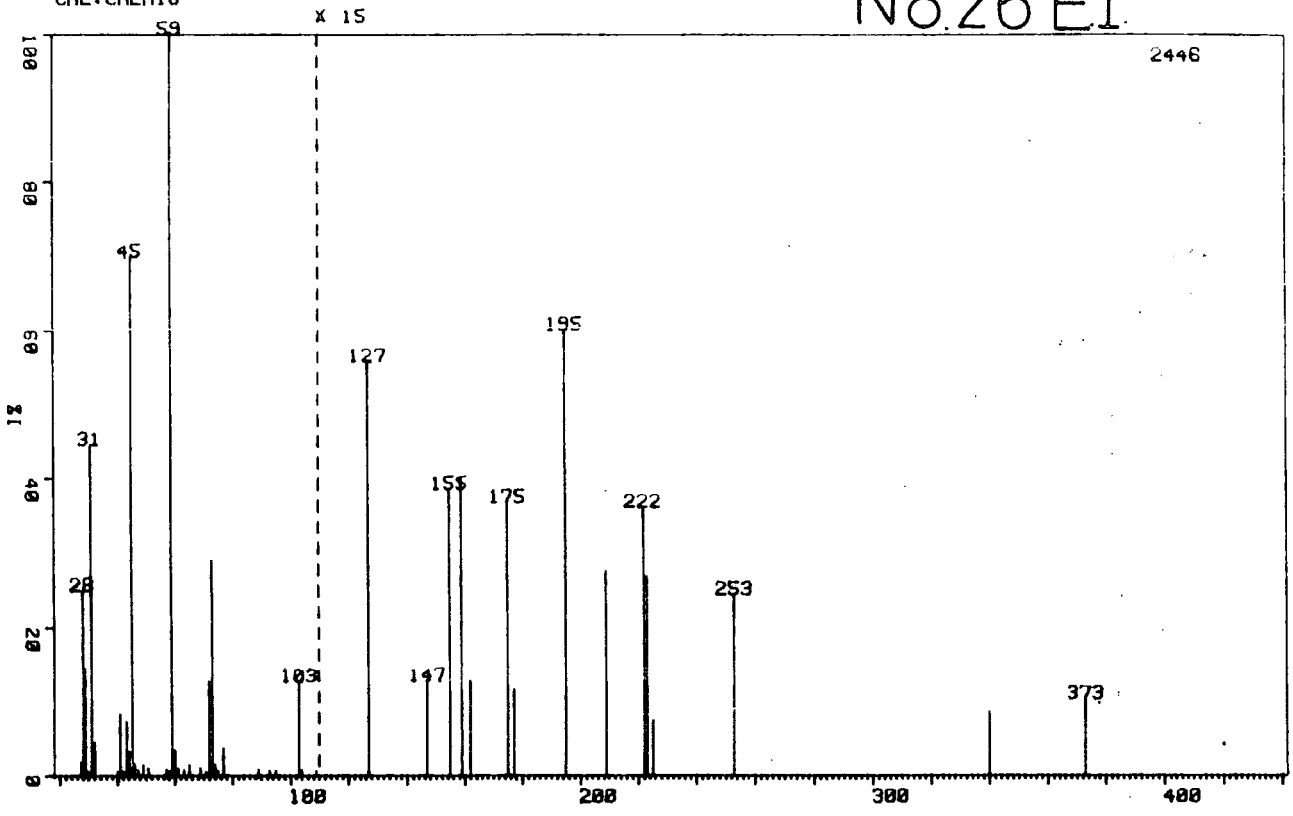


MASS	[illegible] %BASE	MASS	[illegible]
27.24	2.48	101.0[illegible]	0.8[illegible]
28.12	1[illegible]	10[illegible]	[illegible]
29.01	8.31	108.9[illegible]	[illegible]
29.8[illegible]	[illegible].49	116.09	[illegible]
30.92	[illegible]0.52	117.04	1.[illegible]6
32.02	3.[illegible]8	15[illegible].9[illegible]	1.41
35.21	0.77	209.01	0.49
39.94	0.34	222.05	1.01
40.99	5.42	223.02	2.91
42.07	0.55	413.71	1.47
43.12	7.97		
44.16	4.75		
45.17	100.00		
46.16	2.57		
47.13	1.20		
50.95	0.74		
57.12	0.55		
58.09	0.70		
59.03	44.22		
59.95	1.75		
61.02	0.77		
65.12	0.52		
68.95	0.58		
70.99	1.96		
72.04	21.97		
[illegible]	[illegible]		
[illegible]	1.[illegible]		
[illegible]	[illegible]		
[illegible]	[illegible]		
[illegible]	[illegible]		
[illegible]	[illegible]		

PT38C 4 P.T.TELFORD
CAL:CALM18

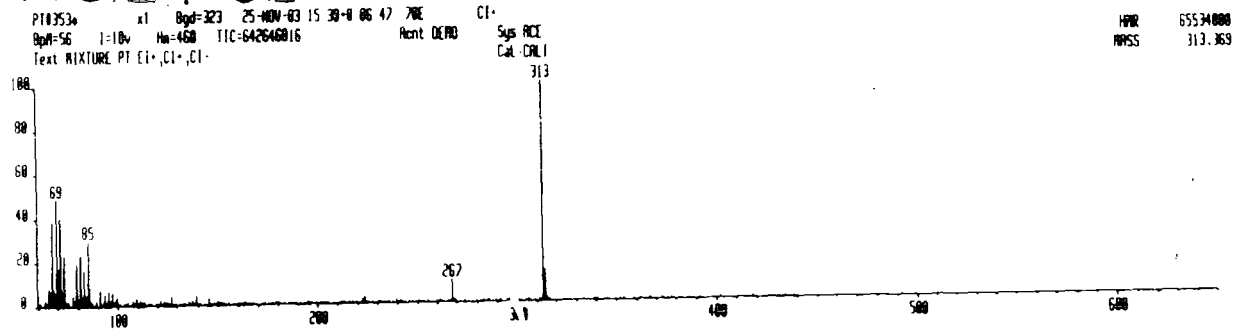
No.26 EI

18-JUN-84

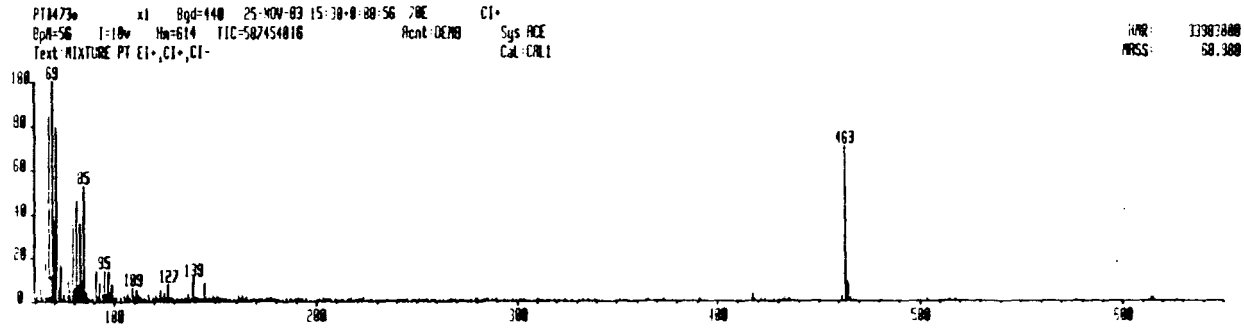


MASS	%HT. BASE	MASS	%HT. BASE
27.25	1.80	88.96	0.86
28.12	25.02	92.99	0.78
29.01	14.51	95.00	0.70
29.85	0.57	103.05	12.80
30.92	44.60	104.07	0.86
32.01	4.54	108.94	0.65
32.13	2.70	126.98	3.72
39.84	0.57	146.98	0.86
40.99	8.30	154.97	2.58
42.07	0.65	158.95	2.66
43.12	7.32	161.95	0.86
44.15	3.31	175.00	2.45
45.17	69.99	176.99	0.78
46.17	1.59	194.98	4.01
47.13	0.86	208.97	1.84
48.97	1.51	222.00	2.41
50.95	1.06	222.98	1.80
57.12	0.94	225.00	0.49
58.09	0.78	253.00	1.64
59.02	100.00	340.00	0.57
59.95	3.43	373.01	0.70
61.01	0.94		
63.09	0.90		
65.12	1.51		
68.95	0.94		
70.98	0.61		
72.04	12.80		
73.08	29.07		
74.11	1.51		
75.06	0.65		
77.00	3.76		

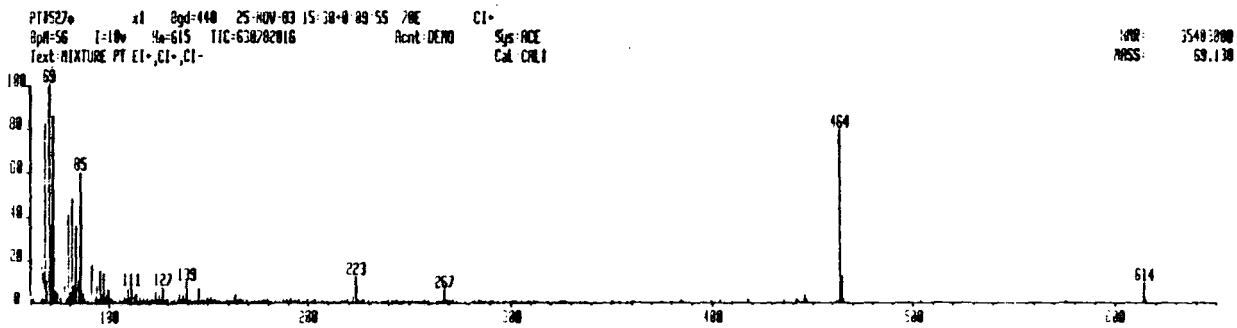
No.24 C.I.



No.25 C.I.

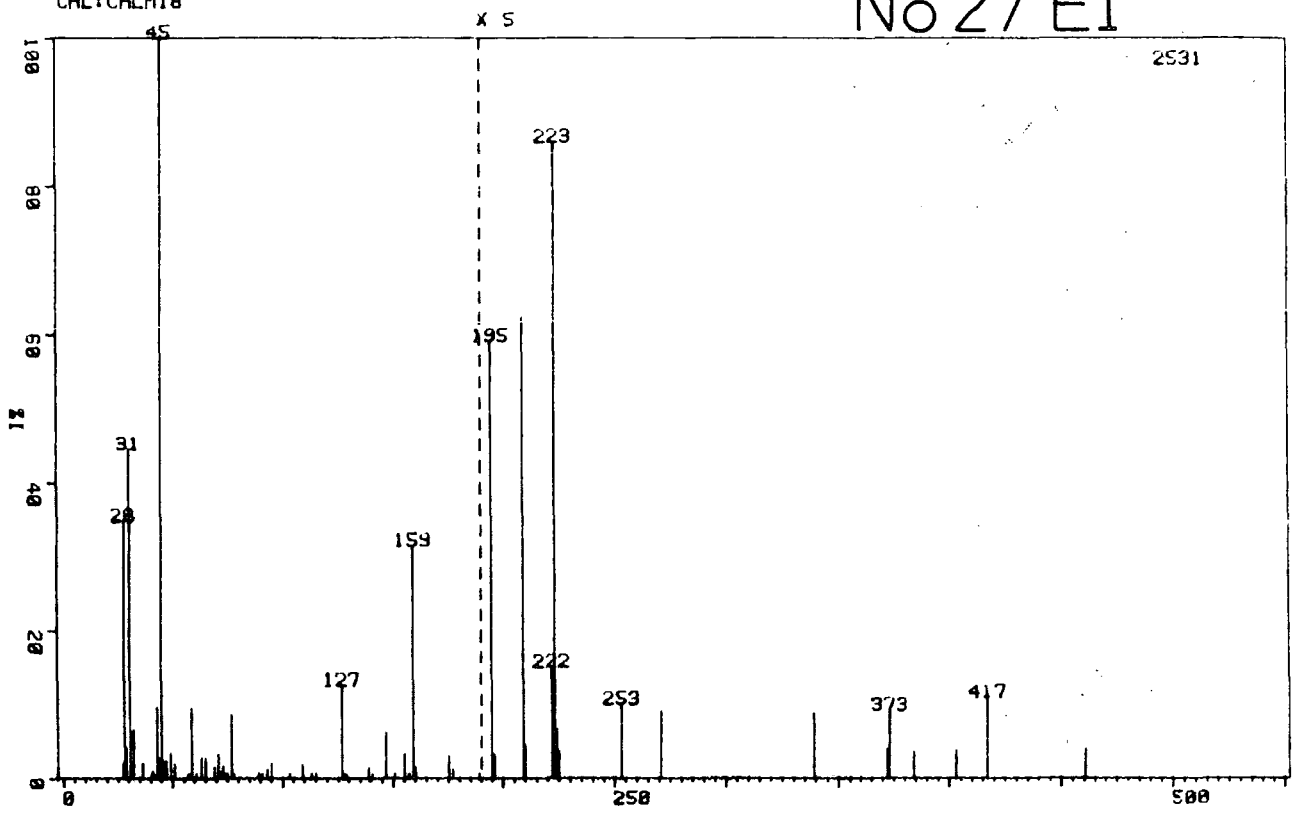


No.26 C.I.



PT38D 4 P.T.TELFORD 38/D 18-JUN-84
CAL:CHLM18

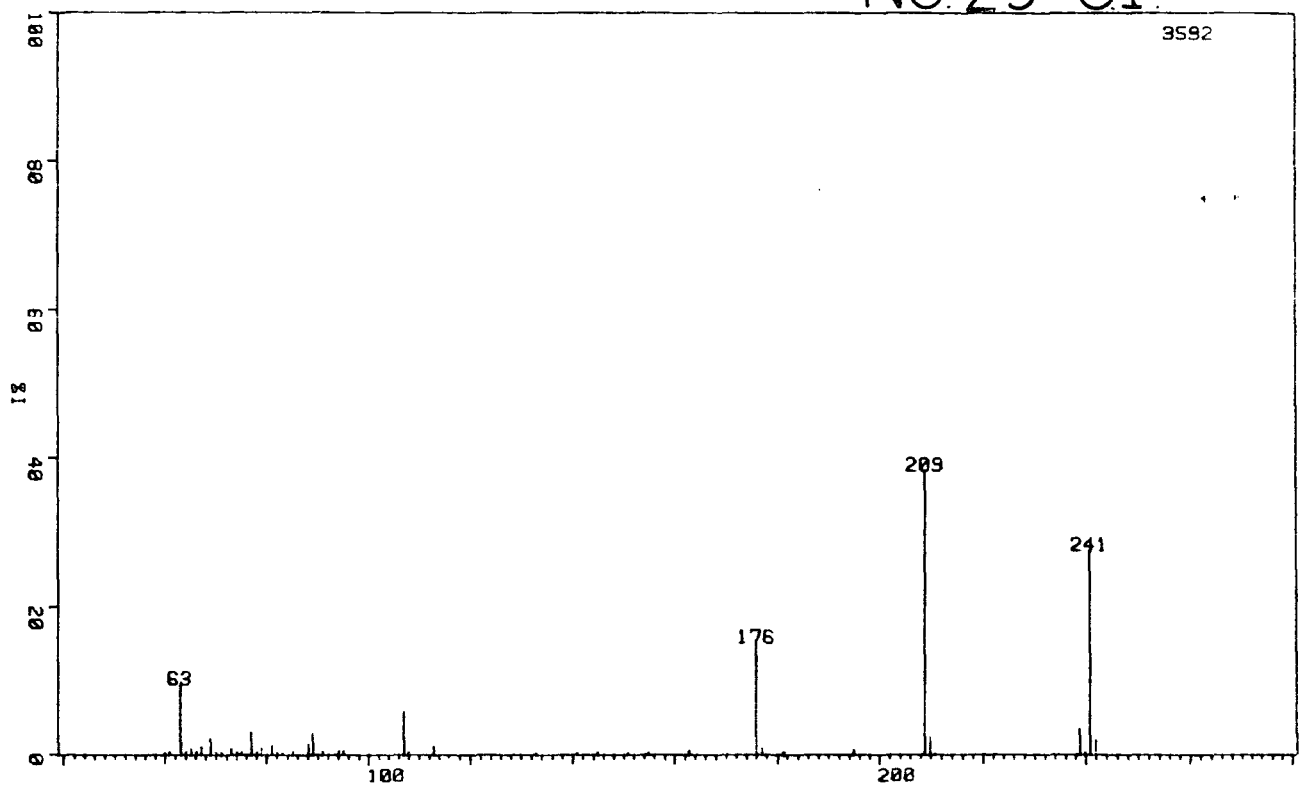
No 27 EI



MASS	%HT. BASE	MASS	%HT. BASE		
27.24	1.98	90.93	0.51	270.97	1.82
28.12	34.85	92.99	1.11	339.05	1.78
29.00	4.35	94.99	1.94	372.01	0.79
30.92	44.45	103.04	0.59	373.01	1.86
32.01	6.64	108.94	1.86	384.02	0.71
36.41	1.94	112.96	0.59	403.04	0.75
39.84	0.55	115.00	0.63	417.00	2.21
40.99	1.07	126.97	12.60	461.00	0.79
42.04	0.40	127.96	0.55		
43.11	9.68	128.93	0.51		
44.14	2.88	138.94	0.95		
45.17	100.00	139.21	1.42		
46.16	2.45	140.91	0.51		
47.13	2.45	146.93	6.20		
48.97	3.44	150.86	0.59		
50.94	1.98	154.98	3.20		
57.12	0.47	156.99	0.51		
58.08	0.67	158.93	31.49		
59.03	9.64	159.90	1.58		
60.99	0.71	174.98	3.04		
63.09	2.88	176.99	1.22		
65.12	2.65	188.98	0.59		
68.95	1.58	194.98	11.81		
70.99	3.24	196.00	0.63		
72.06	0.91	208.98	12.45		
73.08	1.58	209.98	0.91		
74.12	0.59	222.00	3.00		
75.04	0.67	222.99	17.19		
77.06	8.57	224.02	1.34		
77.99	0.59	225.04	0.75		
88.94	0.71	253.01	2.02		

PT21X 9 P.T.TELFORD 2/1 C.I. 26-MAR-85
CAL:CALT31 STA: 1:26

No.29 CI

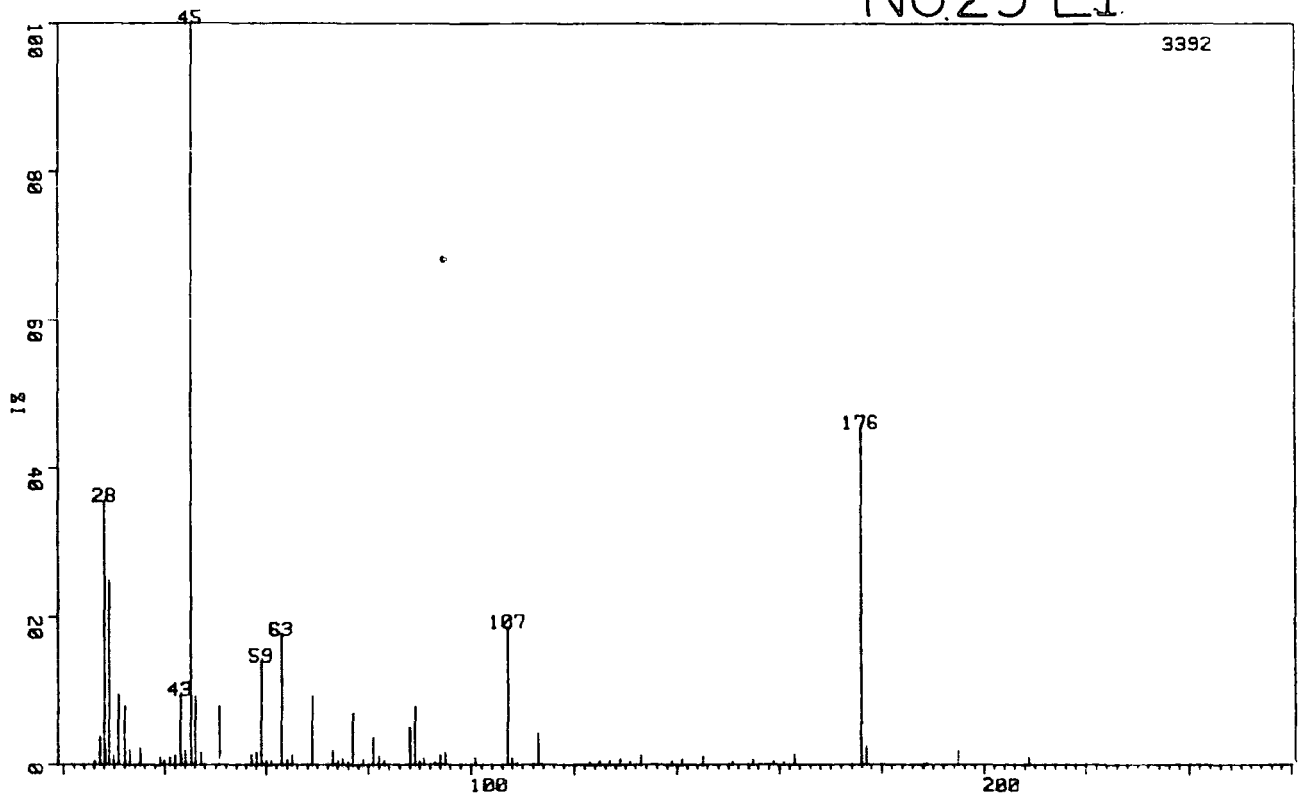


MASS	%HT. BASE	MASS	%HT. BASE
60.89	0.42	154.84	0.31
62.99	9.55	162.82	0.53
64.02	0.36	175.84	15.23
65.03	0.86	176.88	1.06
66.05	0.47	181.05	0.42
67.03	1.17	181.37	0.31
68.91	2.34	194.85	0.75
69.90	0.31	208.84	38.36
70.95	0.39	209.80	2.45
72.98	0.81	210.78	0.25
74.01	0.33	238.78	3.54
75.00	0.36	239.77	0.42
76.97	3.09	240.79	27.78
77.95	0.31	241.81	2.03
78.91	0.97		
80.87	1.42		
81.91	0.39		
83.04	0.31		
85.06	0.47		
87.97	1.56		
88.93	2.87		
90.87	0.56		
93.99	0.53		
94.98	0.53		
106.96	5.99		
107.95	0.42		
112.93	1.31		
132.87	0.33		
140.83	0.31		
144.90	0.39		
150.81	0.33		

PT21X 4 P.T.TELFORD 2/1 E.I.
CAL:CALT31 STA:

No.29 EI

26-MAR-85
0:43

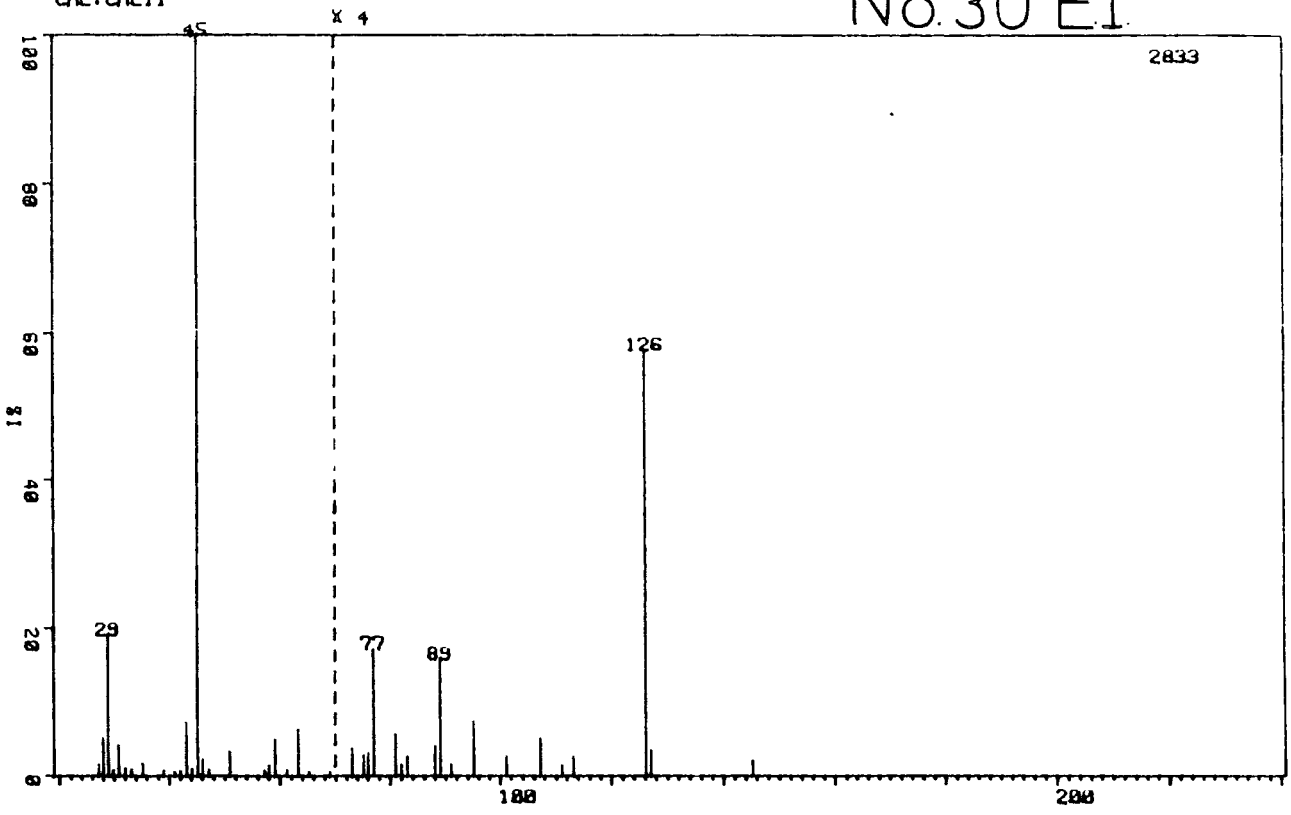


MASS	%HT. BASE	MASS	%HT. BASE		
26.30	0.44	60.93	0.62	130.91	0.41
27.23	3.71	63.04	17.60	132.96	1.24
28.11	35.58	64.06	0.77	138.94	0.47
28.13	2.18	65.07	1.39	140.89	0.88
28.96	24.97	68.94	9.35	145.00	1.21
29.00	4.92	73.03	1.98	150.92	0.41
29.80	1.33	74.06	0.68	154.97	0.65
30.88	9.52	75.04	0.91	158.94	0.44
31.96	7.96	76.04	0.38	160.89	0.38
32.00	0.44	77.02	7.10	162.94	1.44
33.08	1.98	78.92	0.74	175.93	45.37
35.15	2.33	80.92	3.66	176.92	2.54
38.95	1.06	81.95	1.15	188.88	0.27
39.79	0.62	82.98	0.53	194.88	1.95
40.94	1.00	87.99	5.10	208.87	1.00
41.98	1.30	88.96	7.99	219.89	0.41
42.03	0.35	89.91	0.47		
43.05	9.46	90.90	1.00		
43.10	1.36	92.99	0.35		
44.06	0.53	94.02	1.30		
44.10	1.98	95.01	1.71		
45.12	100.00	100.91	0.94		
46.12	9.20	107.00	18.60		
47.09	1.68	107.98	0.94		
50.92	7.99	108.95	0.35		
57.06	1.39	112.98	4.30		
57.10	0.29	122.96	0.29		
58.04	1.74	124.99	0.44		
58.98	14.03	126.97	0.47		
59.92	0.47	128.90	0.80		

PT31 6 P.T.TELFORD 3/1
CAL:CAL11

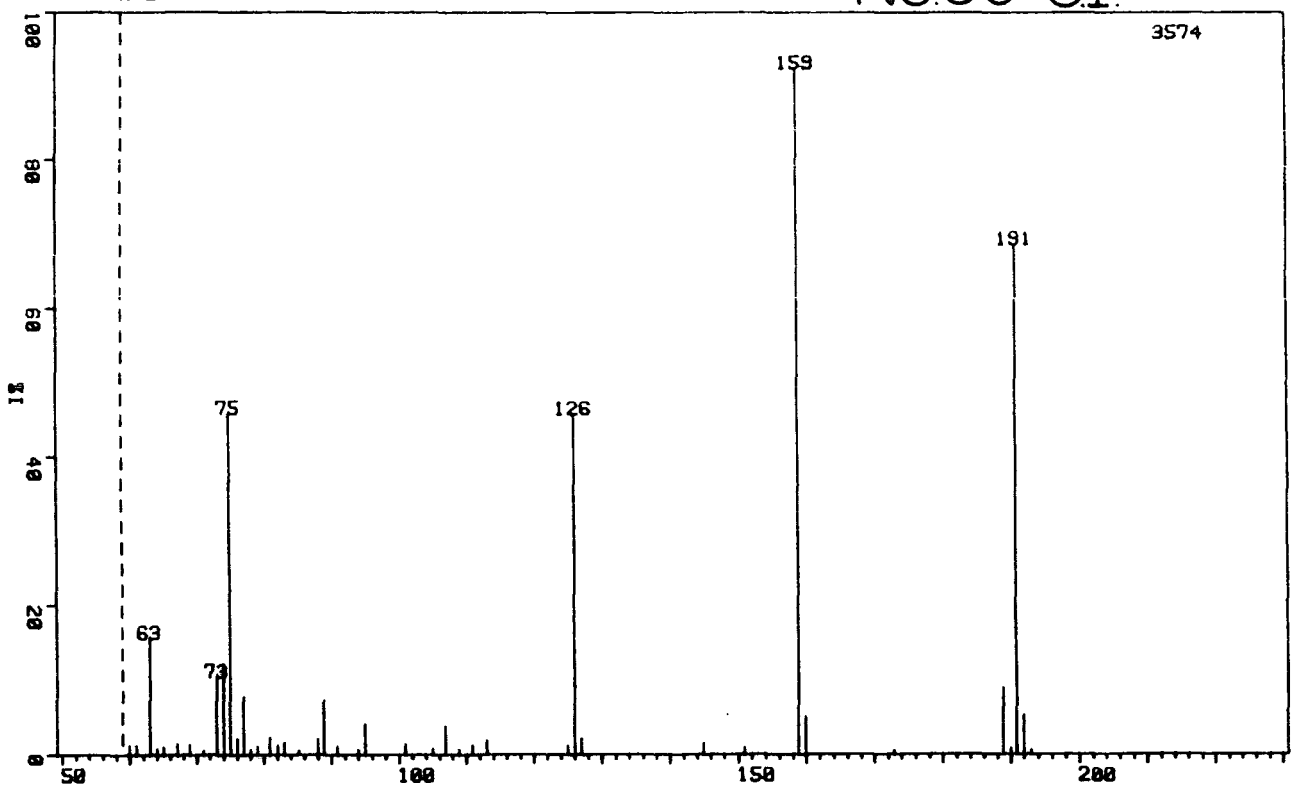
No.30 EI

11-APR-83



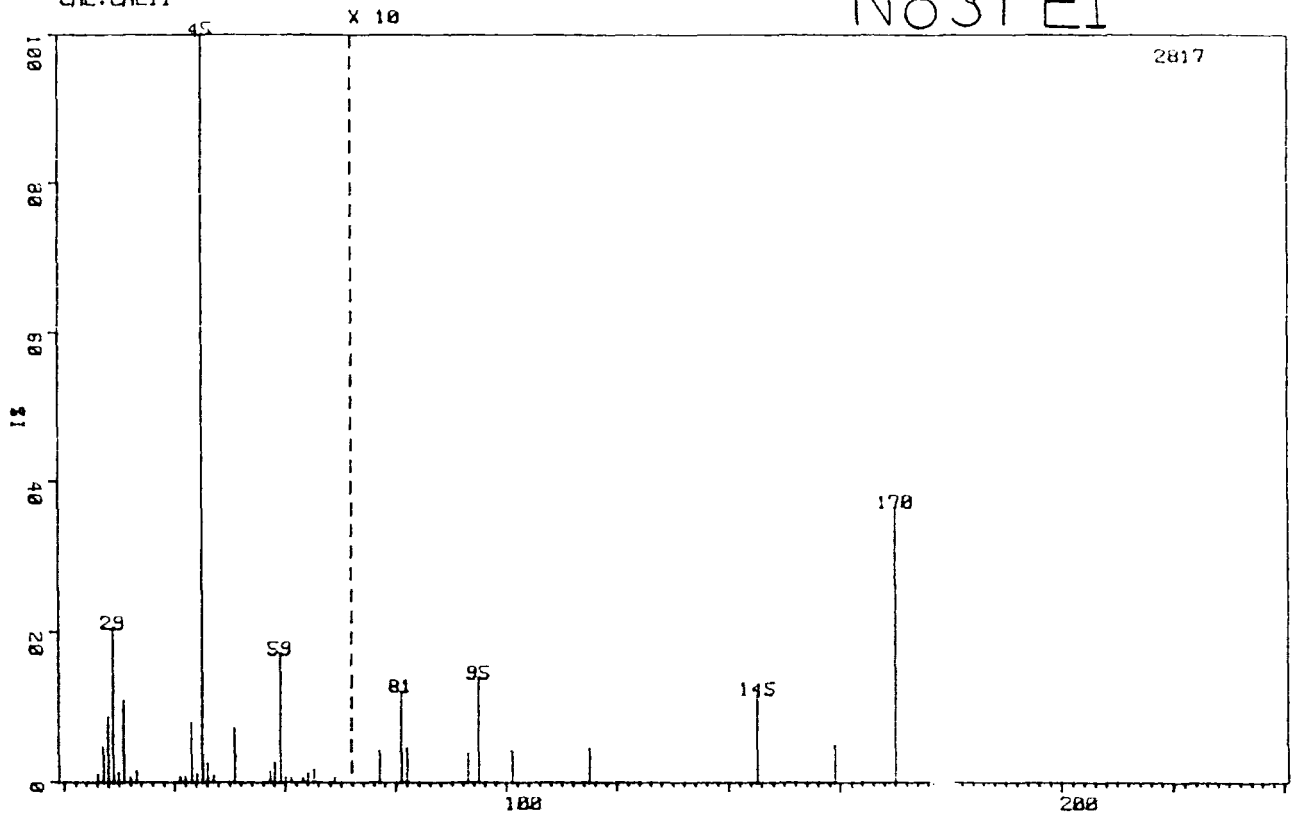
MASS	%HT. BASE	MASS	%HT. BASE
27.22	1.66	88.09	1.02
28.11	5.26	89.06	3.95
28.97	19.13	91.04	0.42
29.82	0.78	95.19	1.87
30.91	4.17	101.13	0.67
32.00	1.09	107.19	1.27
33.13	0.95	111.13	0.39
35.21	1.73	113.19	0.67
39.02	0.81	126.14	14.44
41.02	0.60	127.16	0.88
42.08	0.74	145.22	0.53
43.16	7.31		
44.19	1.02		
45.22	100.00		
46.21	2.40		
47.19	1.02		
51.03	3.35		
57.21	0.85		
58.18	1.52		
59.12	5.05		
61.10	0.88		
63.19	6.39		
65.18	0.60		
68.98	0.53		
73.10	0.95		
75.09	0.74		
76.09	0.81		
77.03	4.31		
80.96	1.45		
81.99	0.42		
83.04	0.67		

PTT31X 11 PTT 3/1 M.W.192 I-BU C.I. No.30 C.I. 03-OCT-84
CAL:CALTS STA: 1:40
X 2



MASS	%HT. BASE	MASS	%HT. BASE
60.04	0.70	124.98	1.12
62.99	3.14	144.92	0.84
64.01	0.48	150.86	0.53
65.03	0.59	158.88	48.24
67.04	0.76	159.90	2.66
68.95	0.76	172.85	0.25
70.97	0.31	172.93	0.28
73.02	5.46	188.87	4.67
74.05	6.38	189.89	0.50
75.06	23.95	190.89	35.87
76.04	1.15	191.91	2.74
76.98	4.09	192.92	0.31
77.96	0.34		
78.92	0.62		
80.87	1.26		
81.93	0.67		
82.96	0.87		
85.05	0.31		
87.93	1.12		
88.93	3.83		
90.88	0.62		
93.99	0.36		
94.99	2.15		
100.87	0.76		
105.00	0.42		
106.99	2.01		
108.93	0.36		
110.88	0.70		
112.98	1.01		
124.98	0.62		
125.98	23.89		

PT31R 6 P.T.TELFORD CF2HCF2CH2OCH2CH2OCH3 No31 EI 11-APR-83
CAL:CAL11

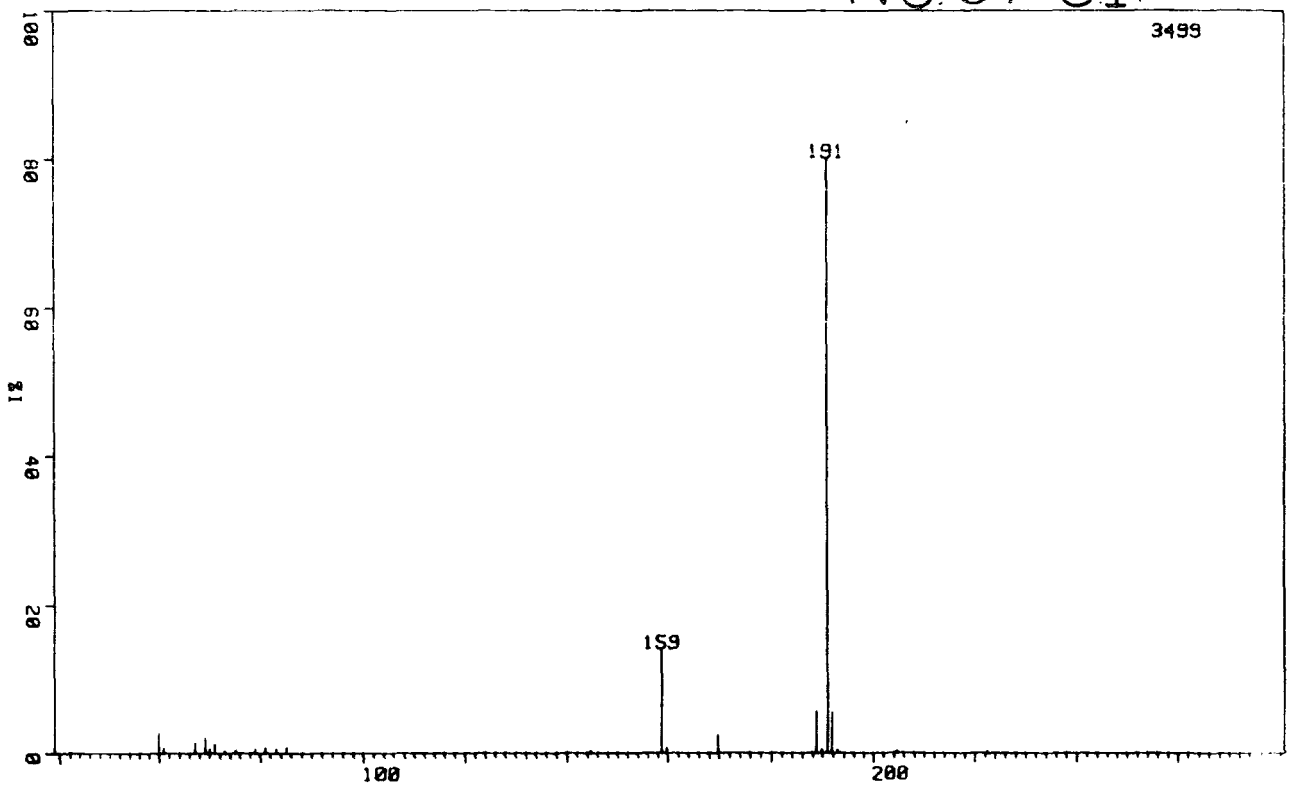


MASS	%HT. BASE	MASS	%HT. BASE
26.26	1.10	115.11	0.46
27.21	4.72	145.17	1.17
28.11	8.73	159.11	0.50
28.97	20.48	170.13	3.66
29.82	1.35		
30.90	10.90		
32.00	0.71		
33.12	1.53		
41.01	0.89		
42.08	0.82		
43.13	8.06		
44.17	1.28		
45.20	100.00		
46.19	2.52		
47.15	0.89		
50.99	7.28		
57.18	1.53		
58.14	2.70		
59.09	17.04		
60.02	0.82		
61.06	0.60		
63.16	0.53		
64.12	1.17		
65.10	1.74		
68.92	0.67		
77.02	0.43		
80.92	1.21		
81.97	0.46		
93.01	0.39		
95.02	1.38		
100.97	0.43		

PT32X 3 P.T.TELFORD 3/2 C.I. I-BU
CAL:CALT31 STA:

No.31 CI

26-MAR-85
0:35

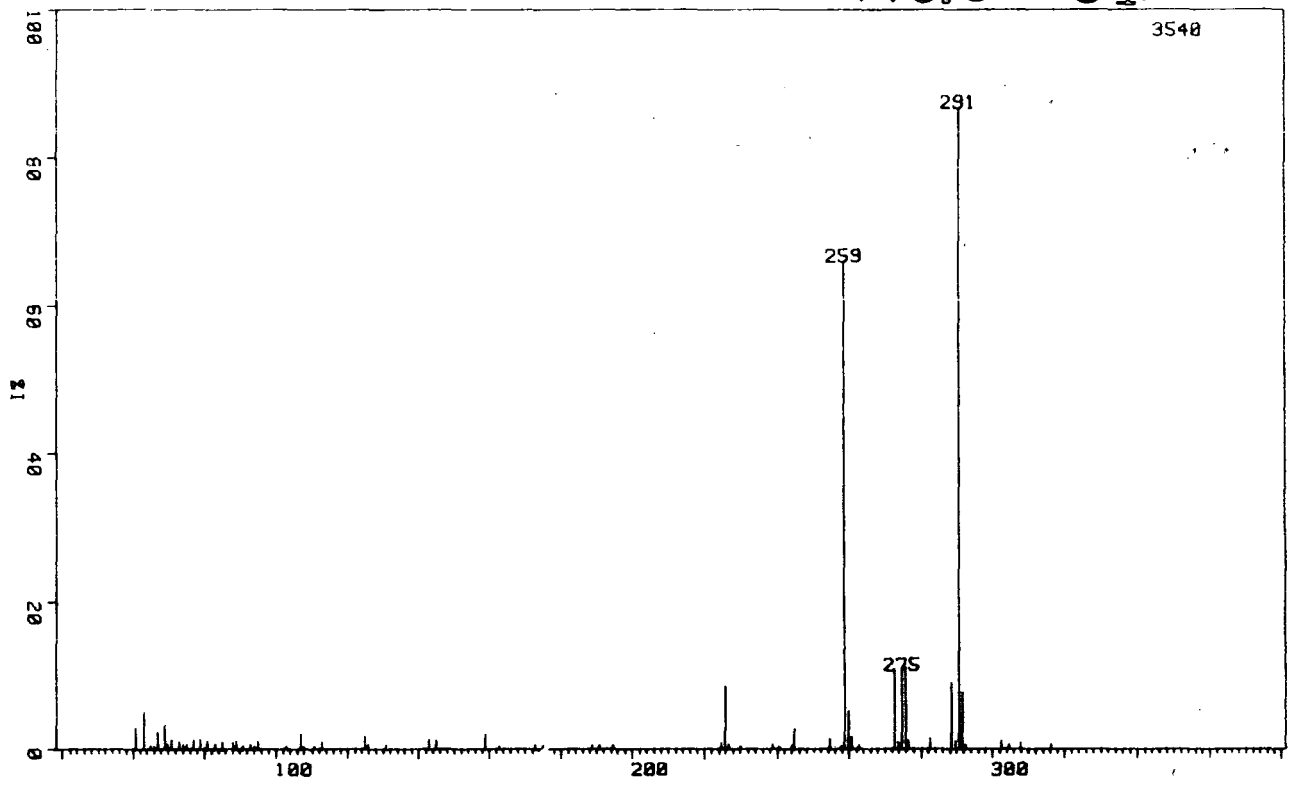


MASS	%HT. BASE
60.89	0.77
67.03	1.46
68.96	2.09
69.91	0.57
70.95	1.31
72.99	0.46
75.02	0.40
78.91	0.54
80.90	0.83
83.01	0.60
85.04	0.86
144.81	0.29
158.74	14.12
159.76	0.80
169.81	2.46
188.80	5.52
189.85	0.46
190.86	80.22
191.84	5.40
192.83	0.46
204.78	0.37
222.73	0.31

PT339 P.T.TELFORD C.I. I-BU
CAL:CALT31 STA:

No.32 C.I.

21-APR-78
1:26

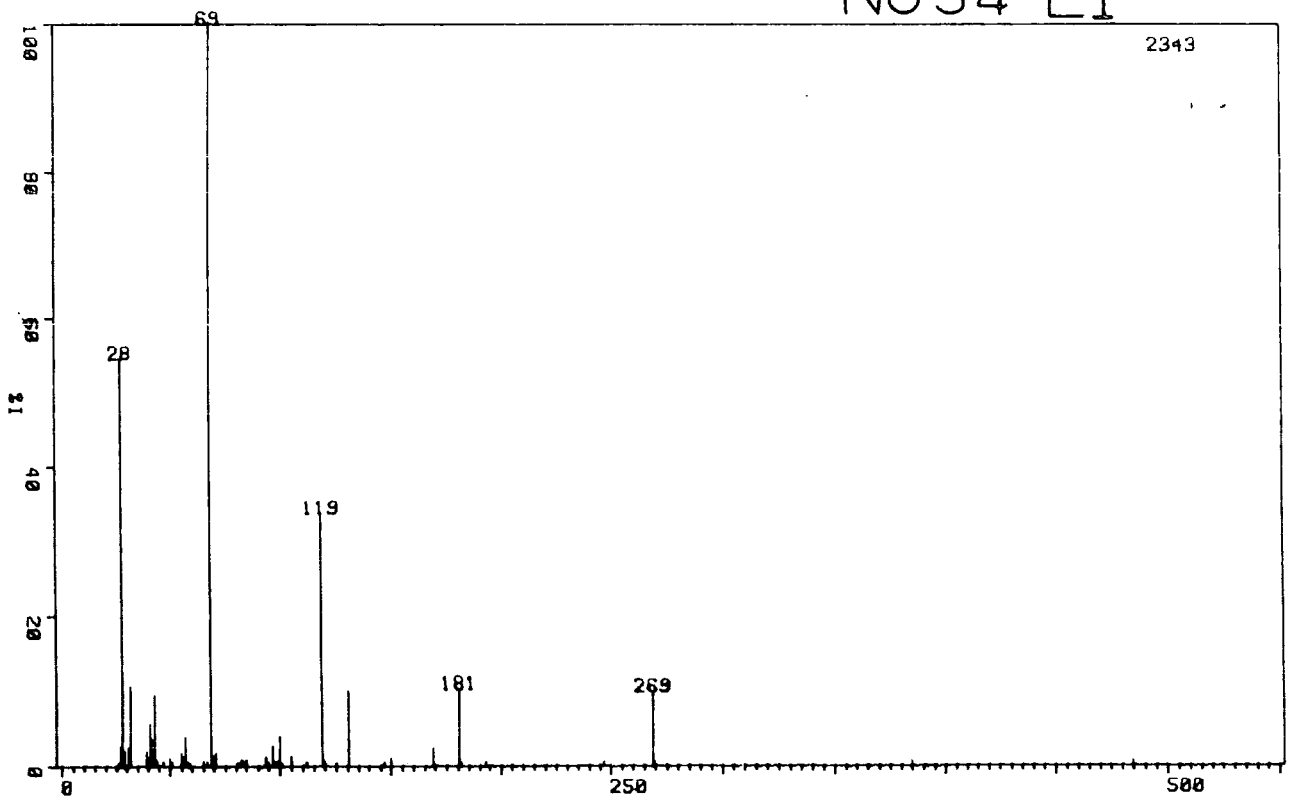


MASS	%HT. BASE	MASS	%HT. BASE		
60.88	3.12	125.90	0.70	273.71	1.10
63.00	5.12	130.81	0.53	274.74	10.91
65.04	0.51	142.88	1.21	275.74	11.53
66.05	0.42	144.95	1.46	276.73	1.12
67.04	1.97	158.86	2.05	282.68	1.27
68.01	0.31	162.87	0.37	288.66	8.80
68.96	3.18	172.86	0.39	289.64	0.87
69.91	0.53	174.88	0.48	290.66	86.39
70.95	1.35	176.89	0.25	291.65	7.56
73.00	1.12	188.80	0.53	292.67	0.62
74.01	0.51	190.84	0.39	302.60	1.18
75.01	0.39	194.84	0.39	304.61	0.56
76.97	1.41	204.81	0.25	307.66	1.18
78.91	1.21	212.74	0.25	316.61	0.98
80.85	0.48	224.73	0.96	318.56	0.48
80.91	1.01	225.79	8.49		
82.99	0.70	226.84	0.56		
85.02	1.04	230.32	0.34		
86.98	0.31	230.74	0.28		
87.92	0.96	238.78	0.62		
88.89	1.21	243.76	0.48		
90.84	0.39	244.75	2.87		
90.89	0.48	246.76	0.39		
92.92	0.76	254.72	1.35		
93.95	0.51	257.72	0.37		
94.95	1.21	258.73	65.21		
102.91	0.25	259.74	5.03		
106.91	1.83	260.71	1.66		
110.81	0.45	262.78	0.42		
112.87	1.01	270.71	0.25		
124.90	2.00	272.71	10.88		

PT664X 11 P.TELFORD 66/4
CAL:CALTS STR:

No 34 EI

12-OCT-84
1:40

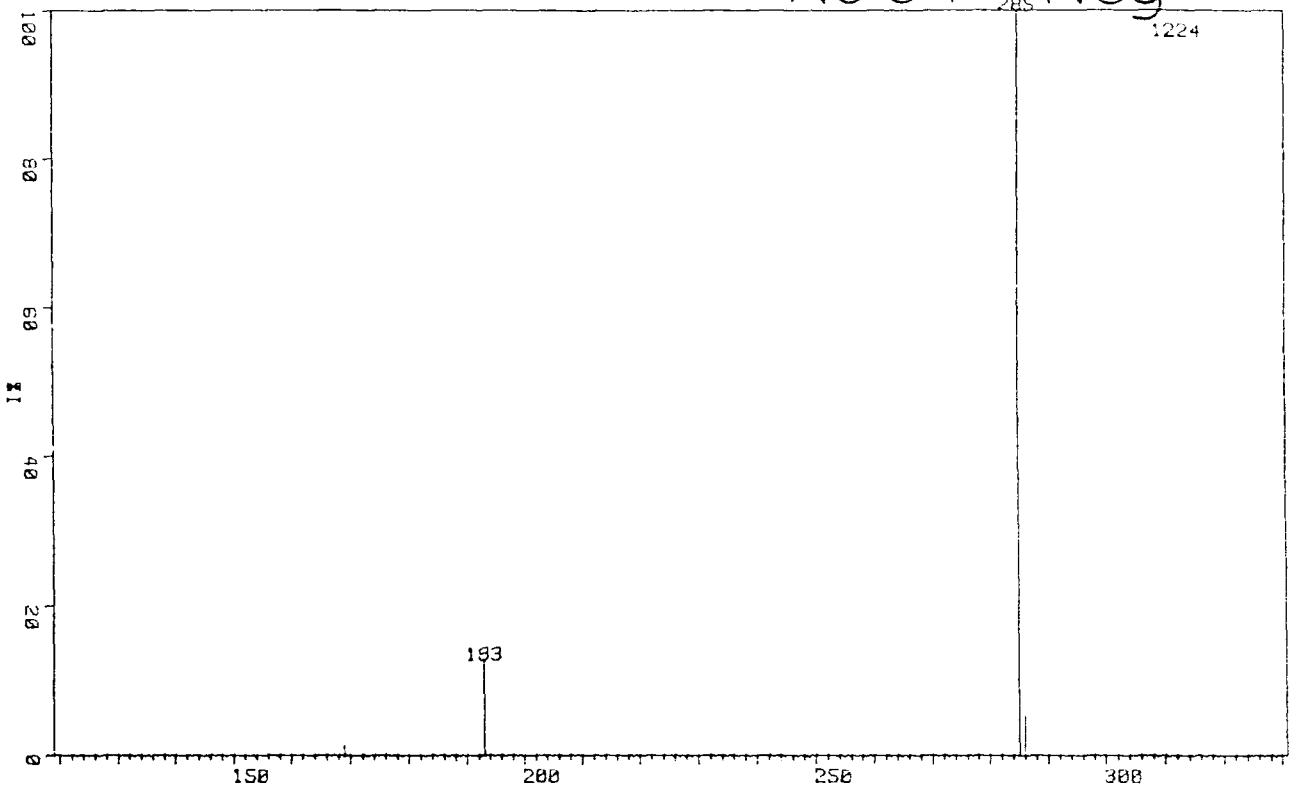


MASS	%HT. BASE	MASS	%HT. BASE
26.21	0.64	82.09	0.98
27.15	2.69	84.12	0.77
28.03	54.63	85.10	0.90
28.89	0.64	92.95	1.02
28.93	2.18	94.01	1.37
30.76	2.52	95.05	0.47
31.87	10.71	96.94	2.69
38.88	2.01	97.06	0.64
39.73	1.11	98.04	0.55
39.78	0.85	98.96	0.81
40.85	5.68	99.84	4.01
41.95	3.67	100.91	0.43
43.02	9.60	105.07	1.41
44.06	0.81	111.92	0.55
46.98	0.77	112.07	0.64
49.80	1.07	118.91	33.80
50.87	0.68	119.87	0.81
55.08	1.79	119.99	0.60
56.08	1.32	125.01	0.39
57.07	3.88	130.92	10.03
58.01	0.55	146.94	0.55
58.95	0.43	147.07	0.38
65.07	0.73	149.87	1.07
67.06	0.73	168.91	2.43
68.93	100.00	180.86	10.29
69.00	1.20	181.91	0.55
69.88	1.11	192.93	0.51
69.98	1.41	246.83	0.63
71.04	1.84	268.79	9.86
80.93	0.55	269.85	0.73
82.03	0.43	384.62	0.81
		484.38	0.68

PT664 9 I-BU NEG. 193 REF.
CAL:CALN18 STA:

No 34 Neg

26-SEP-84
1:19

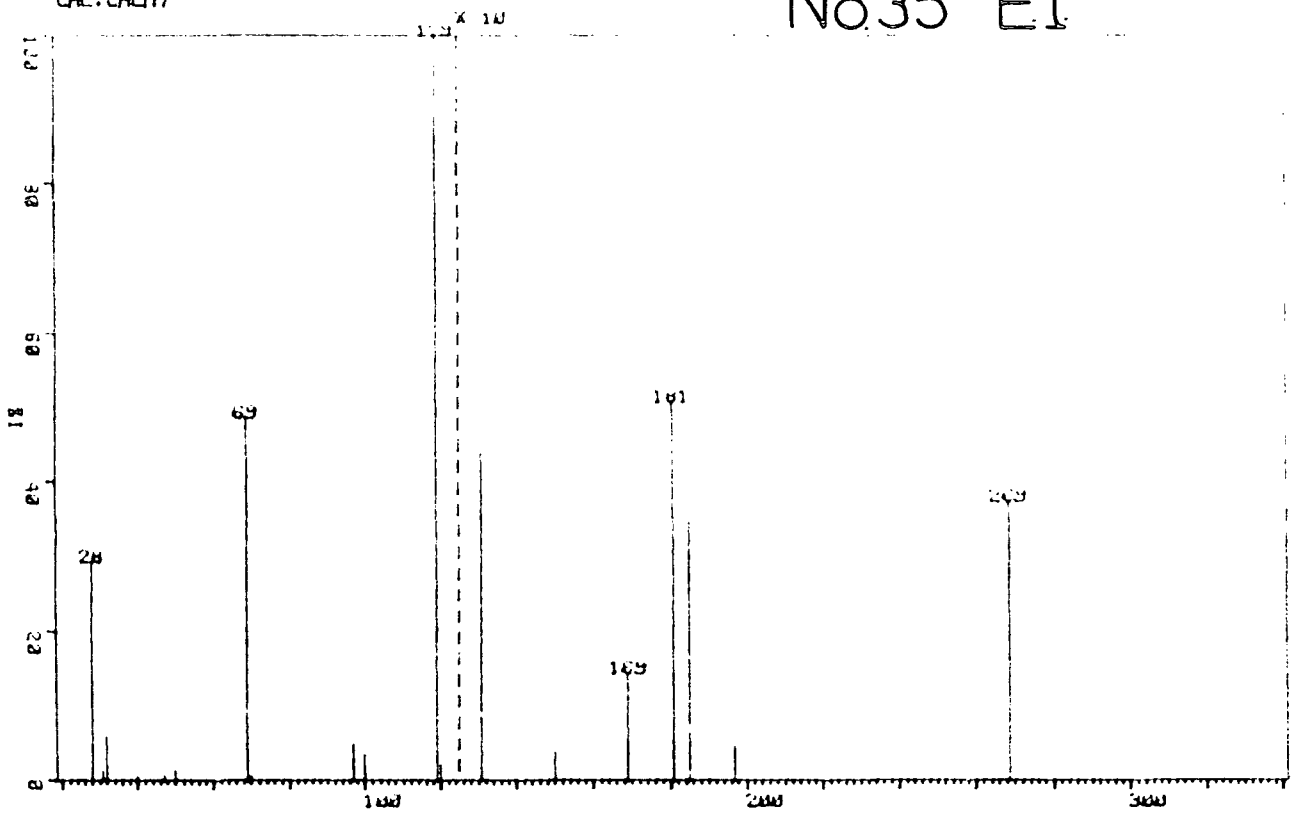


MASS	%HT. BASE
169.06	1.23
193.01	12.83
285.10	100.00
286.09	5.31

PTF131 8 P.T.TELFORD F13/1

CHL:CHLM7

No35 EI

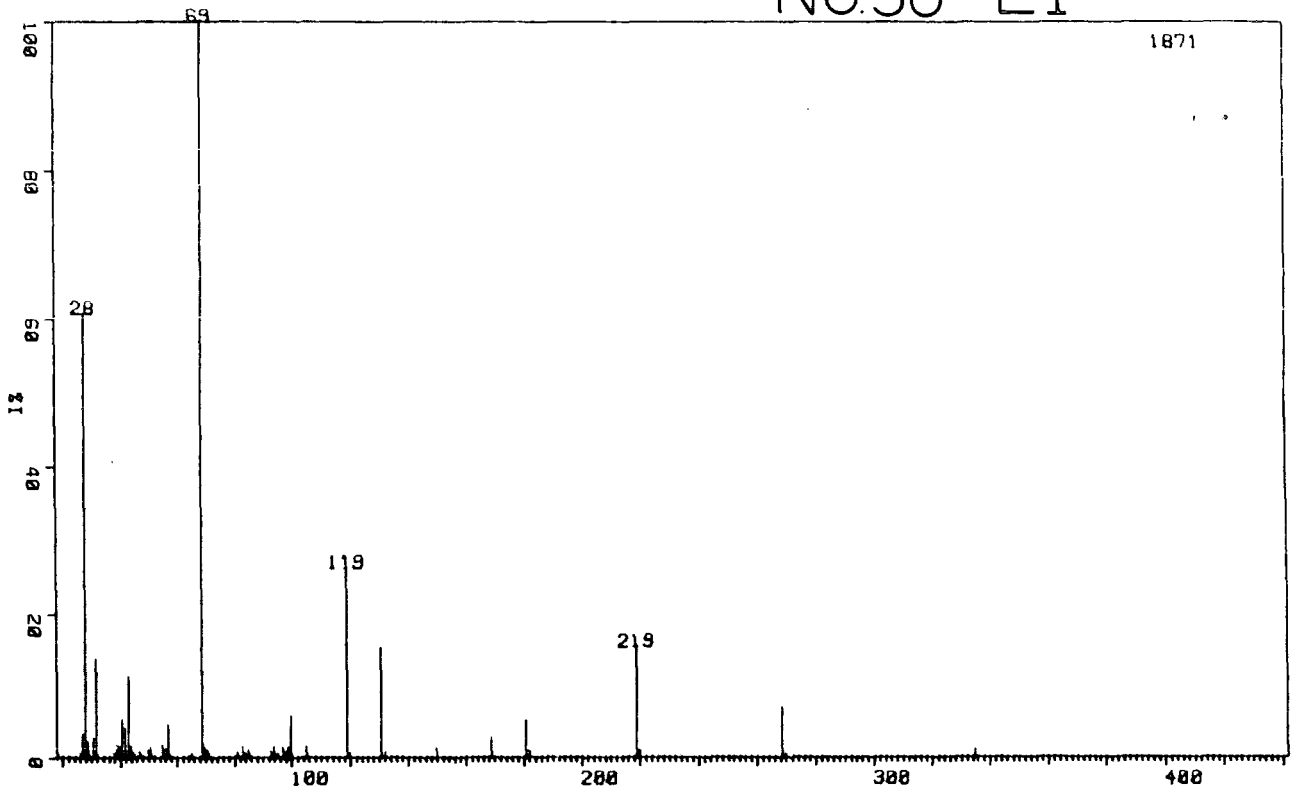


MASS	%HT. BASE
28.14	29.29
30.93	1.29
32.03	5.95
39.85	0.63
47.10	0.63
49.36	1.29
68.96	48.60
69.90	0.70
96.98	4.86
99.89	3.43
118.94	100.00
119.91	2.06
130.94	4.37
149.93	0.38
168.95	1.43
180.89	5.07
184.96	3.46
196.96	0.45
268.82	3.74

PTS02X 8 P.TELFORD 50/2
CAL:CALTS STA:

No.36 EI

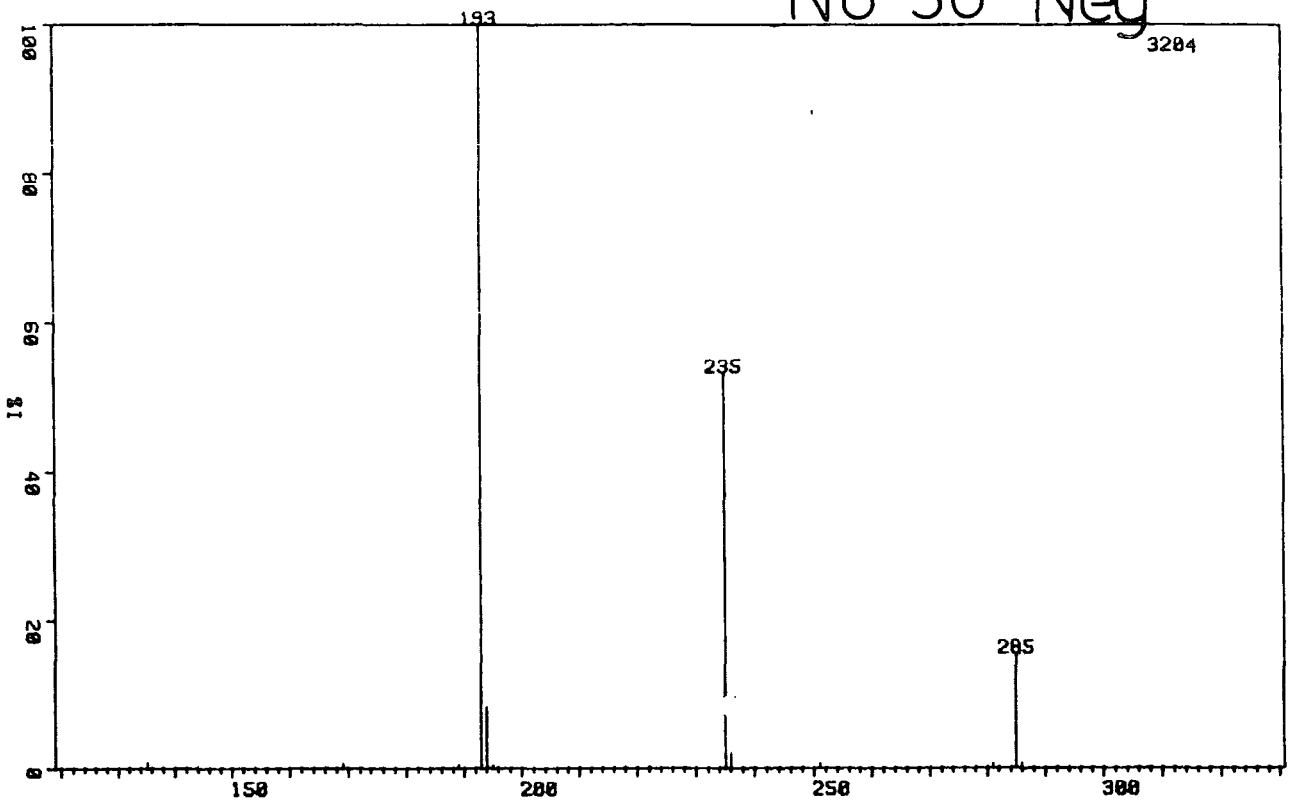
12-OCT-84
1:14



MASS	%HT. BASE	MASS	%HT. BASE
26.22	0.75	83.08	1.55
27.15	3.24	84.11	0.59
28.03	60.66	85.10	1.18
28.89	1.12	92.94	0.96
28.92	2.30	94.00	1.55
30.77	2.94	95.05	0.59
31.87	13.95	96.93	1.44
37.96	0.59	97.04	1.18
38.88	1.98	97.98	0.91
39.72	1.76	98.96	1.55
39.78	0.80	99.84	5.99
40.85	5.24	105.05	1.55
41.95	4.17	118.89	26.30
43.02	11.54	119.89	0.75
43.99	0.75	130.92	15.45
44.06	1.76	131.96	0.86
45.06	0.80	149.87	1.23
46.98	0.80	168.89	2.67
49.79	1.02	180.88	5.18
50.87	1.44	181.90	1.02
55.07	1.76	218.85	15.55
56.07	1.34	219.87	1.02
57.06	4.54	268.79	7.06
65.06	0.59	269.80	0.64
68.92	100.00	334.74	1.12
68.99	1.87		
69.86	1.39		
69.97	1.12		
71.03	1.12		
80.91	0.91		
80.99	0.69		

PTS02 7 P.TELFORD 50/2 NH3 NEG. 193 REF. 11-OCT-84
CAL:CALN18 STA: 1.5

No 36 Neg

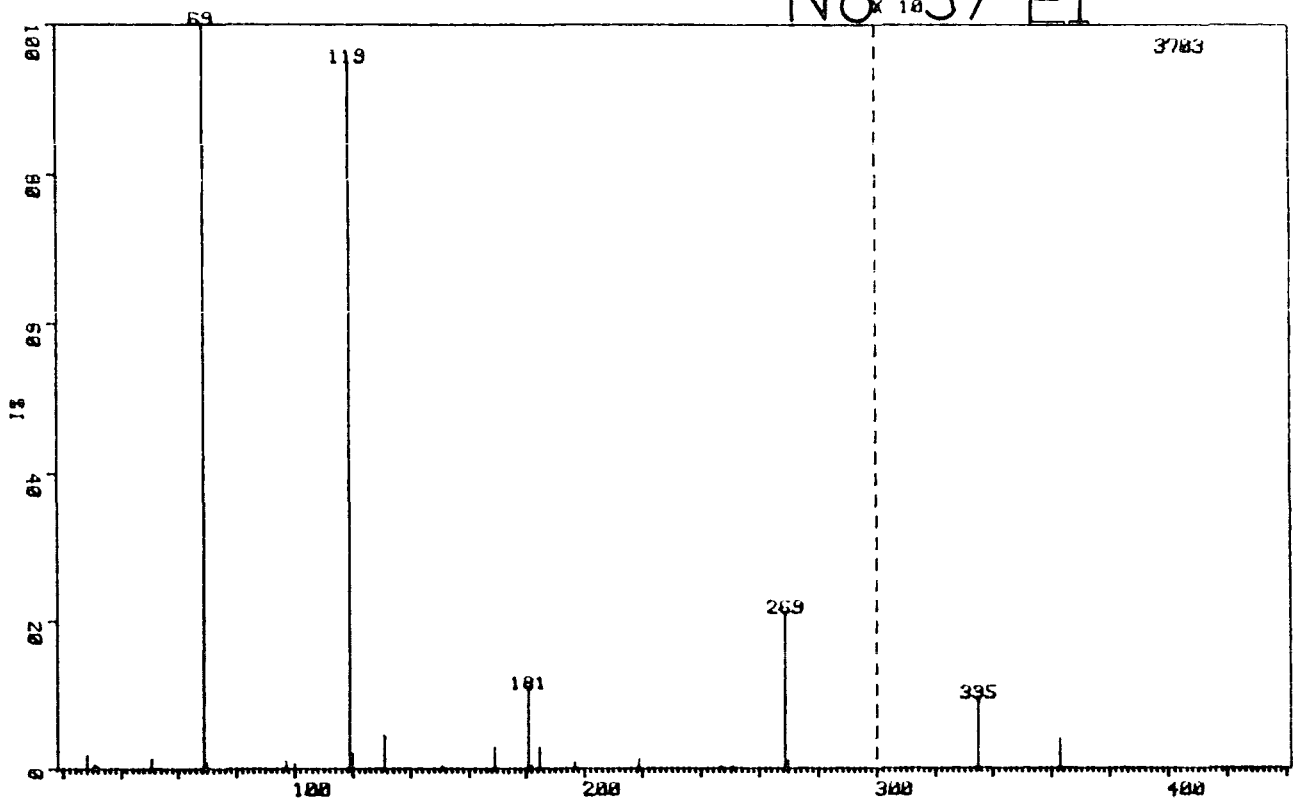


MASS	ZHT. ABL.
135.14	0.84
167.10	0.66
189.01	0.50
193.01	100.00
194.03	8.36
195.02	0.34
235.00	53.40
236.09	9.12
251.02	0.78
281.00	0.59
285.01	15.64
286.01	0.73

PTTTT 10 P.T.TELFORD F13/3C
CAL:CALM13

No 37 EI

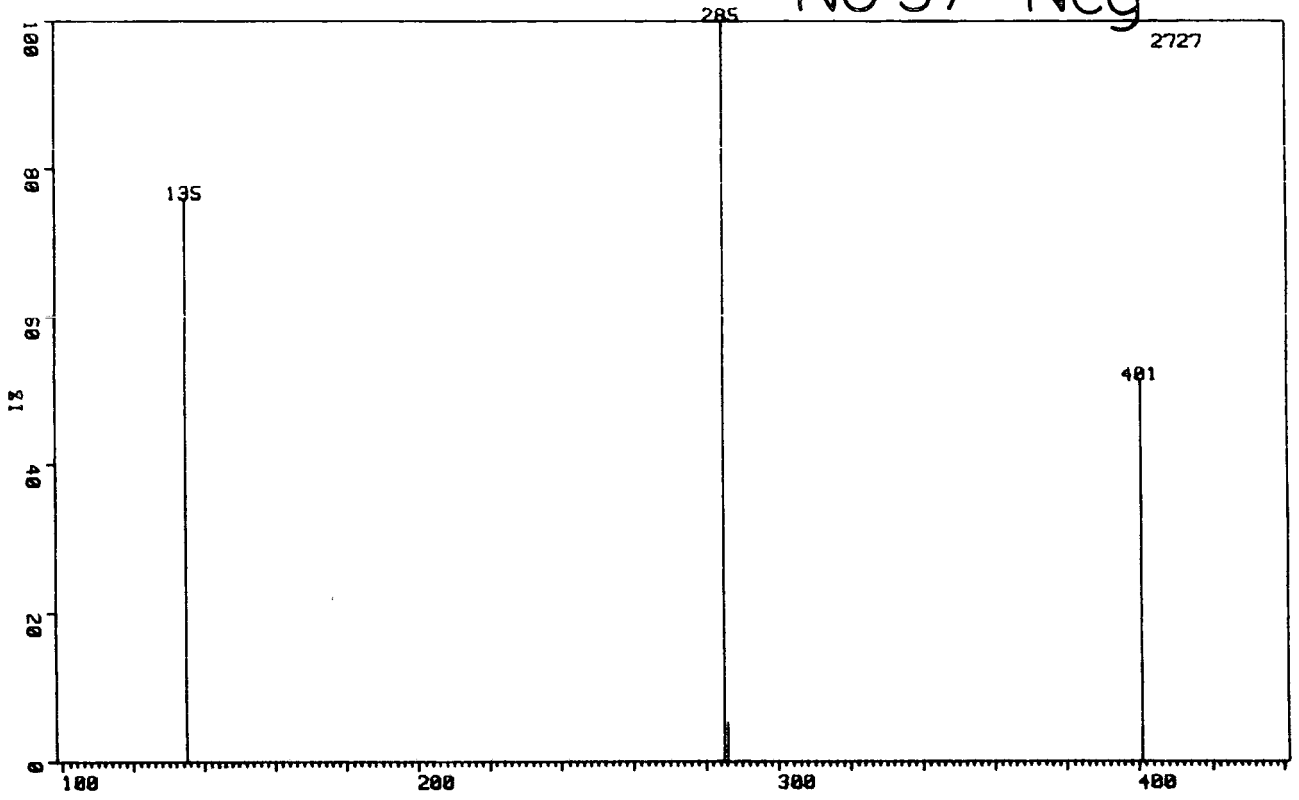
21-MAR-84



MASS	%HT. BASE
28.07	1.92
30.83	0.68
31.95	0.46
50.93	1.43
68.95	100.00
69.89	1.00
97.01	1.11
99.93	0.65
118.94	95.06
119.93	2.08
130.96	4.54
150.97	0.30
168.94	2.97
180.93	10.91
182.00	0.49
184.96	2.94
196.93	0.92
218.90	1.35
246.95	0.35
250.96	0.32
268.89	21.17
269.90	1.19
334.99	0.95
362.91	0.41

PF133X S P.T.TELFORD F13/3C I-BU NEG. 04-DEC-85
CAL:CALN20 STA: 0:52

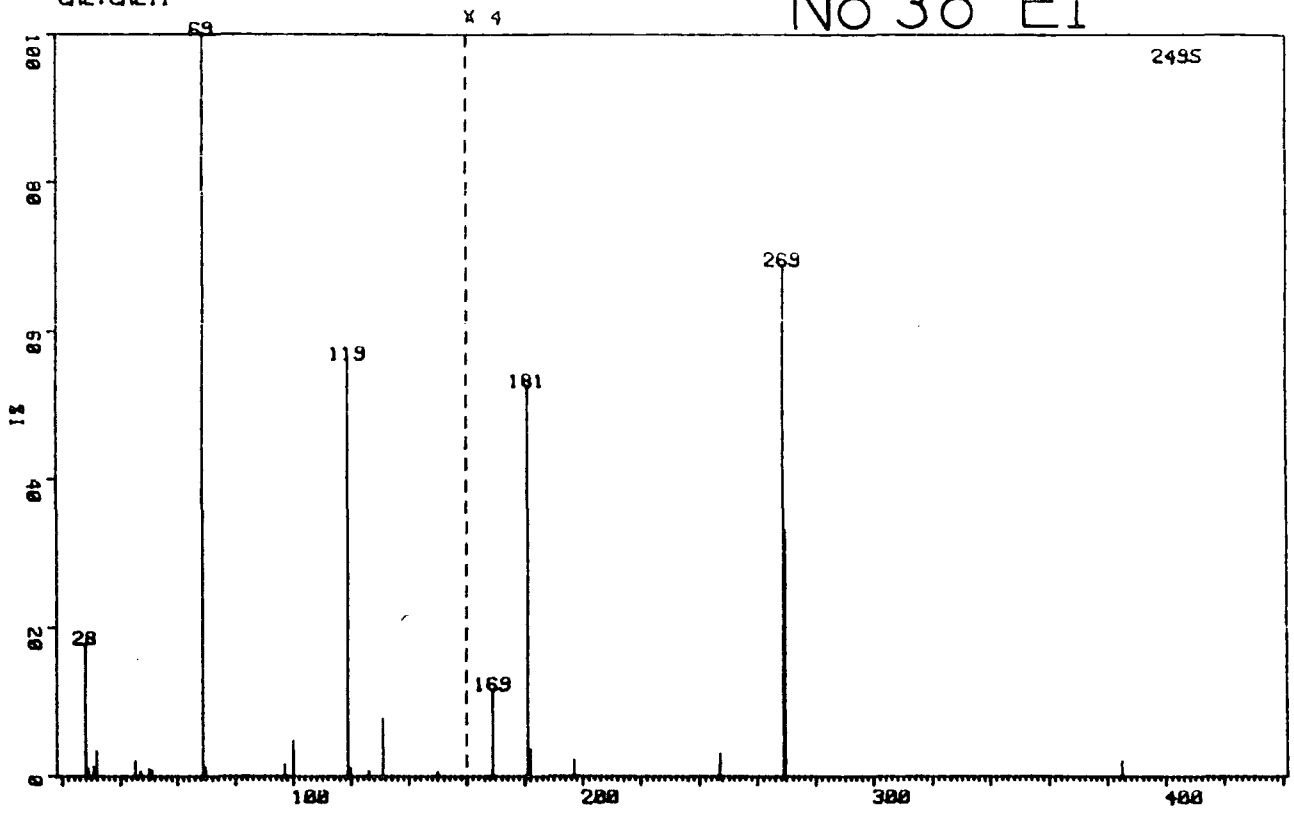
No 37 Neg



MASS	%HT. BASE
135.09	75.94
285.01	100.00
286.05	5.35
400.93	51.49

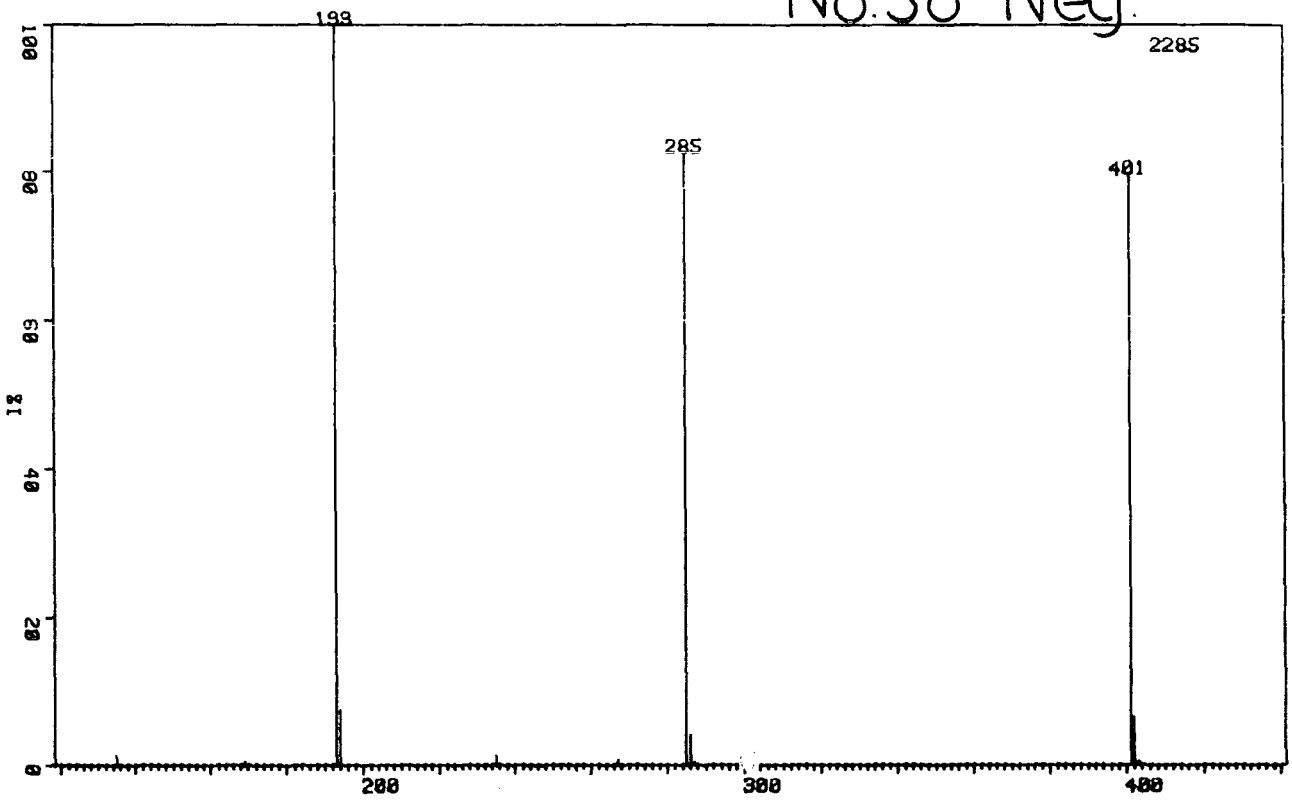
PF134F 6 P.T.TELFORD F13/4F 11-APR-83
CAL:CAL11

No 38 EI



MASS	%HT. BASE
28.11	17.84
28.97	1.12
30.88	1.40
32.00	3.41
45.17	2.00
47.08	0.60
49.88	1.08
50.96	0.80
68.93	100.00
69.87	1.24
97.05	1.68
99.98	4.81
119.00	56.23
119.95	1.20
126.09	0.72
131.02	7.90
149.98	0.60
168.98	2.93
180.99	13.15
182.05	0.92
197.08	0.56
247.11	0.80
269.07	17.23
269.60	8.30
385.01	0.52

PTFB4F 9 P.T.TELFORD F13/4F NH3 NEG. No.38 Neg. 22-OCT-84
CAL:CALN18 STA: 1:23

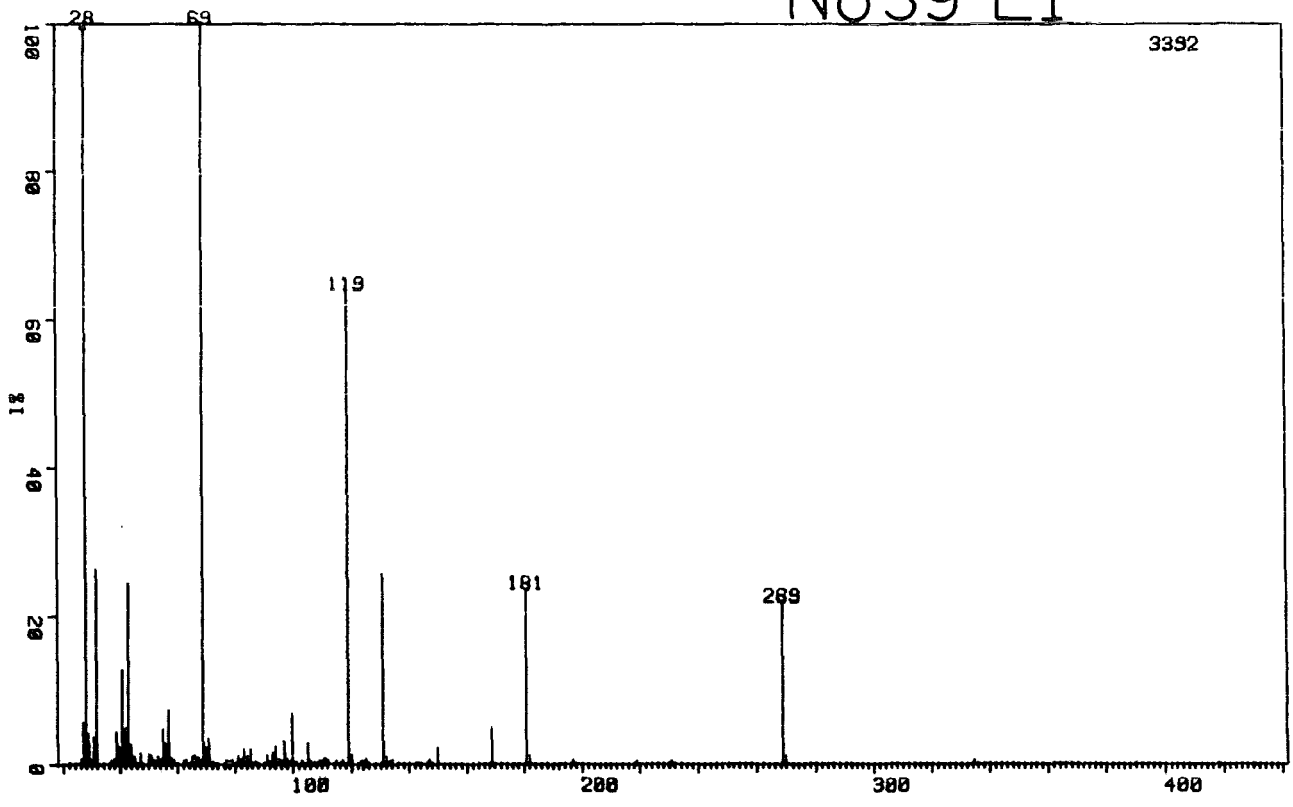


MASS	%HI. BASE
155.08	1.40
169.06	0.53
193.03	100.00
193.99	7.53
235.08	1.40
267.03	0.79
285.07	82.63
286.06	4.07
287.06	0.39
401.07	79.82
402.05	6.48
403.07	0.52

PT806 5 P.TELFORD 80/6
CAL:CALTS STA:

No39 EI

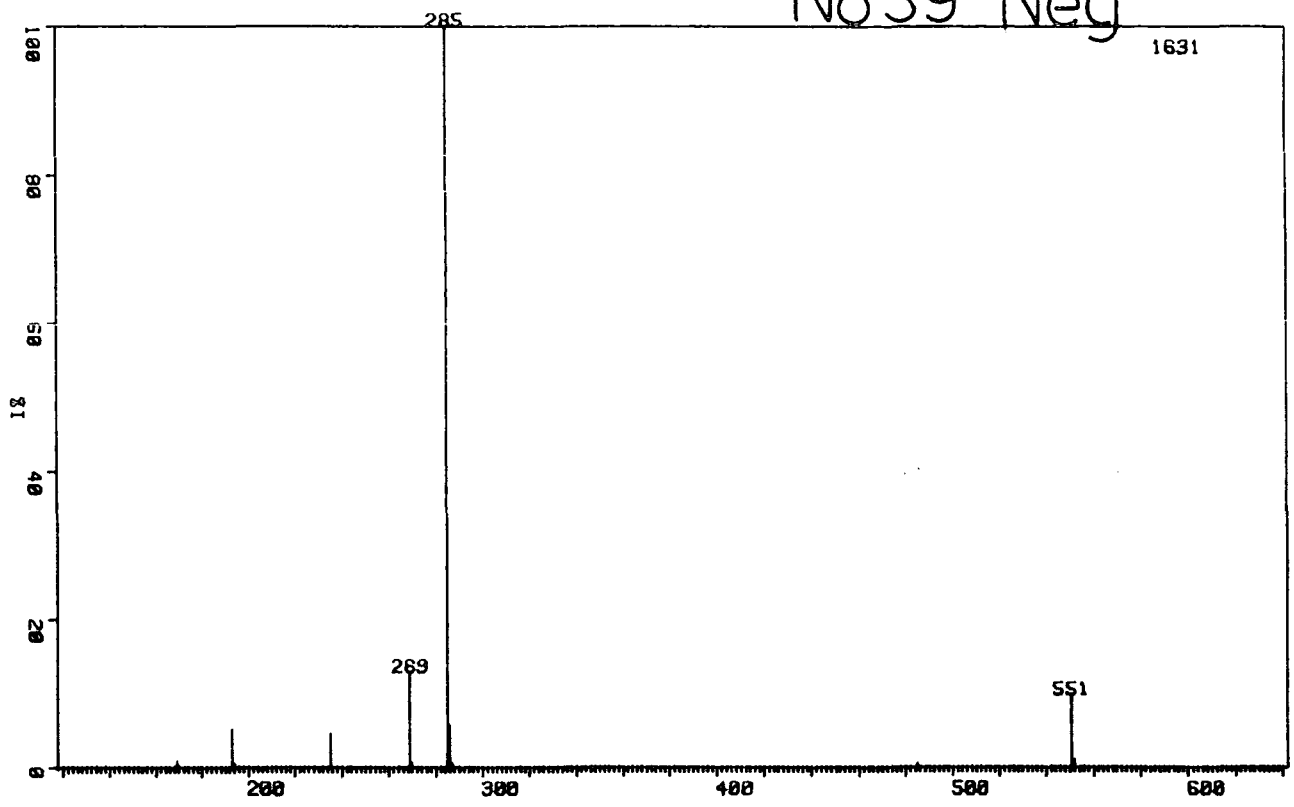
12-OCT-84
0:49



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.22	0.78	58.00	0.86	95.04	0.81	142.91	0.25
27.15	5.55	58.92	0.59	96.04	0.47	146.91	0.39
28.03	100.00	61.93	0.42	96.93	3.04	147.04	0.70
28.05	1.03	62.99	0.59	97.03	1.42	149.85	2.20
28.89	1.25	65.05	1.06	98.02	0.84	168.86	4.68
28.93	3.99	66.05	1.20	98.99	0.59	180.85	22.41
29.76	0.47	67.04	0.98	99.82	6.61	181.92	1.20
30.77	3.69	68.01	0.64	100.89	0.36	196.88	0.59
31.87	24.77	68.90	94.54	103.00	0.59	218.85	0.53
37.01	0.50	69.87	2.31	105.05	2.90	230.83	0.42
37.95	0.81	69.97	2.03	106.05	0.42	268.77	20.76
38.68	4.26	71.03	3.34	107.04	0.31	269.80	1.14
39.72	2.37	72.08	0.31	108.90	0.50	334.70	0.59
39.78	1.39	73.09	0.25	109.03	0.45		
40.84	12.12	77.06	0.67	110.00	0.42		
41.94	4.71	77.98	0.56	111.03	0.86		
43.01	23.16	78.03	0.56	111.93	0.64		
43.98	2.70	78.99	0.64	112.05	0.42		
44.02	0.31	80.91	1.09	115.02	0.42		
44.06	1.17	81.00	0.75	117.03	0.59		
45.04	1.14	82.03	0.72	118.90	60.62		
46.98	1.48	82.93	0.42	119.87	1.34		
49.79	1.37	83.08	1.92	120.00	1.06		
50.85	1.14	84.10	1.03	123.10	0.45		
51.94	0.50	85.11	1.95	124.11	0.28		
53.00	1.03	87.04	0.33	124.99	0.81		
54.01	2.45	90.94	1.14	125.12	0.39		
55.03	0.45	91.98	0.31	130.91	24.33		
55.06	4.52	92.93	1.42	131.94	0.95		
56.06	2.81	93.00	0.36	133.06	0.36		
57.05	6.94	94.00	2.34	134.08	0.70		

PT806 12 PTT80/6 I-BU NEG. 193 REF 12-OCT-84
CAL:CALN18 STA: 1:48

No 39 Neg

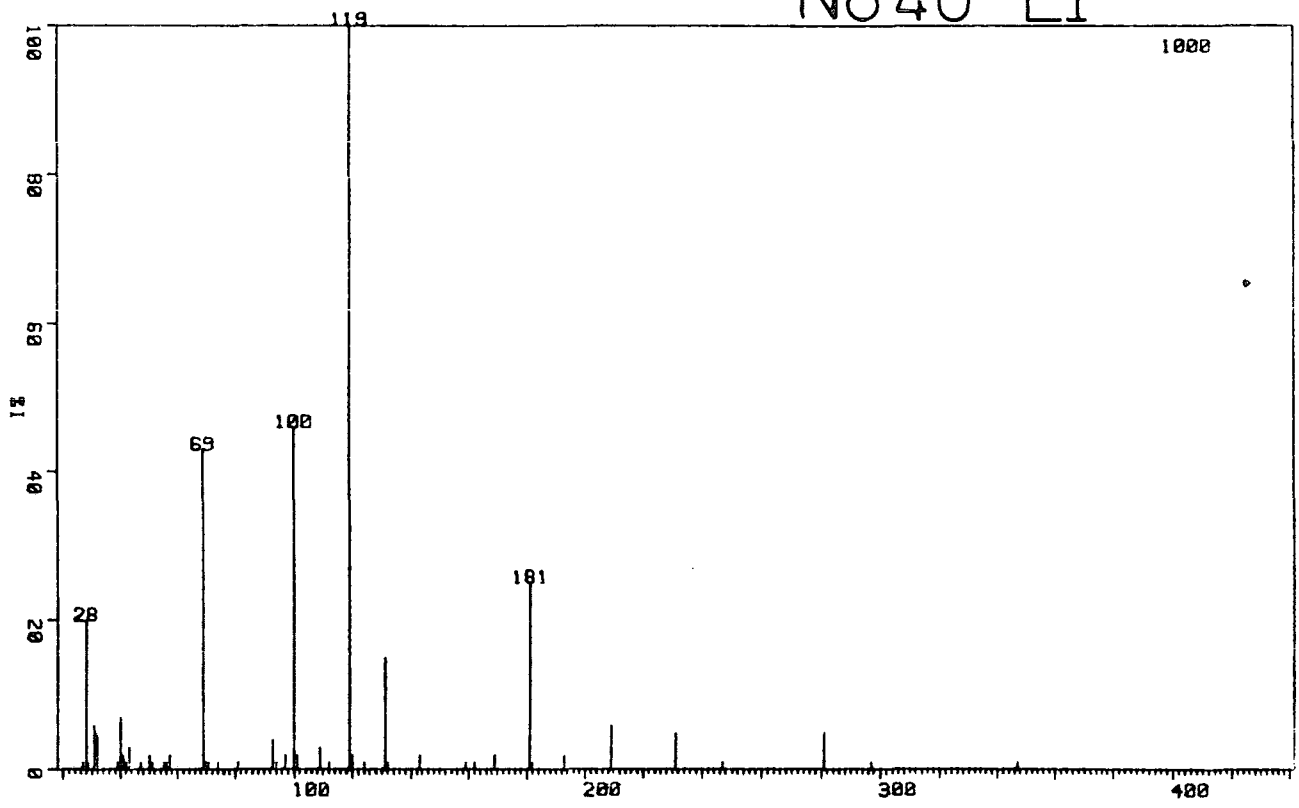


MASS	%HT. BASE
169.03	0.98
183.01	5.21
194.01	0.67
235.08	4.60
268.97	12.94
269.97	0.80
284.99	100.00
286.01	5.82
287.01	0.61
484.88	0.67
550.78	9.81
551.86	1.16

PT1093 0
CAL:LIB STA:

No40 EI

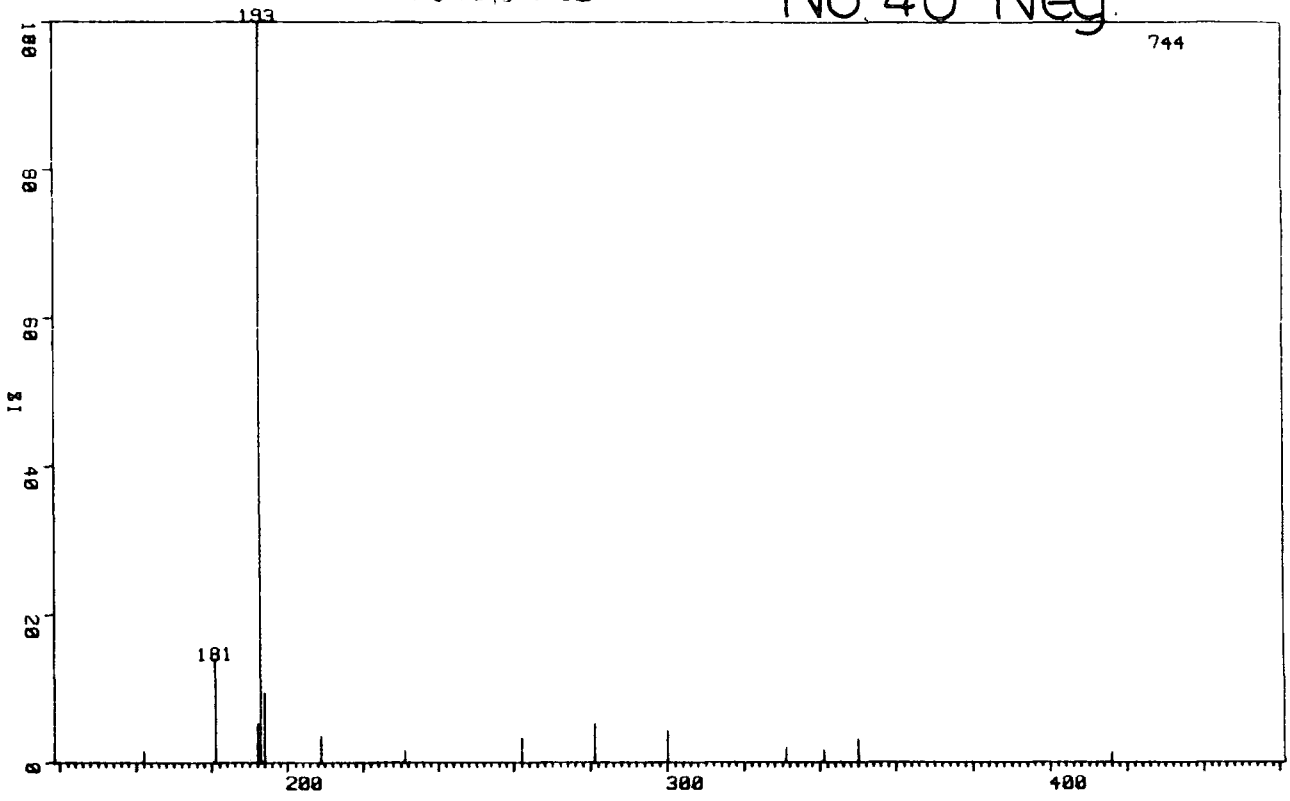
25-MAR-85
0:0



MASS	%HT. BASE	MASS	%HT. BASE
27.30	0.82	119.88	2.07
28.17	20.00	124.00	0.43
29.06	0.66	130.93	14.57
30.93	5.47	131.96	0.51
32.03	4.57	142.97	1.29
38.99	0.59	158.92	0.43
39.82	6.60	161.94	1.13
40.97	1.52	168.90	1.95
42.06	0.82	180.91	25.20
43.13	3.09	181.93	1.05
47.07	0.66	192.95	1.84
49.87	1.60	208.89	5.55
50.94	0.47	230.90	4.73
55.14	0.82	246.93	0.90
56.14	0.59	280.85	4.34
57.12	1.29	296.90	0.66
68.95	43.28	346.84	0.90
69.02	0.59		
69.89	0.66		
69.99	0.43		
71.06	0.62		
74.07	0.59		
80.97	0.74		
93.04	4.10		
94.10	0.51		
97.02	1.64		
99.92	45.59		
100.96	1.37		
108.94	3.05		
111.96	0.86		
118.91	100.00		

P1093X 22 PT109/3 PREP 3 NEG.(NH3) 17-MAY-85
CAL:CALN16 STA: 193 Reference 1:11

No. 40 Neg.

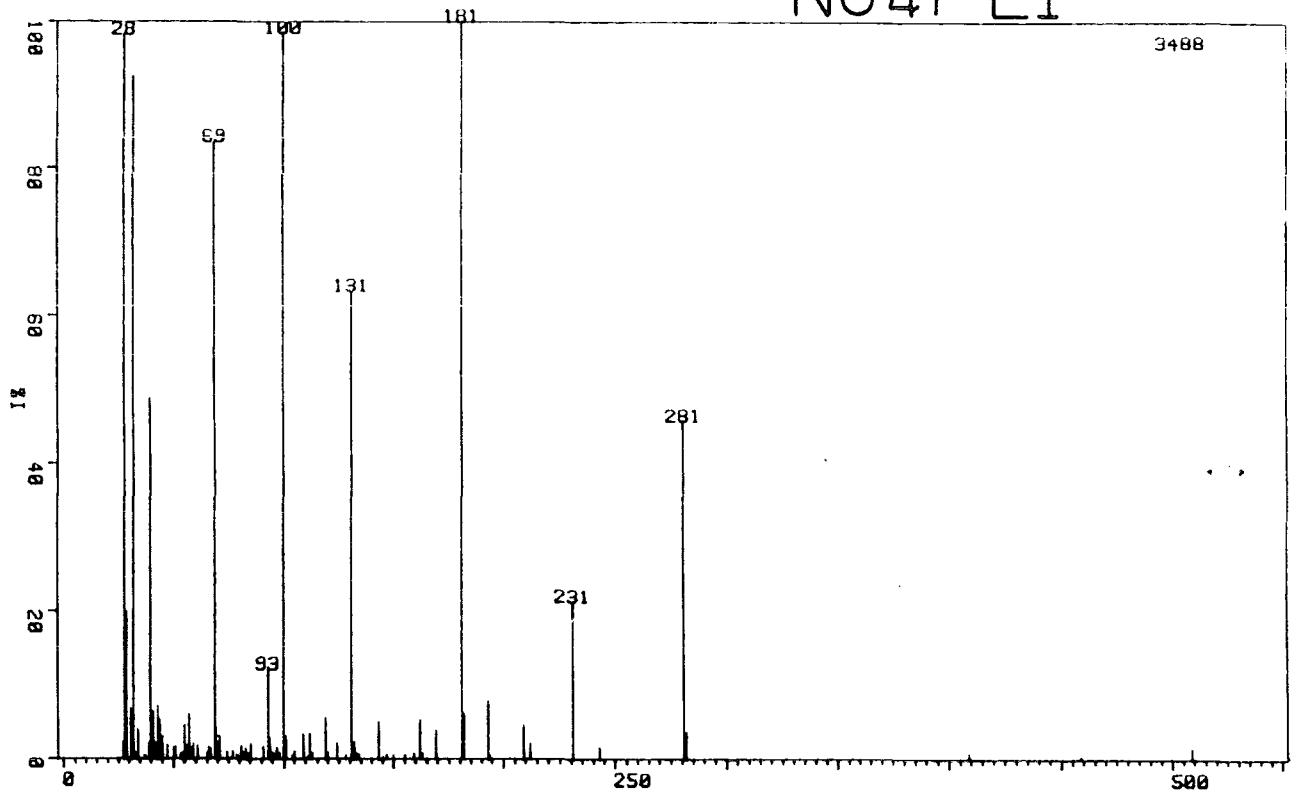


MASS	%HT. BASE
162.03	0.37
181.00	3.23
192.04	1.24
193.02	23.08
194.04	2.20
209.00	0.87
231.00	0.40
262.05	0.78
281.02	1.21
299.97	1.02
331.01	0.50
341.06	0.40
350.00	0.74
416.04	0.34

PT1022 4 P.T.TELFORD 102/2
CAL:CAL26 STA:

No41 EI

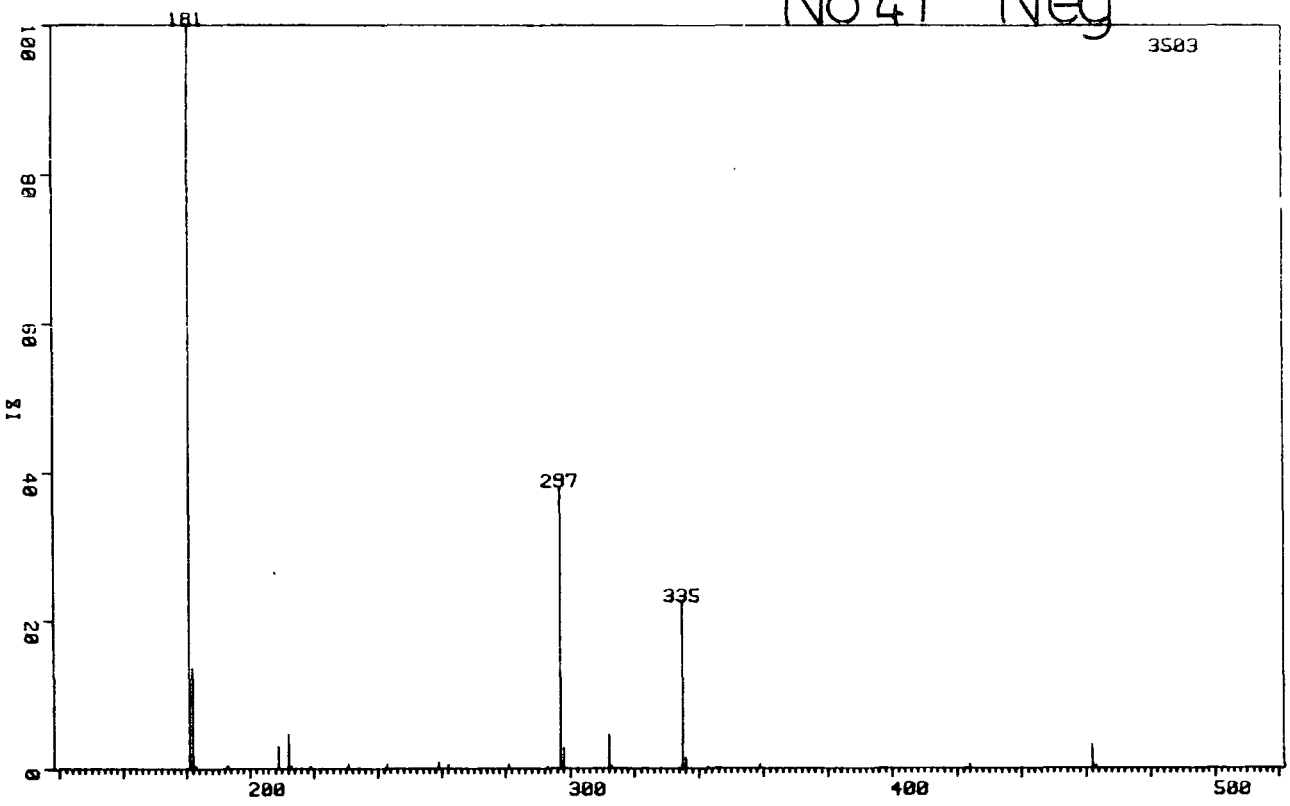
26-APR-85
0:41



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
31.95	92.52	69.86	0.66	119.00	1.46
33.05	0.75	69.97	2.09	119.87	0.29
34.10	4.04	71.04	3.18	119.96	0.89
37.09	0.43	74.04	0.95	123.98	2.15
38.96	2.21	74.11	0.77	127.94	0.49
39.80	48.82	77.01	1.00	130.90	63.30
39.86	1.15	78.95	0.60	131.96	2.41
40.94	6.42	80.86	1.81	133.10	0.80
42.04	2.26	80.98	1.83	134.09	0.66
43.07	1.72	81.95	0.43	142.97	5.05
43.11	7.20	82.01	0.97	145.08	0.34
44.08	5.36	83.08	1.49	146.94	0.63
44.12	0.60	84.12	0.77	149.89	0.46
45.14	3.12	85.11	2.04	154.99	0.54
47.07	1.86	90.97	1.69	158.93	0.72
49.87	1.58	92.97	12.13	161.95	5.30
50.95	1.66	94.03	2.81	163.00	0.80
53.10	0.83	95.09	0.86	168.95	3.99
54.13	0.86	96.09	0.54	180.94	100.00
55.11	0.66	96.98	1.61	181.95	6.19
55.16	4.56	97.09	1.12	192.96	7.91
56.16	1.83	98.05	0.86	193.98	0.52
57.10	0.60	99.89	98.37	208.93	4.59
57.14	6.05	100.95	3.18	211.96	2.12
58.07	1.49	104.10	0.57	230.95	21.30
59.02	2.09	105.11	1.09	242.97	1.63
60.98	1.83	108.92	3.41	280.94	45.73
65.12	1.00	111.05	0.43	281.95	3.67
66.09	1.66	111.96	3.38	408.91	0.86
67.07	1.46	112.10	0.75	458.92	0.34
68.92	83.49	112.96	0.89	508.85	1.52
69.00	4.27	118.91	5.56		

P1022X 5 P.T.TELFORD NH3 NEG. 09-MAY-85
CAL:CALN8 STA: 0:51

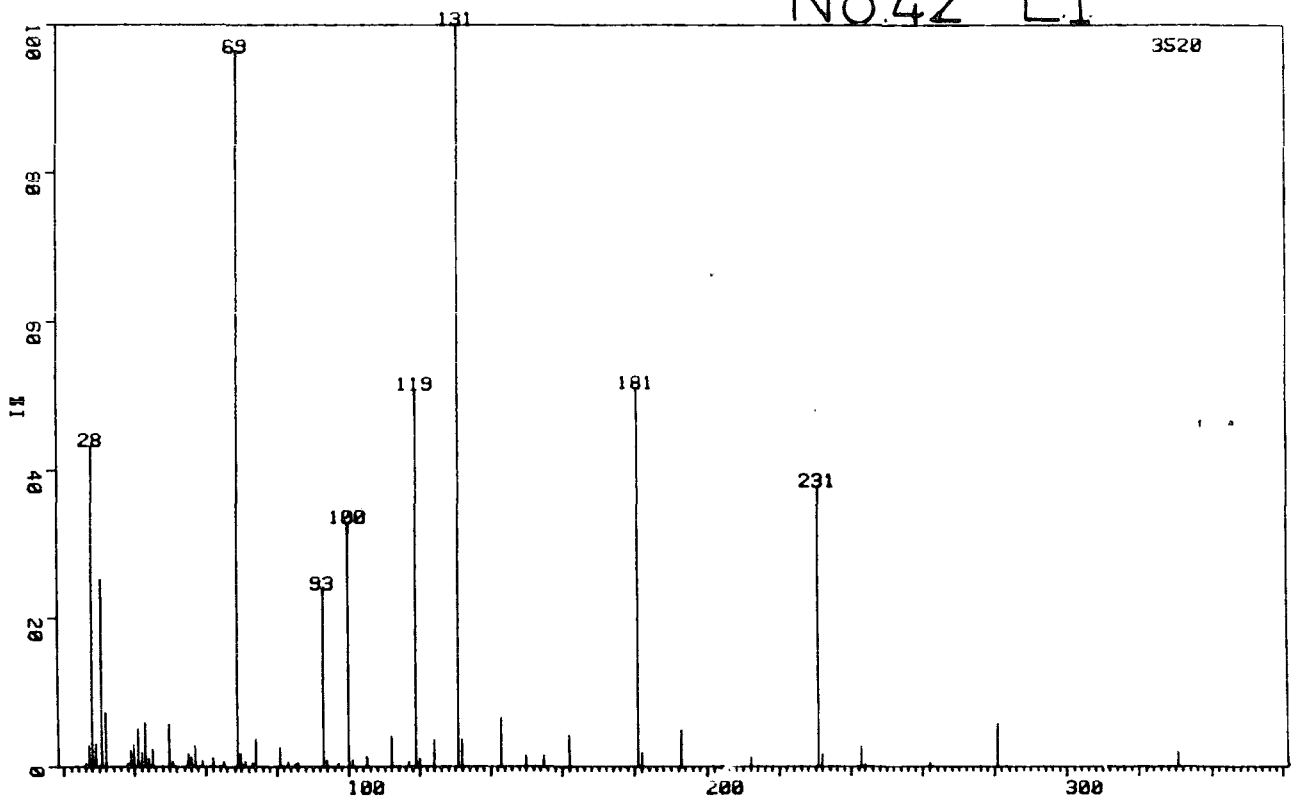
No 41 Neg



MASS	%HT. BASE
180.98	100.00
182.00	13.62
183.02	0.34
193.02	0.49
208.99	3.05
212.01	4.77
212.98	0.31
218.94	0.31
230.95	0.74
242.99	0.69
258.92	0.94
261.94	0.71
280.93	0.66
292.92	0.31
296.96	38.11
297.95	2.83
311.94	4.60
312.94	0.37
334.95	22.61
335.95	1.60
342.91	0.26
358.88	0.63
423.91	0.60
461.86	3.17
462.92	0.37

P1012X 5 P.T.TELFORD 09-MAY-85
CAL:CAL26 STR: 0:50

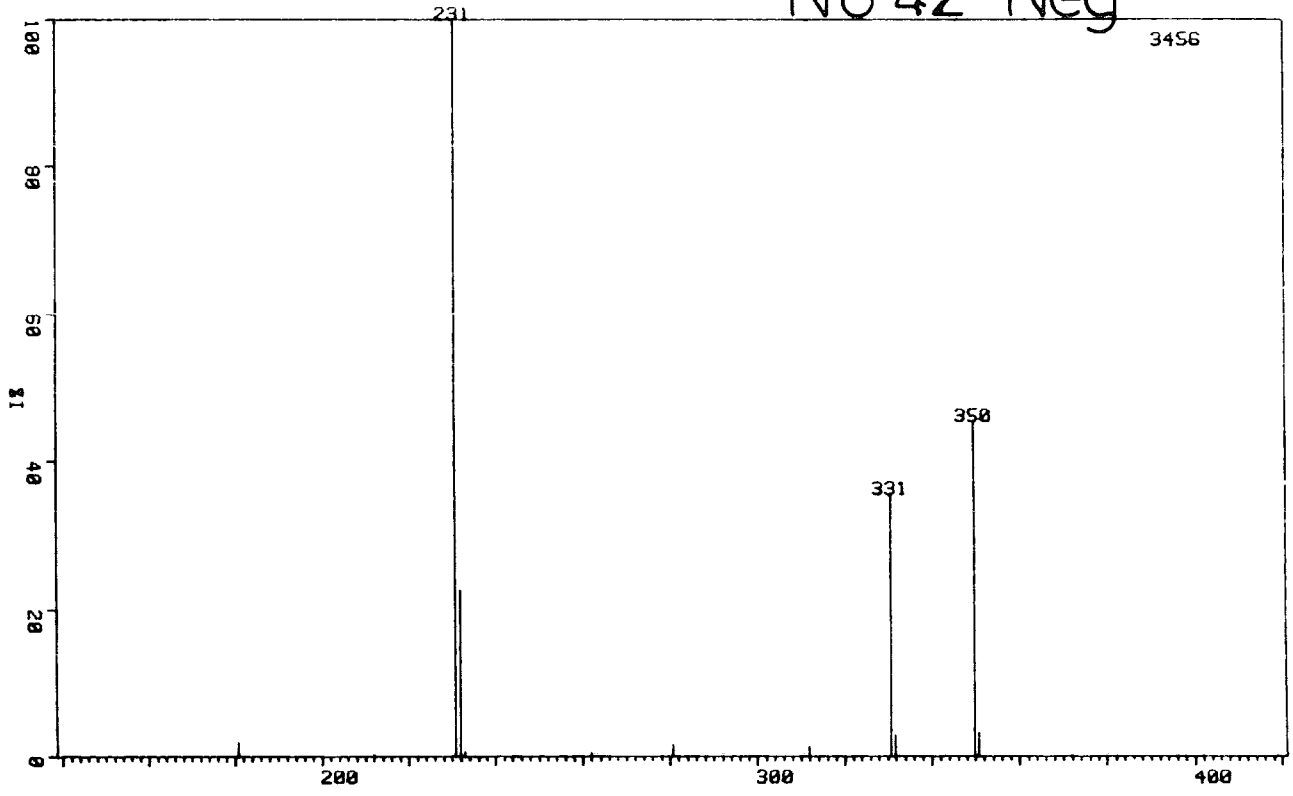
No.42 EI



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
26.28	0.43	69.98	0.57	211.97	1.34
27.21	2.98	71.04	0.77	230.95	37.93
28.09	43.30	73.08	0.60	231.97	1.70
28.11	0.77	74.03	3.78	242.99	2.78
28.95	0.94	80.90	2.64	244.00	0.31
28.98	3.12	81.01	0.48	261.95	0.51
30.84	25.31	83.10	0.65	280.93	5.80
31.95	7.24	85.12	0.40	330.92	2.05
38.02	0.48	86.02	0.57		
38.95	2.22	93.02	24.06		
39.79	3.01	94.06	0.99		
39.85	0.43	97.13	0.37		
40.93	5.14	99.94	32.95		
42.02	1.99	100.98	1.05		
43.06	1.22	105.06	1.39		
43.09	5.99	105.13	0.99		
44.06	1.11	111.97	4.09		
44.10	0.40	117.00	0.74		
45.13	2.30	118.95	50.88		
49.86	5.68	119.05	0.68		
50.92	0.77	119.92	1.16		
55.08	1.05	124.01	3.64		
55.14	1.82	130.94	100.00		
56.14	1.31	131.97	3.72		
57.12	2.84	142.98	6.68		
59.01	0.82	149.90	1.51		
61.99	1.19	155.01	1.56		
65.10	0.71	161.99	4.26		
68.94	96.34	180.97	51.14		
69.01	1.56	181.99	1.96		
69.88	1.85	192.99	5.00		

P1012X 2 P.TELFORD NH3 NEG. 09-MAY-85
CAL:CALN8 STA: 0:25

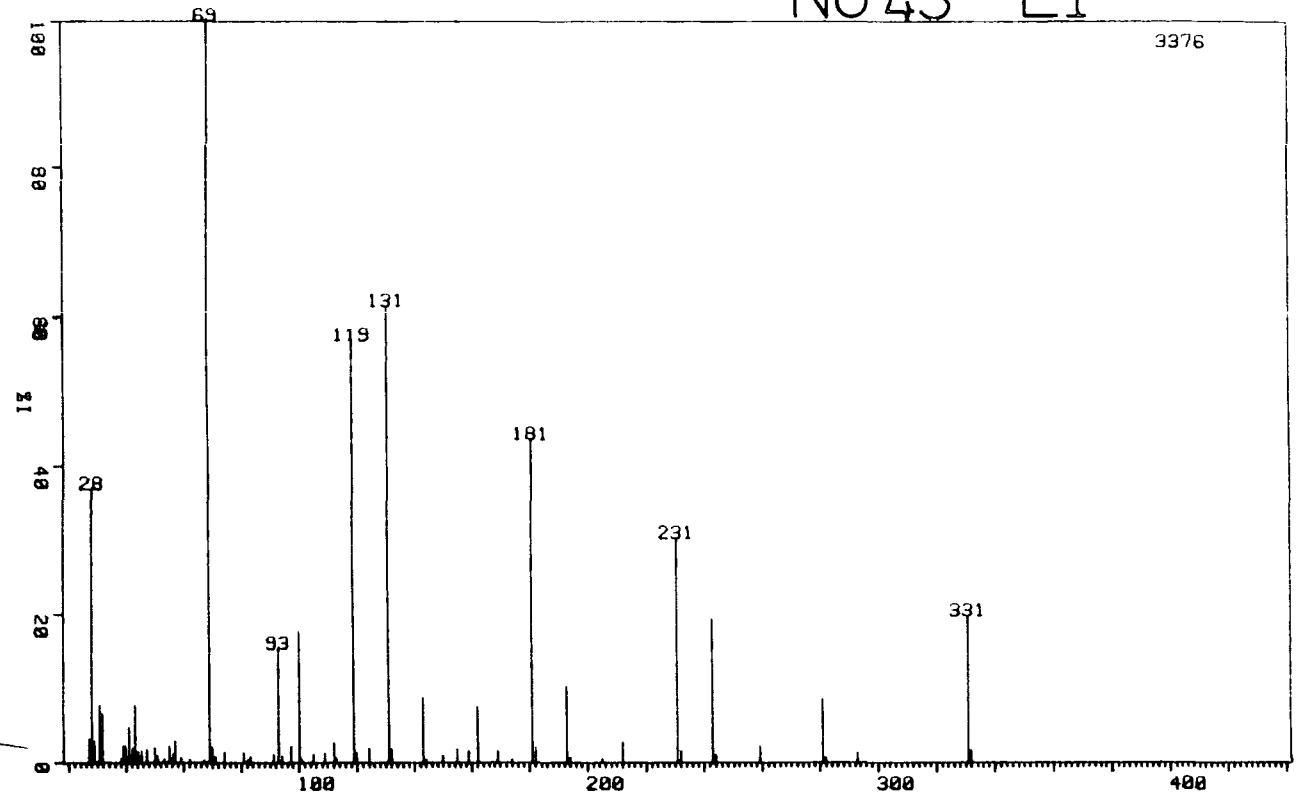
No 42 Neg



MASS	%HT. BASE
180.88	2.03
211.86	0.35
230.84	100.00
231.86	22.71
232.86	0.67
261.81	0.55
280.79	1.65
311.76	1.36
330.74	35.62
331.77	2.98
349.73	45.49
350.75	3.24

P1013X S P.T.TELFORD 09-MAY-85
CAL:CAL26 STA: 0:51

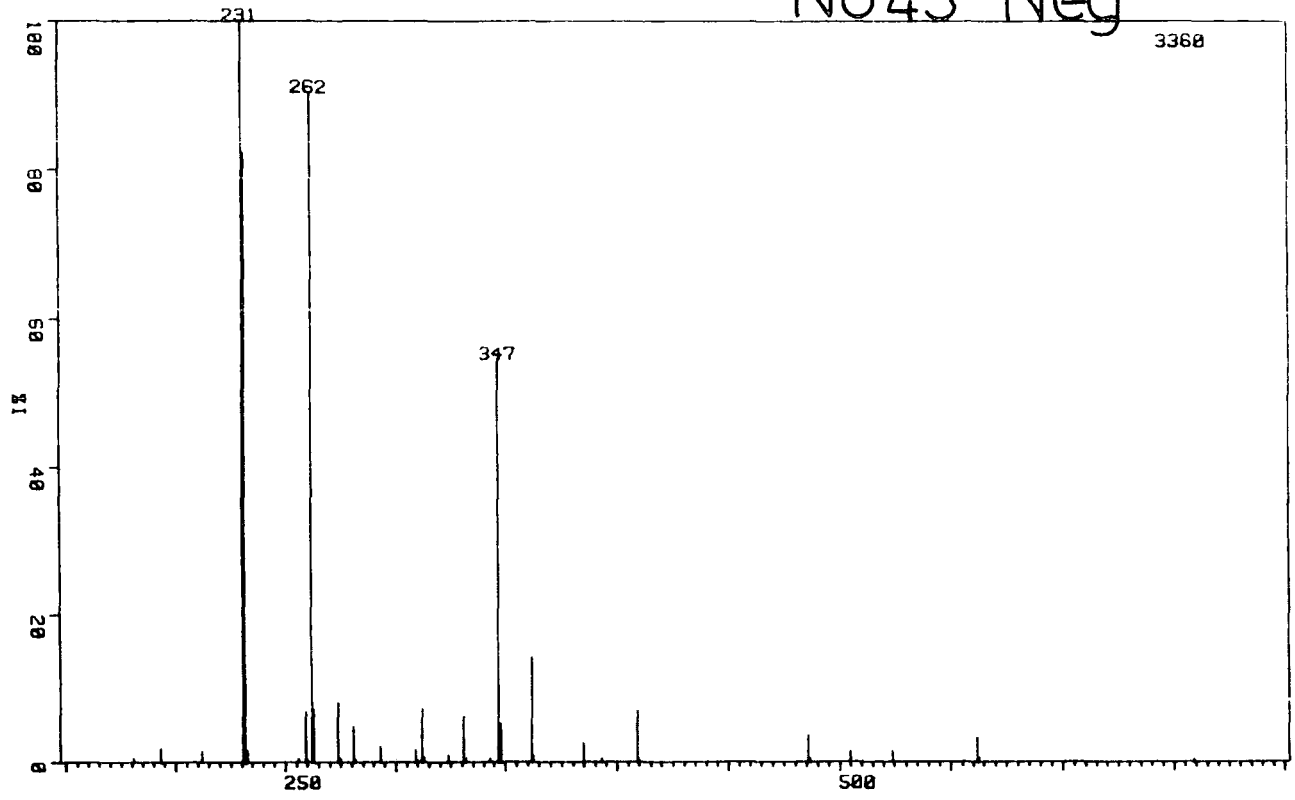
No 43 EI



MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
27.21	3.35	70.94	0.27	181.99	2.07
28.09	36.97	71.04	0.98	192.99	10.43
28.11	0.74	74.04	1.57	193.99	0.83
28.95	0.86	80.90	1.45	204.99	0.62
28.98	3.11	82.02	0.41	211.97	2.90
30.85	7.85	83.10	0.95	230.97	30.33
31.95	6.84	91.01	1.16	231.99	1.66
38.02	0.59	93.02	15.46	242.99	19.40
38.95	2.46	94.09	1.04	244.00	1.18
39.79	2.49	97.03	2.28	258.95	2.34
39.85	0.68	99.94	17.77	280.95	8.86
40.93	4.89	100.98	0.59	281.96	0.77
42.03	2.19	105.05	0.65	292.96	1.36
43.06	1.04	105.13	1.18	330.95	19.91
43.09	7.79	108.95	1.42	331.97	1.75
44.06	1.69	111.97	2.81		
45.13	1.69	113.01	0.50		
47.05	1.90	118.96	56.87		
49.86	2.13	119.92	1.48		
50.93	0.98	124.01	1.95		
53.08	0.44	130.94	61.46		
55.14	2.34	131.97	1.98		
56.14	1.21	142.98	8.92		
57.12	3.05	143.99	0.44		
59.01	0.74	149.90	1.01		
62.00	0.53	155.01	1.93		
67.08	0.41	158.97	1.69		
68.94	100.00	161.99	7.70		
69.01	1.39	168.97	1.69		
69.88	2.28	174.03	0.41		
69.98	1.07	180.97	43.57		

P1013X 9 P.T.TELFORD NH3 NEG. 09-MAY-85
CAL:CALN8 STA: 1:25

No43 Neg

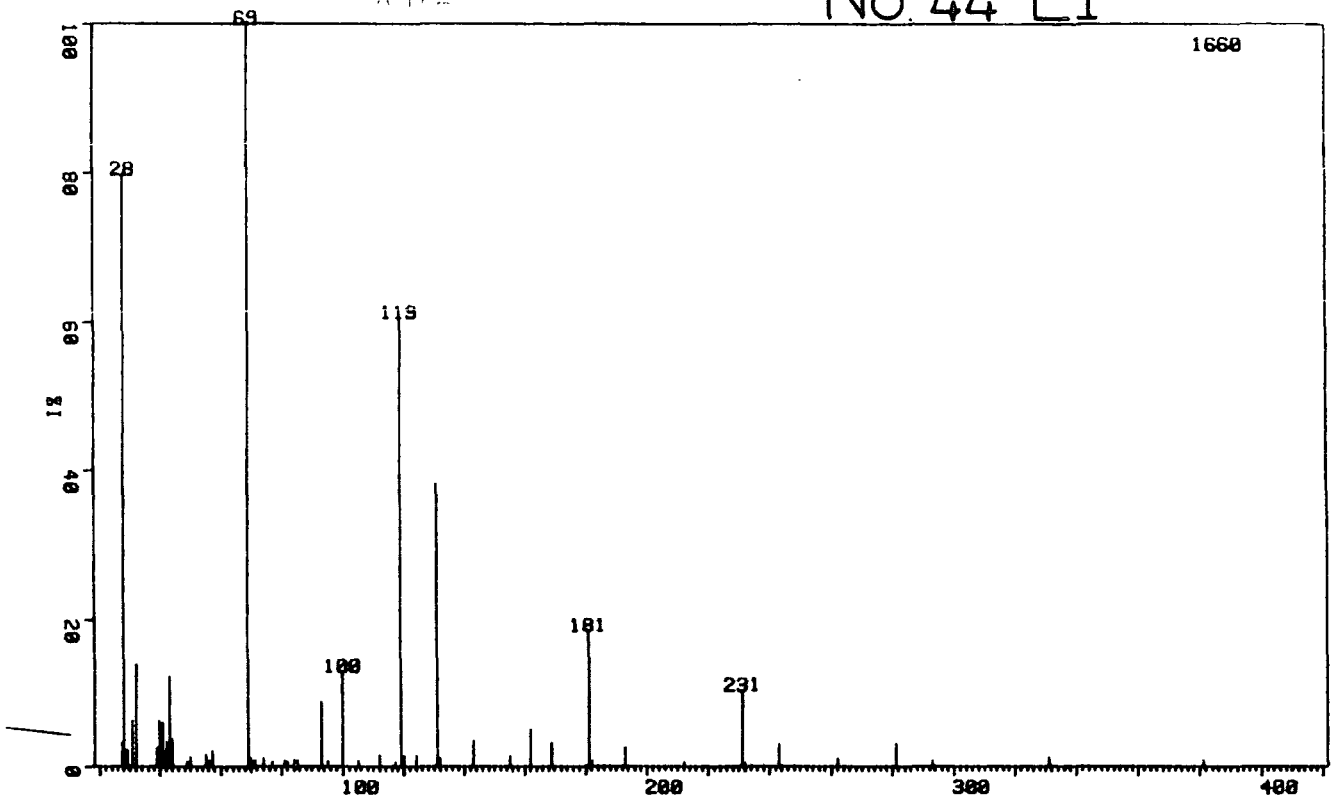


MASS	%HT. BASE	MASS	%HT. BASE
180.96	0.60	409.88	0.54
193.02	1.82	485.86	3.61
211.99	1.45	486.87	0.54
230.95	95.48	504.93	1.45
231.52	0.43	523.92	1.53
231.99	78.55	561.92	3.18
232.99	1.62	562.89	0.57
256.00	0.54	658.86	0.40
258.95	6.56		
259.92	0.37		
261.94	86.16		
262.96	6.82		
273.98	7.84		
274.96	0.57		
280.95	4.66		
281.94	0.37		
292.95	2.10		
308.92	1.68		
311.94	6.93		
312.91	0.63		
323.94	0.99		
330.93	5.97		
331.93	0.60		
342.95	0.48		
346.92	52.06		
347.95	5.09		
361.92	13.58		
362.90	0.77		
384.92	2.47		
392.87	0.40		
408.91	6.68		

PT472X 6 P.T.TELFORD EI
CAL:CALT31 STA:

No 44 EI

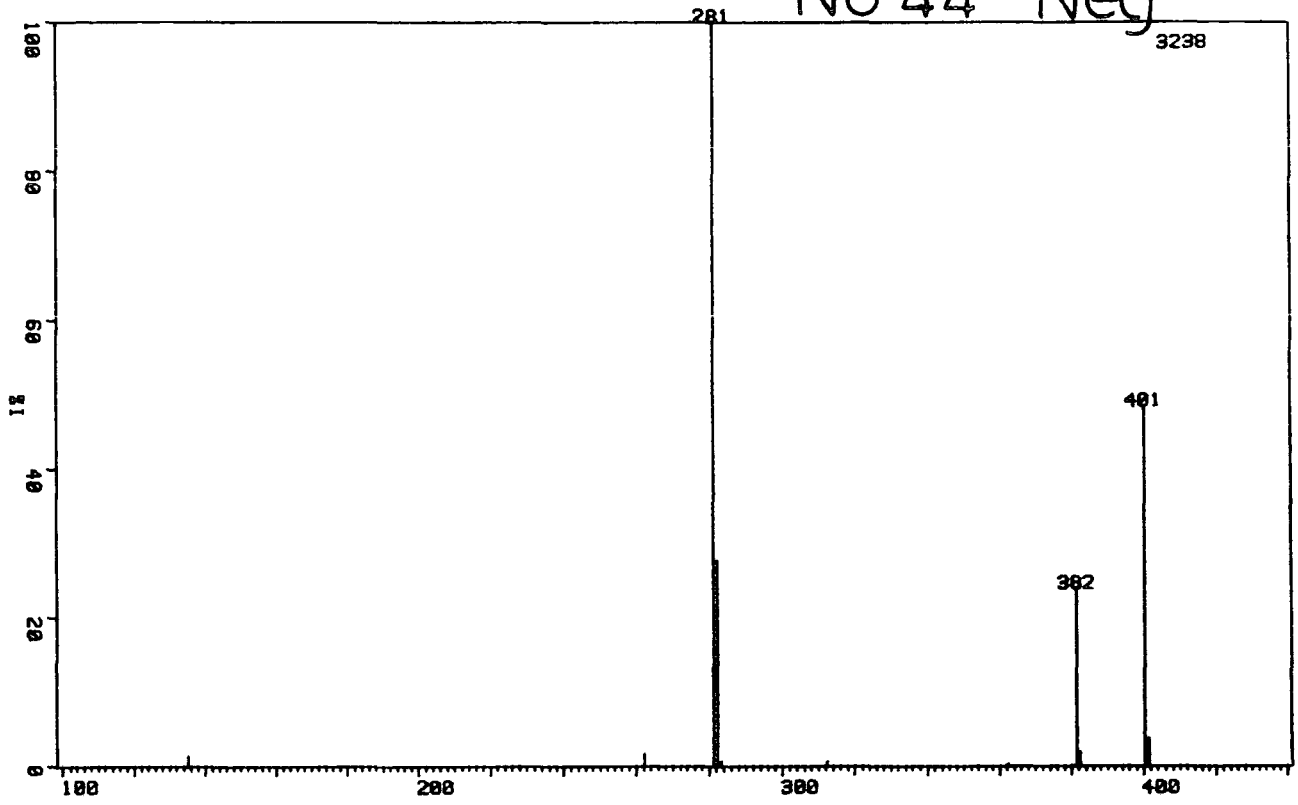
22-NOV-85
1:0



MASS	%HT. BASE	MASS	%HT. BASE
27.23	3.37	99.88	12.95
28.11	79.70	105.12	0.90
28.97	1.20	111.99	1.63
29.00	2.35	117.02	0.60
30.86	6.33	118.97	60.48
31.97	13.92	119.93	1.57
38.97	2.59	124.04	1.63
39.80	6.27	130.98	38.19
40.95	6.02	132.03	1.14
42.04	3.43	143.04	3.55
43.11	12.29	155.08	1.45
44.09	3.73	162.05	5.12
44.16	0.66	169.02	3.25
48.95	0.72	181.04	18.49
49.88	1.33	182.07	0.72
55.16	1.75	193.09	2.59
56.17	0.90	212.09	0.66
57.15	2.17	231.11	10.42
69.00	100.00	232.10	0.60
69.08	1.27	243.11	3.01
69.95	1.33	262.10	1.14
70.03	0.78	281.07	3.19
71.10	0.96	293.12	0.90
74.11	1.14	331.19	1.33
77.10	0.66	381.21	1.02
80.97	0.84		
82.07	0.66		
84.16	1.02		
85.14	0.90		
92.98	8.92		
94.95	0.78		

PT472X 3 P.T.TELFORD NH3 NEG. 22-NOV-85
CAL:CALN16 STA: 0:35

No 44 Neg

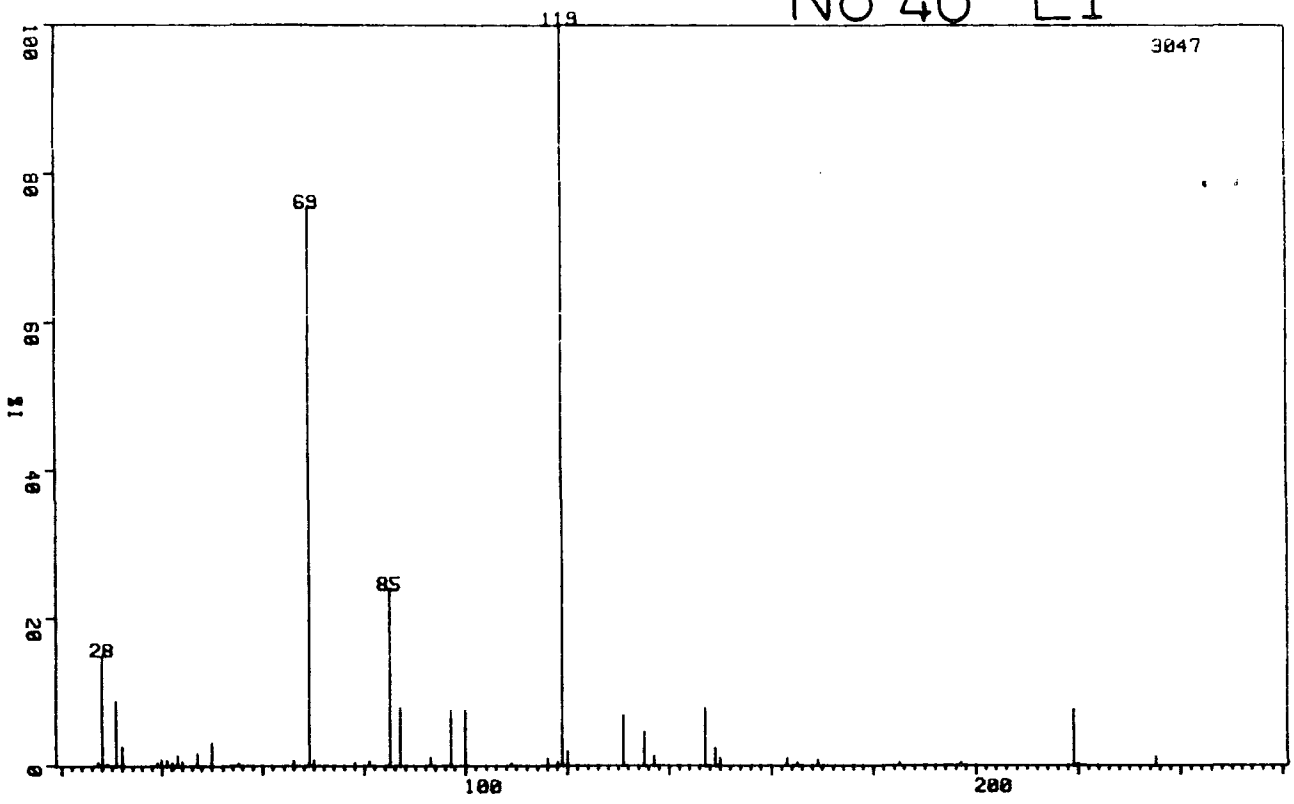


MASS	%HT. BASE
135.21	1.39
262.37	1.73
281.37	100.00
282.41	27.73
283.42	0.77
312.45	0.71
362.52	0.34
381.51	23.93
382.54	2.07
400.54	48.55
401.59	3.83

PT482X S P.T.TELFORD EI 148/2
CAL:CALT31 STA:

No 46 EI

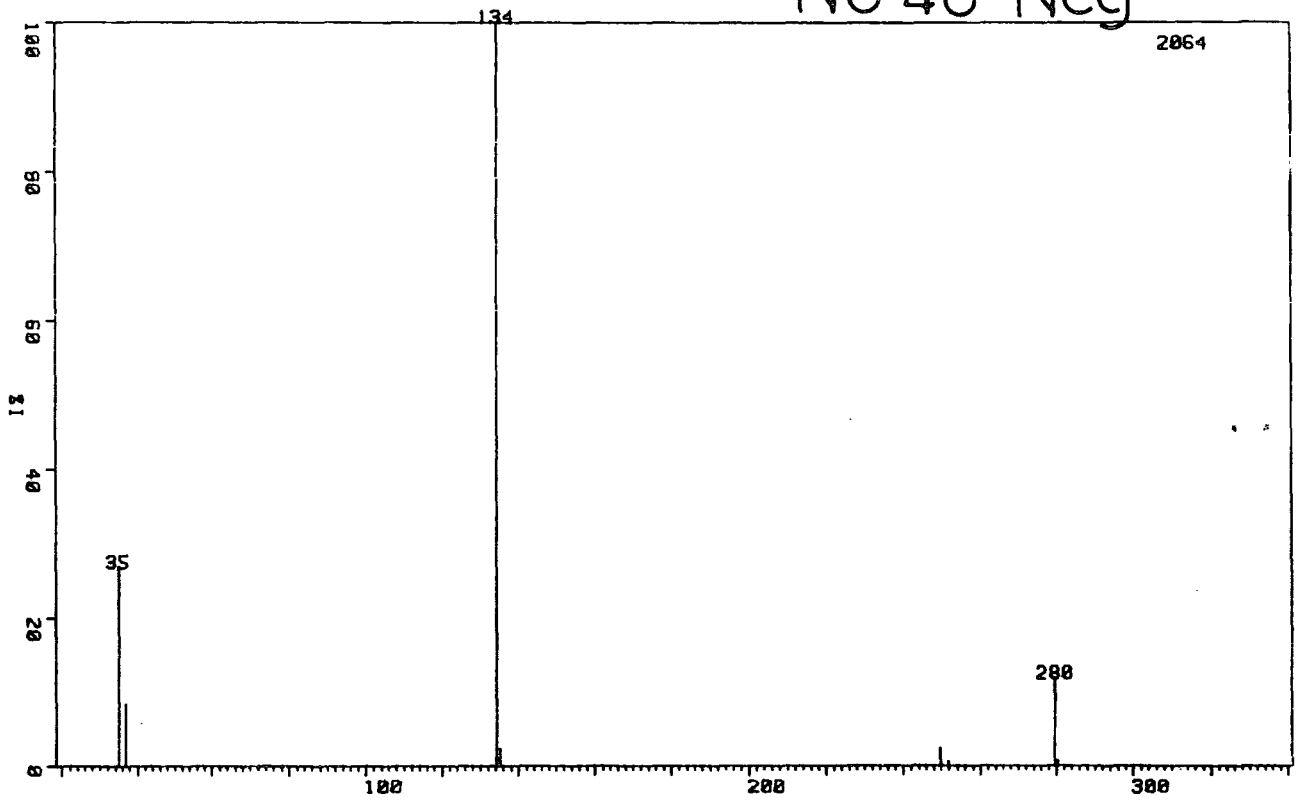
22-NOV-85
0:52



MASS	%HT. BASE		
27.23	2.10	117.98	0.50
28.11	80.52	118.97	100.00
28.13	0.65	119.94	2.02
28.97	0.80	130.97	8.08
29.00	0.61	134.99	4.35
30.86	9.30	136.98	1.52
31.97	14.30	146.98	8.73
35.10	0.42	148.93	3.47
38.96	1.45	149.93	1.49
39.80	2.21	162.96	1.26
40.94	2.67	164.96	0.50
42.03	1.98	168.94	0.88
43.10	4.54	196.95	0.50
44.07	0.88	218.91	7.62
45.13	0.50	234.89	1.41
47.06	2.02		
49.86	3.85		
55.14	0.50		
57.13	0.53		
62.00	0.57		
66.04	0.80		
68.96	79.91		
69.92	0.69		
80.94	0.99		
85.01	26.31		
86.98	8.73		
93.00	1.37		
97.00	7.36		
99.90	9.49		
108.97	0.42		
116.01	1.11		

P1482X 6 P.T.TELFORD 148/2 NEG. NH3 26-MAR-85
CAL:CALN22 STA: 1:8

No 46 Neg

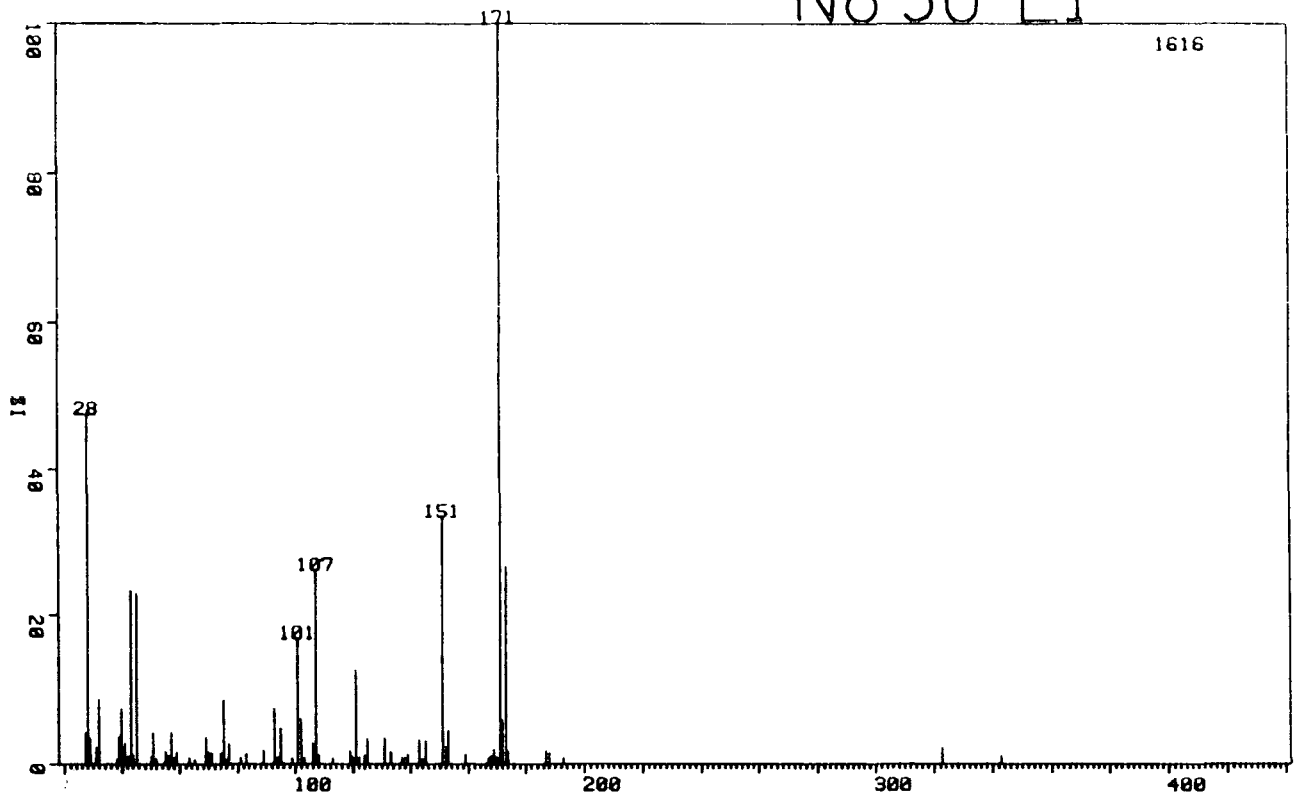


MASS	%HT. BASE
35.12	26.84
37.03	8.38
134.41	100.00
135.41	2.37
249.72	2.47
251.71	0.78
279.57	11.82
280.57	0.78

PT111X S P.T.TELFORD 111/1
CAL:CALT1 STA:

No 50 EI

03-JUL-85
0:50

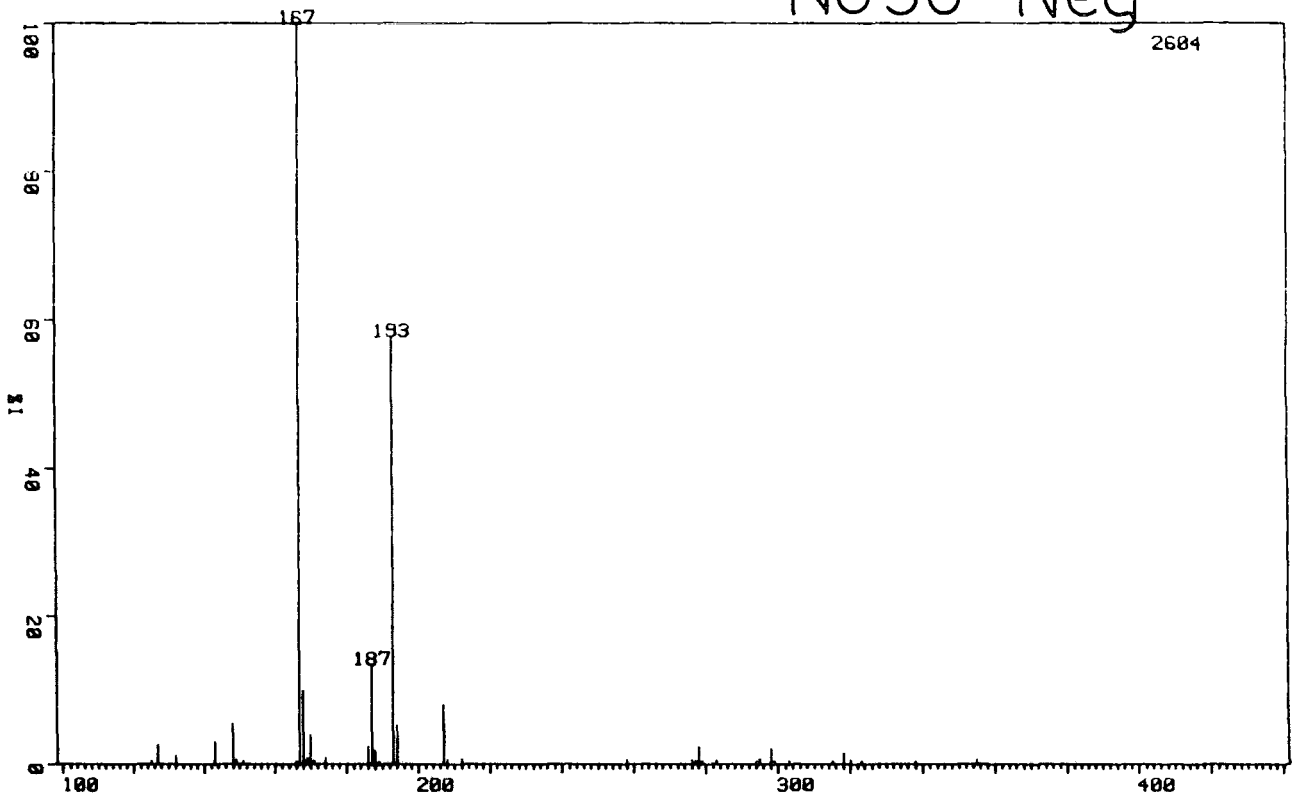


MASS	%HT. BASE	MASS	%HT. BASE	MASS	%HT. BASE
27.29	4.39	69.91	1.67	142.96	3.28
28.17	47.52	70.97	1.61	143.97	0.74
28.19	0.99	74.04	1.67	145.00	3.16
29.02	3.59	75.06	8.60	150.94	33.54
29.05	1.30	76.06	0.62	151.97	2.29
30.93	2.35	77.05	2.66	152.98	4.52
32.03	8.73	80.96	0.87	158.94	1.42
38.07	0.74	83.05	1.42	166.97	0.87
38.99	3.84	88.98	1.92	167.96	1.18
39.82	7.36	93.01	7.49	168.94	2.04
40.97	3.09	94.04	1.05	169.90	1.05
42.02	0.87	95.05	4.83	170.95	100.00
42.06	1.18	98.97	0.80	171.98	6.13
43.09	23.45	100.98	16.89	172.97	26.73
43.13	6.19	102.02	6.13	173.99	1.79
44.09	1.30	103.05	0.93	186.98	1.79
44.13	0.93	106.02	2.91	187.98	1.49
45.15	23.02	107.02	26.24	192.94	0.80
49.88	1.05	108.00	1.24	322.78	2.17
50.94	4.27	112.99	0.93	342.85	1.18
52.03	0.80	118.93	1.79		
55.14	1.67	119.90	1.05		
56.08	1.18	120.96	12.69		
57.07	4.33	122.00	0.99		
57.12	2.17	123.99	1.30		
58.05	0.87	125.00	3.40		
58.98	1.67	130.93	3.53		
63.06	0.87	133.01	1.67		
65.09	0.68	136.97	0.87		
68.95	3.71	137.98	0.87		
69.02	1.05	138.95	1.30		

PT111X S P.T.TELFORD 111/1 -VE EI I.BU
CAL:CALN1 STA:

No50 Neg

03-JUL-85
0:51



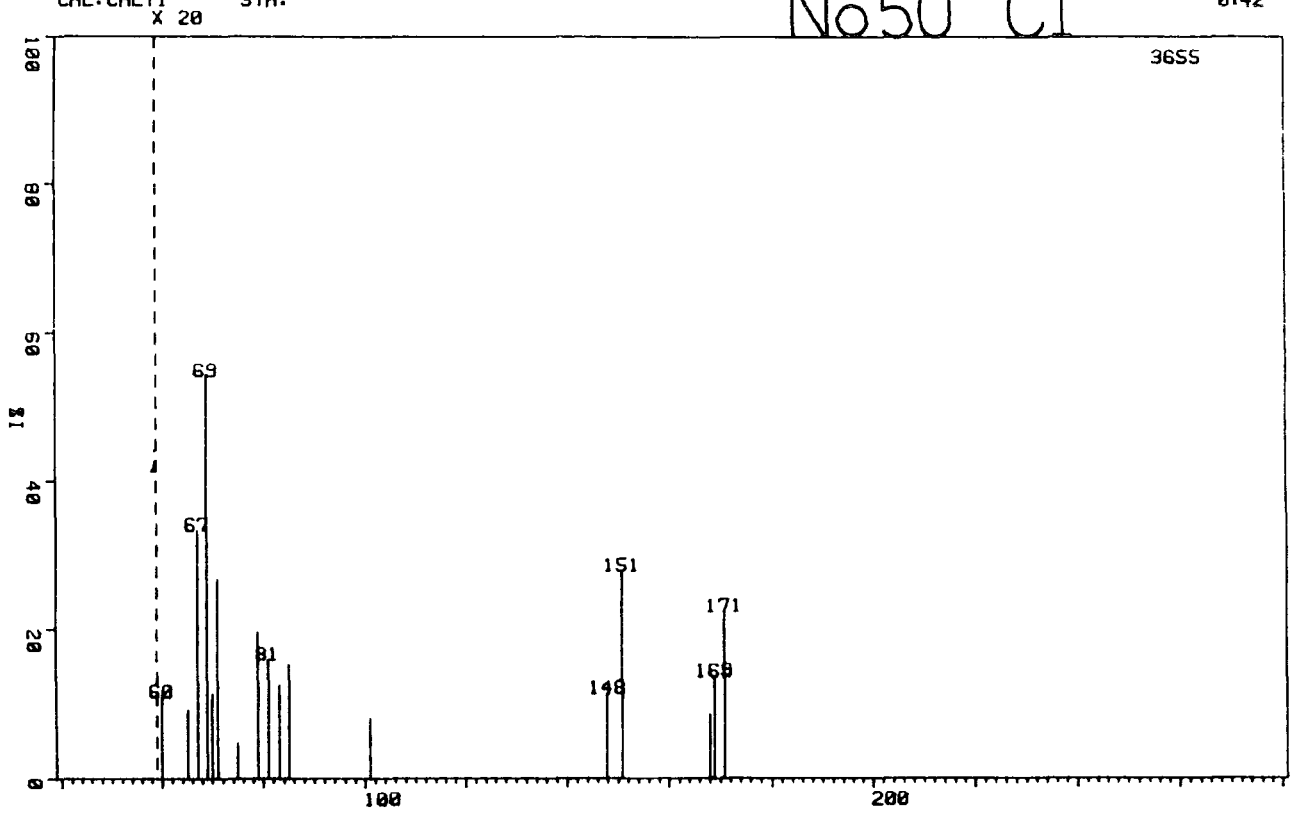
MASS	%HT. BASE	MASS	%HT. BASE
39.02	1.57	295.04	0.77
125.03	0.42	298.02	2.11
126.94	2.61	299.04	0.42
132.04	1.19	302.99	0.46
143.03	3.07	315.03	0.42
148.03	5.49	318.03	1.61
149.01	0.61	320.00	0.54
151.02	0.38	323.03	0.42
166.05	0.38	338.04	0.42
167.03	100.00	355.05	0.69
168.02	9.95		
169.01	0.84		
169.97	3.96		
170.98	0.46		
174.03	0.96		
186.04	2.50		
187.04	13.44		
188.01	1.96		
189.01	0.35		
193.02	57.72		
194.02	5.30		
207.03	8.14		
208.02	0.65		
211.99	0.73		
258.03	0.65		
276.03	0.54		
277.04	0.46		
278.02	2.38		
278.99	0.38		
283.02	0.46		
294.05	0.42		

PT111X 4 P.T.TELFORD 111/1 CI I.BU

CAL:CALT1 STA:

No50 CI

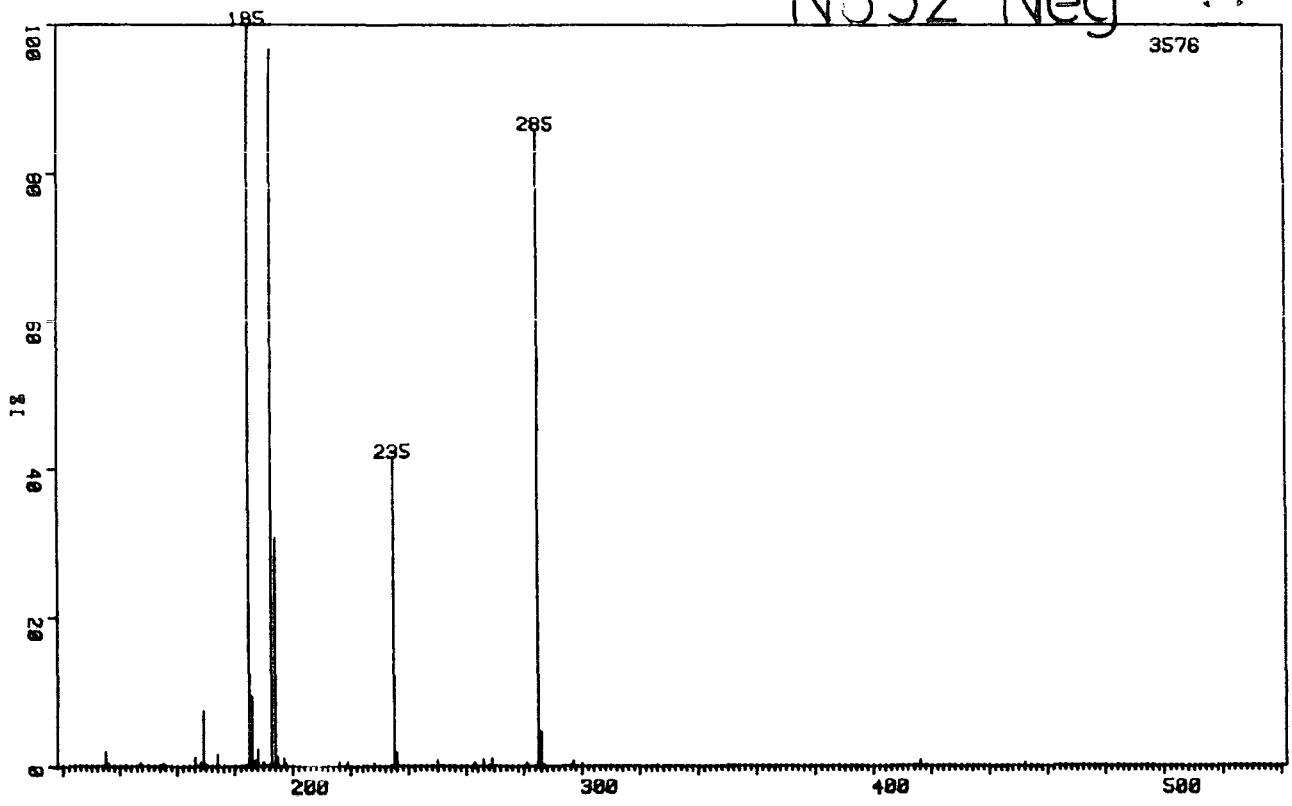
03-JUL-85
0:42



MASS	%HT. BASE
65.03	0.47
67.01	1.67
68.94	2.71
69.89	0.57
70.97	1.34
75.00	0.25
78.95	0.98
80.96	0.79
83.05	0.63
85.08	0.77
100.89	0.41
147.84	0.57
150.82	1.40
167.90	0.44
168.85	0.68
170.86	1.12

PTT662 S I-BU NEG. 193 REF 26-SEP-84
CAL:CALN18 STA: P:49

No52 Neg



MASS	%HT. BASE	MASS	%HT. BASE
135.12	1.93	236.06	4.70
136.14	0.34	237.14	0.31
147.15	0.48	297.10	0.64
155.21	0.34	300.06	0.36
166.14	1.26	414.29	0.28
168.16	0.45	416.18	0.89
169.10	7.47	452.17	0.48
170.14	0.31		
174.14	1.73		
185.07	100.00		
186.10	9.42		
187.03	0.64		
188.09	2.24		
190.04	0.50		
193.01	96.64		
194.05	30.65		
195.08	1.23		
197.03	1.09		
198.07	0.31		
212.01	0.42		
216.02	0.67		
219.00	0.70		
228.15	0.36		
235.12	41.53		
236.12	1.96		
250.06	0.89		
253.11	0.39		
266.07	0.98		
269.06	1.01		
281.07	0.53		
285.06	85.91		

RESEARCH COLLOQUIA, SEMINARS AND LECTURES

A. Lectures and Seminars organised by the Department of Chemistry during the period 1982-1985

*	13.10.82	Dr. W.J. Feast (Durham) "Approaches to the Synthesis of Conjugated Polymers"
	14.10.82	Prof. H. Suhr (Tubingen, FRG) "Preparative Chemistry in Nonequilibrium Plasmas"
	27.10.82	Dr. C.E. Housecroft (Oxford High School/Notre Dame) "Bonding capabilities of butterfly-shaped Fe_4 units. Implications for C-H bond activation in hydrocarbon complexes"
*	28.10.82	Prof. M.F. Lappert, FRS (Sussex) "Approaches to Asymmetric Synthesis and Catalysis using electron-rich olefins and some of their metal complexes"
*	15.11.82	Dr G. Bertrand (Toulouse, France) "Curtius Rearrangement in Organometallic Series: A route for new hybridised species"
	24.11.82	Prof. F.R. Hartley (R.M.C.S., Shrivenham) "Supported Metal-Complex Hydroformulation Catalysts"
	24.11.82	Prof. G.G. Roberts (Applied Physics, Durham) "Langmuir-Blodgett films: Solid state polymerisation of diacetylenes"
	8.12.82	Dr. G. Wooley (Trent) "Bonds in transition metal-cluster compounds"
	12. 1.83	Dr. D.C. Sherrington (Strathclyde) "Polymer-supported phase transfer catalysts"
	9. 2.83	Dr. P. Moore (Warwick) "Mechanistic studies in solution by stopped flow F.T.-NMR and high pressure NMR line broadening"
	21. 2.83	Dr. R. Lynden-Bell (Cambridge) "Molecular motion in the cubic phase of NaCN"
	2. 3.83	Dr. D. Bloor (Queen Mary College, London) "The solid-state chemistry of diacetylene monomers and polymers"
	8. 3.83	Prof. D.C. Bradley, FRS (Queen Mary College, London) "Recent Developments in Organo-Imido-Transition Metal Chemistry"
	9. 3.83	Dr. D.M.J. Lilley (Dundee) "DNA, Sequence, Symmetry, Structure and Supercoiling"

* 11. 3.83 Prof. H.G. Viehe (Louvain, Belbium)
"Oxidations on Sulphur" and
"Fluorine substitutions in radicals"
(The W.K.R. Musgrave Lecture)

* 16. 3.83 Dr. I. Gosney (Edinburgh)
"New extrusion reactions: Organic synthesis in a hot-tube"

25. 3.83 Prof. F.G. Baglin (Nevada, USA)
"Interaction induced Raman Spectroscopy in Supracritical ethane"

* 21. 4.83 Prof. J. Passmore (New Brunswick, Canada)
"Novel selenium-iodine cations"

4. 5.83 Prof. P.H. Plesch (Keele)
"Binary ionisation equilibria between two ions and two molecules. What Ostwald never thought of"

*10. 5.83 Prof. W. Burger (Munich, FRG)
"New reaction pathways from trifluoromethyl-substituted heterodienes to partially fluorinated heterocyclic compounds"

11. 5.83 Dr. N. Isaacs (Reading)
"The application of high pressures to the theory and practice of organic chemistry"

13. 5.83 Dr. R. de Koch (Michigan/Amsterdam)
"Electronic structural calculations in organo-metallic cobalt cluster molecules. Implications for metal surfaces"

13. 5.83 Dr. T.B. Marder (UCLA/Bristol)
"The Chemistry of Metal-carbon and metal-metal multiple bonds"

* 16. 5.83 Prof. R.J. Lagow (Texas, USA)
"The chemistry of polylithium organic compounds. An unusual class of matter"

18. 5.83 Dr. D.M. Adams (Leicester)
"Spectroscopy at very high pressures.

25. 5.83 Dr. J.M. Vernon (York)
"New heterocyclic chemistry involving lead tetraacetate"

15. 6.83 Dr. A. Pietrzykowski (Warsaw/Strathclyde)
"Synthesis, structure and properties of Aluminoxanes"

22. 6.83 Dr. D.W.H. Rankin (Edinburgh)
"Floppy molecules - the influence of phase on structure"

5. 7.83 Prof. J. Miller (Camfinas, Brazil)
"Reactivity in nucleophilic substitution reactions"

5.10.83 Prof. J.P. Maier (Basel, Switzerland)
"Recent approaches to spectroscopic characterization of cations"

12.10.83 Dr. C.W. McLeland (Port Elizabeth, Australia)
"Cyclization of aryl alcohols through the intermediacy of alkoxy radicals and aryl radical cations"

19.10.83 Dr. N.W. Alcock (Warwick)
"Aryl tellurium (IV) compounds, patterns of primary and secondary bonding"

26.10.83 Dr. R.H. Friend (Cavendish, Cambridge)
"Electronic properties of conjugated polymers"

30.11.83 Prof. I.M.G. Cowie (Stirling)
"Molecular interpretation of non-relaxation processes in polymer glasses"

* 2.12.83 Dr. G.M. Brooke (Durham)
"The fate of the ortho-fluorine in 3,3-sigmatropic reactions involving polyfluoro-aryl and -hetero-aryl systems"

14.12.83 Prof. R.J. Donovan (Edinburgh)
"Chemical and physical processes involving the ion-pair states of the halogen molecules"

10. 1.84 Prof. R. Hester (York)
"Nanosecond Laser Spectroscopy of Reaction Intermediates"

18. 1.84 Prof. R.K. Harris (UEA)
"Multi-nuclear solid state magnetic resonance"

8. 2.84 Dr. B.T. Heaton (Kent)
"Multi-nuclear NMR studies"

15. 2.84 Dr. R.M. Paton (Edinburgh)
"heterocyclic Syntheses using Nitrile Sulphides"

7. 3.84 Dr. R.T. Walker (Birmingham)
"Synthesis and Biological Properties of some 5-substituted Uracic Derivatives; yet another example of serendipity in Anti-viral Chemotherapy"

21. 3.84 Dr. P. Sherwood (Newcastle)
"X-ray photoelectron spectroscopic studies of electrode and other surfaces"

21. 3.84 Dr. G. Beamson (Durham/Kratos)
"EXAFS: General Principles and Applications"

23. 3.84 Dr. A. Ceulemans (Leuven)
"The Development of Field-Type models of the Bonding in Molecular Clusters"

* 2. 4.84 Prof. K. O'Driscoll (Waterloo)
"Chain Ending reactions in Free Radical Polymerisation"

3. 4.84 Prof. C.H. Rochester (Dundee)
"Infrared Studies of Adsorption at the Solid-Liquid Interface"

25. 4.84 Dr. R.M. Acheson (Biochemistry, Oxford)
"Some Heterocyclic Detective Stories"

27. 4.84 Dr. T. Albright (Houston, U.S.A.)
"Sigmatropic Rearrangements in Organometallic Chemistry"

* 14. 5.84 Prof. W.R. Dolbier (Florida, USA)
"Cycloaddition Reactions of Fluorinated Allenes"

16. 5.84 Dr. P.J. Garratt (UCL)
"Synthesis with Dilithiated Vicinal Diesters and Carboximides"

22. 5.84 Prof. F.C. de Schryver (Leuven)
"The use of Luminescence in the study of micellar aggregates" and
"Configurational and Conformational control in excited state complex formation"

* 23. 5.84 Prof. M. Tada (Waseda, Japan)
"Photochemistry of Dicyanopyrazine Derivatives"

* 31. 5.84 Dr. A. Haaland (Oslo)
"Electron Diffraction Studies of some organo-metallic compounds"

* 11. 6.84 Dr. J.B. Street (IBM, California)
"Conducting Polymers derived from Pyrroles"

* 19. 9.84 Dr. C. Brown, (IBM, California)
"New Superbase reactions with organic compounds"

21. 9.84 Dr. H.W. Gibson (Signal UOP, Illinois)
"Isomerization of Polyacetylene"

* 19.10.84 Dr. A. Germain (Languedoc, Montpellier)
"Anodic Oxidation of Perfluoro Organic Compounds in Perfluoroalkane Sulphonic Acids"

24.10.84 Prof. R.K. Harris (Durham)
"N.M.R. of Solid Polymers"

28.10.84 Dr. R. Snaith (Strathclyde)
"Exploring Lithium Chemistry: Novel Structures, Bonding and Reagents"

7.11.84 Prof. W.W. Porterfield (Hampden-Sydney College, USA)
"There is no Borane Chemistry (only Geometry)"

7.11.84 Dr. H.S. Munro (Durham)
"New Information from ESCA Data"

21.11.84 Mr. N. Everall (Durham)
"Picosecond Pulsed Laser Raman Spectroscopy"

* 27.11.84 Dr. W.J. Feast (Durham)
"A Plain Man's Guide to Polymeric Organic Metals"

28.11.84 Dr. T.A. Stephenson (Edinburgh)
"Some recent studies in Platinum Metal Chemistry"

12.12.84 Dr. K.B. Dillon (Durham)
"^{31}P N.M.R. Studies of some Anionic Phosphorus Complexes"

* 11. 1.85 Emeritus Prof. H. Suschitzky (Salford)
"Fruitful Fissons of Benzofuroxanes and Isobenzimidazoles (umpolung of o-phenylenediamine)"

13. 2.85 Dr. G.W.J. Flett (Oxford)
"Synthesis of some Alkaloids from Carbohydrates"

* 19. 2.85 Dr. D.J. Mincher (Durham)
"Stereoselective Synthesis of some novel Anthracyclinones related to the anti-cancer drug Adriamycin and to the Steffimycin Antibiotics"

* 27. 2.85 Dr. R.E. Mulvey (Durham)
"Some unusual Lithium Complexes"

6. 3.85 Dr. P.J. Kocienski (Leeds)
"Some Synthetic Applications of Silicon-Mediated Annulation Reactions"

7. 3.85 Dr. P.J. Rodgers (I.C.I. plc. Agricultural Division, Billingham)
"Industrial Polymers from Bacteria"

12. 3.85 Prof. K.J. Packer (B.P. Ltd./East Anglia)
"N.M.R. Investigations of the Structure of Solid Polymers"

* 14. 3.85 Prof. A.R. Katritzky F.R.S.(Florida)
"Some Adventures in Heterocyclic Chemistry"

20. 3.85 Dr. M. Poliakoff (Nottingham)
"New Methods for detecting Organometallic Intermediates in Solution"

28. 3.85 Prof. H. Ringsdorf (Mainz)
"Polymeric Liposomes as Models for Biomembranes and Cells?"

24. 4.85 Dr. M.C. Grossel (Bedford College, London)
"Hydroxypyridone dyes -Bleachable one-dimensional Metals?"

* 25. 4.85 Major S.A. Shackelford (U.S. Air Force)
"In Situ Mechanistic Studies on Condensed Phase Thermochemical Reaction Processes: Deuterium Isotope Effects in HMX Decomposition, Explosives and Combustion"

* 1. 5.85 Dr. D. Parker (I.C.I. plc, Petrochemical and Plastics Division, Wilton)
"Applications of Radioisotopes in Industrial Research"

* 7. 5.85 Prof. G.E. Coates (formerly of University of Wyoming, U.S.A.)
"Chemical Education in England and America: Successes and Deficiencies"

8. 5.85 Prof. D. Tuck (Windsor, Ontario)
"Lower Oxidation State Chemistry of Indium"

* 8. 5.85 Prof. G. Williams (U.C.W. Aberystwyth)
"Liquid Crystalline Polymers"

* 9. 5.85 Prof. R.K. Harris (Durham)
"Chemistry in a Spin: Nuclear Magnetic Resonance"

14. 5.85 Prof. J. Passmore (New Brunswick, U.S.A.)
"The Synthesis and Characterisation of some Novel Selenium-Iodine Cations, aided by ^{77}Se N.M.R. Spectroscopy"

* 15. 5.85 Dr. J.E. Packer (Auckland, New Zealand)
"Studies of Free Radical Reactions in squeous solution using Ionising Radiation"

17. 5.85 Prof. I.D. Brown (McMaster University, Canada)
"Bond Valence as a Model for Inorganic Chemistry"

21. 5.85 Dr. D.L.H. Williams (Durham)
"Chemistry in Colour"

* 22. 5.85 Dr. M. Hudlicky (Blacksburg, U.S.A.)
"Preferential Elimination of Hydrogen Fluoride from Vicinal Bromofluorocompounds"

22. 5.85 Dr. R. Grimmett (Otago, New Zealand)
"Some Aspects of Nucleophilic Substitution in Imidazoles"

4. 6.85 Dr. P.S. Belton (Food Research Institute, Norwich)
"Analytical Photoacoustic Spectroscppy"

13. 6.85 Dr. D. Woolins (Imperial College, London)
"Metal - Sulphur - Nitrogen Complexes"

14. 6.85 Prof. Z. Rappoport (Hebrew University, Jerusalem)
"The Rich Mechanistic World of Nucleophilic Cinylic Substitution"

19. 6.85 Dr. T.N. Mitchell (Dortmund)
"Some Synthetic and NMR - Spectroscopic Studies of Organotin Compounds"

* 26. 6.85 Prof. G. Shaw (Bradford)
"Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin"

12. 7.85 Dr. K. Laali (Hydrocarbon Research Institute, University of Southern California)
"Recent Developments in Superacid Chemistry and Mechanistic Considerations in Electrophilic Aromatic Substitutions; a Progress Report"

B. Lectures Organised by Durham University Chemical Society during the period 1982-1985

*14.10.82 Mr. F. Shenton (County Analyst, Durham)
"There is death in the pot"

28.10.82 Prof. M.P. Lappert, F.R.S. (Sussex)
"The Chemistry of Some Unusual Subvalent Compounds of the Main Group IV and V Elements"

4.11.82 Dr. D.H. Williams (Cambridge)
"Studies on the Structures and Modes of Action of Antibiotics"

11.11.82 Dr. J. Cramp (I.C.I. plc)
"Lasers in Industry"
(Joint Lecture with the Society of Chemical Industry)

25.11.82 Dr. D.H. Richards, P.E.R.M.E. (Ministry of Defence)
"Terminally Functional Polymers - their Synthesis and Uses"

* 27. 1.83 Prof. D.W.A. Sharp (Glasgow)
"Some Redox Reactions in Fluorine Chemistry"

3. 2.83 Dr. R. Manning (Dept. Zoology, Durham)
"Molecular Mechanisms of Hormone Action"

10. 2.83 Sir G. Allen, F.R.S. (Unilever Ltd.)
"U.K. Research"

17. 2.83 Prof. A.G. MacDiarmid (Pennsylvania)
"Metallic Covalent Polymers (SN)x and (CH)x and their Derivatives" (R.S.C. Centenary Lecture)

3. 4.83 Prof. A.C.T. North (Leeds)
"The Use of a Computer Display System in Studying Molecular Structures and Interactions"

20.10.83 Prof. R.B. Cundall (Salford)
"Explosives"

* 3.11.83 Dr. G. Richards (Oxford)
"Quantum Pharmacology"

10.11.83 Prof. J.H. Ridd (U.C.L.)
"Ipso-Attack in Electrophilic Aromatic Substitution"

* 17.11.83 Dr. J. Harrison (Sterling Organic)
"Applied Chemistry and the Pharmaceutical Industry"
(Joint Lecture with the Society of Chemical Industry)

24.11.83 Prof. D.A. King (Liverpool)
"Chemistry in 2-Dimensions"

1.12.83 Dr. J.D. Coyle (The Open University)
"The Problem with Sunshine"

26. 1.84 Prof. T.L. Blundell (Birkbeck College, London)
"Biological Recognition: Interactions of Macromolecular surfaces"

2. 2.84 Prof. N.B.H. Jonathan (Southampton)
"Photoelectron Spectroscopy - A Radical Approach"

* 12. 6.84 Prof. D. Phillips (The Royal Institution)
"Luminescence and Photochemistry - A Light Entertainment"

* 23. 2.84 Prof. F.G.A. Stone F.R.S. (Bristol)
"The Use of Carbene and Carbyne Groups to Synthesise Metal Clusters"
(The Waddington Memorial Lecture)

* 1. 3.84 Prof. A.J. Leadbetter (Rutherford Appleton Labs.)
"Liquid Crystals"

3. 3.84 Prof. D. Chapman (Royal Free Hospital School of Medicine, London
"Phospholipids and Biomembranes, Basic Science and Future Technique"

28. 3.84 Prof. H. Schmidbaur (Munich, F.R.G.)
"Ylides in Coordination Sphere of Metal: Synthetic, Structural and Theoretical Aspects"
(R.S.C. Centenary Lecture)

* 18.10.84 Dr. N. Logan (Nottingham)
"N_2O_4 and Rocket Fuels"

* 23.10.84 Dr. W.J. Feast (Durham)
"Syntheses of Conjugated Polymers. How and Why?"

8.11.84 Prof. B.J. Aylett (Queen Mary College, London)
"Silicon - Dead Common or Refined?"

* 15.11.84 Prof. B.T. Golding (Newcastle-upon-Tyne)
"The Vitamin B_{12} Mystery"

* 22.11.84 Prof. D.T. Clark (I.C.I. New Science Group)
"Structure, Bonding, Reactivity and Synthesis as Revealed by ESCA"
(R.S.C. Tilden Lecture)

* 29.11.84 Prof. C.J.M. Stirling (University College of North Wales)
"Molecules taking the Strain"

* 6.12.84 Prof. R.D. Chambers (Durham)
"The Unusual World of Fluorine"

24. 1.85 Dr. A.K. Covington (Newcastle-upon-Tyne)
"Chemistry with Chips"

* 31. 1.85 Dr. M.L.H. Green (Oxford)
"Naked Atoms and Negligee Ligands"

7. 2.85 Prof. A. Ledwith (Pilkington Bros.)
"Glass as a High Technology Material"
(Joint Lecture with the Society of Chemical Industry)

* 14. 2.85 Dr. J.A. Salthouse (Manchester)
"Son et Lumiere"

21. 2.85 Prof. P.M. Maitlis, F.R.S. (Sheffield)
"What Use is Rhodium?"

* 7. 3.85 Dr. P.W. Atkins (Oxford)
"Magnetic Reactions"

* Lectures attended

(C) Research Conferences attended

Graduate Symposium, Durham, April 1983

17th Sheffield Symposium on "Modern Aspects of Stereochemistry", Sheffield, 21 December 1983

Graduate Symposium, Durham, April 1984

International Symposium on "Chemistry of Carbanions", University of Durham, 16-20 July 1984

Graduate Symposium, Durham, April 1985

(D) First Year Induction Course, October 1982

This course consists of a series of one hour lectures on the services available in the department.

1. Departmental organisation
2. Safety matters
3. Electrical appliances and infrared spectroscopy
4. Chromatography and Microanalysis
5. Atomic absorptiometry and inorganic analysis
6. Library facilities
7. Mass spectrometry
8. Nuclear magnetic resonance spectroscopy
9. Glassblowing technique.

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