Free radical approaches to fluorinated derivatives of Amines

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UNIVERSITY OF DURHAM

A THESIS

entitled

FREE RADICAL APPROACHES TO FLUORINATED DERIVATIVES OF AMINES

submitted by

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To Mum, Dad, Gareth and

Gran

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MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1988 and September 1991. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

NOMENCLATURE

Throughout this thesis an "F" in the centre of a ring is used to denote that all unmarked bonds are attached to fluorine.

ABSTRACT

Free Radical Approaches to Fluorinated Derivatives of Amines

by

P.H.Whitby

The work contained in this thesis is divided into three sections.

A. The C-H bond is used as a functional group in free radical addition of nitrogen containing compounds to a variety of fluoroalkenes. Substituent effects are explained using the trimethylsilyl and acetyl derivatives of a range of both aliphatic and alicyclic amines, and studies are described on the effect of introducing a second heteroatom on the reactivity of these derivatives. Further reactions of some of the adducts gave synthetic routes to fluorinated amines.

B. Attempts at direct fluorination of tertiary amide models for **RDX** explosives are described using a range of techniques from high pressure to UV initiation.

C. Reactions of fluorinated aldehydes and ammonia result in the formation of fluorinated oligomers, and also to the formation of a fluorinated heterocycle.

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THE USE OF FREE RADICAL REACTIONS IN THE MODIFICATION OF EXPLOSIVE MATERIALS

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I.1. Explosive Materials

I.1.A. Introduction

An explosion has been defined as 'a chemical reaction or change of state which is effected in an exceedingly short space of time with the generation of a high temperature and generally a large quantity of gas'[1].

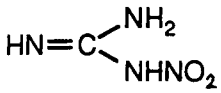
The first useful propellant and explosive was probably gunpowder, comprising an intimate mixture of charcoal and sulphur as fuel, with potassium nitrate as a solid oxidizing agent. Thermal decomposition of gunpowder causes the formation of hot gaseous products, the explosion spreading by a combination of conduction and diffusion. The introduction of molecules in which fuel / oxidizing agent were part of the same molecule coupled with the subsequent discovery of detonation has lead to the remarkably varied array of explosives and explosive mixtures available today. There are reviews available on explosives[2,3], detonation theory[4] and methods for the detection of explosives[5], although it is not the aim of this study to discuss these here. Explosives can be broadly divided by chemical composition into the following categories[6]:- (1) Nitro compounds, (2) Nitrate esters, (3) Nitramines, (4) Salts of nitric, chloric and perchloric acids, (5) Azides, (6) Mixtures.

The class of particular interest to this study are the nitramines (Table 1.1). Of this class 1,3,5-trinitrohexahydro-s-triazine (**RDX**) and 1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine (**HMX**) have received the most interest, and reviews are available[7,8].

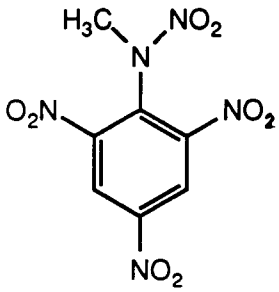
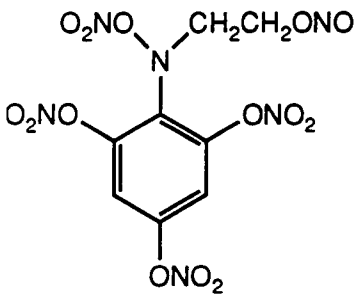
Table 1.1 (5)

Explosive Materials

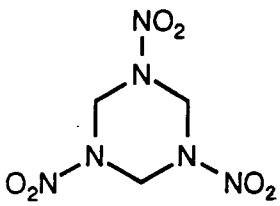
Aliphatic

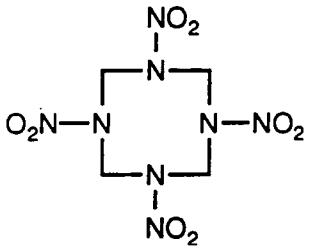
NH_2NO_2	Nitramine
CH_3NHNO_2	Methylnitramine
$(CH_3)_2NNO_2$	Dimethylnitramine
	Nitroguanidine

Aromatic

	*N*-methyl-*N*-nitro-2,4,6-trinitroaniline (Tetryl)
	2,4,6-trinitrosophenyl-nitraminoethylnitrate (Pentyl, Pentryl)

Heterocyclic

	1,3,5-trinitrohexahydro-s-triazine (**RDX**)



1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine

(HMX)

I.1.B. Nitramine Explosives

I.1.B.(1). 1,3,5-Trinitrohexahydro-s-triazine (RDX, Hexogen, T4, Cyclonite)

RDX (named for research department explosive) achieved great importance during World War II as a constituent of many explosive mixtures which required high power.

RDX was first patented in 1899 by Henning[9], from the action of nitric acid on hexamethylenetetramine (henceforth referred to as hexamine) nitrate. The author gave few details and did not propose a structure, recommending the product as a medicine, although in later patents he proposed the use of **RDX** as a smokeless propellant[10]. In 1921 Herz[11] modified Henning's method by nitrating hexamine itself, and proposed the correct structure for the compound, and in 1925 Hale[12] reported improved directions for the preparation of **RDX** using 98-100% nitric acid, [1.1].

$$C_6H_{12}N_4 + 3HNO_3 \longrightarrow \underset{\textbf{RDX}}{C_3H_6O_6N_6} + 3HCHO + NH_3 \text{ -[1.1]}$$

Both during and after the war numerous methods were developed and operated on an industrial scale, and in 1949 Bachmann and Sheehan[13] combined the process of Hale[12] and Ross and Schiesler[14] using modified experimental conditions to yield twice the amount of **RDX**.

RDX is a white, crystalline solid which exists in the orthorhombic crystal system[15], crystallising in two polymorphic forms, although the second is unstable. In 1950 McCrone reported a complete structural morphology[16], and a final complete structural assignment was made in 1972 by Choi and Prince[17].

I.1.B.(2). 1,3,5,7-Tetranitrooctahydro-1,3,5,7-tetrazocine (Octogen, HMX)

HMX (designated for high melting explosive) was first prepared by Bachmann and Sheehan[13] in 1949 as a by-product of **RDX** production, in a yield of originally 0-10%. Wright and co-workers were able to prepare **HMX** from 1,5-methylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane (**DPT**)[18a,b], and the yield was subsequently increased using **DPT** to 28% by Bachmann and co-workers[19a,b]. More recently in 1981 Gilbert and co-workers[20] devised routes to **HMX** starting from the initial acetylation of hexamine to give the diacetyl derivative 3,7-diacetyl-1,3,5,7-tetraazabicyclo[3.3.1]nonane (**DAPT**), or the tetraacetyl derivative 1,3,5,7-tetraacetyloctahydro-1,3,5,7-tetrazocine (**TAT**), followed by nitration.

HMX is a white crystalline solid which exists in four polymorphic forms[21], of which the monoclinic β-form[22] is the most common form stable at room temperature. At present **HMX** is the highest energy solid explosive produced on a large scale, primarily for military use.

I.1.C. The Mechanism of RDX and HMX Formation

The mechanisms of **RDX** and **HMX** production have received a good deal of interest[7,23] and are thought to involve either (1) selective cleavage of bonds within the hexamine molecule, or (2) the total cleavage (in the presence of an electrophile) of the molecule to smaller fragments followed by recombination[13,19a,b,24,25]. Evidence for the latter pathway in the Bachmann nitration has been obtained from ^{14}C and ^{15}N tracer studies[26,27]. The ^{14}C data showed that nitration involved the complete non-selective degradation of hexamine to fragments containing chemically equivalent methylene groups, and that methylene groups derived from paraformaldehyde could enter into a common pool with those of hexamine to form the final product[26]. Later work[28] did not elucidate these simple fragments other than to say that one amino nitrogen was present, and that the formation of **RDX** may be logically ascribed to the condensation of three hydroxymethylnitramine molecules, [1.2].

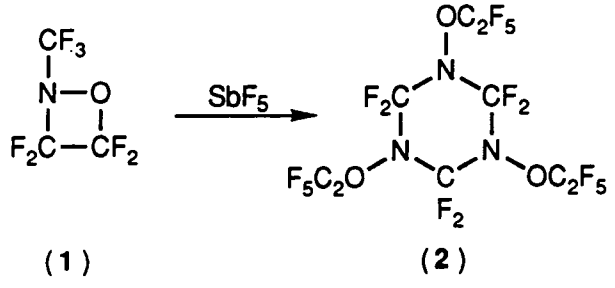
$$3(HOCH_2NHNO_2) \longrightarrow \underset{\textbf{RDX}}{C_3H_6O_6N_6} + 3H_2O \quad \text{-[1.2]}$$

Wright and co-workers[18a] prepared **DPT**, a structural derivative of **HMX**, by the reaction of nitramide with formaldehyde and ammonia, and there is evidence to suggest that at the low temperatures used for the reaction that nitramide is stable over several hours[29]. Isotopic studies[17b,26] indicated that the conversion of **DPT** to **HMX** involved the complete non-selective cleavage of bonds within **DPT**.

Acetolysis on the other hand seems to be a selective process and ^{15}N studies[30] indicated very little isotopically mixed product in the conversion of **DAPT** to **TAT**, indicative of simple cleavage of the methylene bridge.

I.1.D. The Introduction of Fluorine into Explosive Materials

The introduction of a 2-fluoro-2,2-dinitroethoxy structure in ethers and acetals[31] represents an important class of energetic compounds, and it was proposed that the introduction of either fluoro or fluoroalkyl groups into the analagous acetamide derivatives of **RDX** and **HMX** would give novel compounds with improved explosive potential. Desmarteau and Malacrida[32] prepared a close fluorinated structural analogue to **RDX** from 3,3,4,4-tetrafluoro-2-(trifluoromethyl)-1,2-oxazetidine (**1**) using SbF_5 to give 2,2,4,4,6,6,-hexafluoro-1,3,5-tris(1,1,2,2,2-pentafluoroethoxy)-1,3,5-triazine (**2**), [1.3].

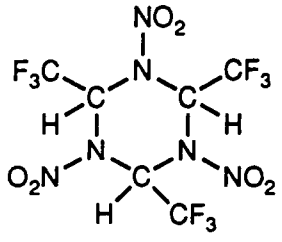


[1.3]

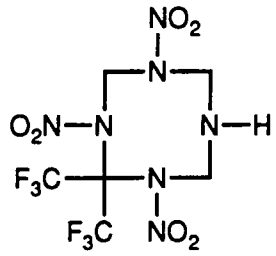
(1) (2)

and in 1971 Young and co-workers[33] claimed that the desired compound (**3**) had been made from a perfluorinated aldehyde and ammonia and that (**4**) had been prepared from

methylenedinitramine (MEDINA), formaldehyde and 2,2-diaminohexafluoropropane [1.4].



(3)



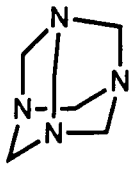
(4)

[1.4]

In this study (see Chapter 2) acetyl derivatives have been used as non-explosive models for **RDX** and **HMX**, and a brief discussion of these derivatives is given.

I.1.E. Derivatives and Intermediates for the Nitramine Explosives RDX and HMX

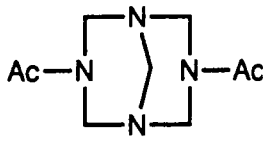
I.1.E.(1). Hexamethylenetetramine (Hexamine, Urotropine, Formin, Aminoform, Methenamine)



Hexamine may be formed quantitatively from the formaldehyde / ammonia reaction[34]. This reaction has received limited detailed study and understanding of the complex reaction mechanism is fairly tentative, although mechanistic studies[35,36,37] have been undertaken.

Hexamine is a colourless, odourless compound which crystallises in rhombic dodecahedrons[38]. The ^1H NMR exhibits a singlet at 4.75ppm, illustrating the equivalence of the six methylene groups[37]. The major use of hexamine was as a medicine and in resin manufacture.

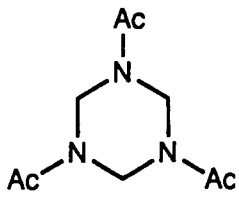
I.1.E.(2). **3,7-Diacetyl-1,3,5,7-tetraazabicyclo[3,3,1]nonane (DAPT)**



DAPT (named for DiAcetylPentamethyleneTetramine) was prepared in 1949 by Aristoff and co-workers[24] from the action of acetic anhydride on hexamine in a yield of 6%. In 1972 Hodge cited a yield of 9-45%[39], and in 1973 Gilbert and co-workers[40] produced **DAPT** in 34% yield, following modified conditions this yield was subsequently increased to over 90%[41].

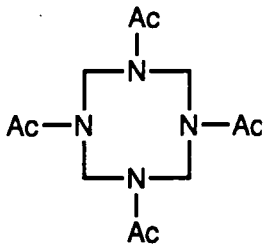
DAPT is a white, crystalline solid, crystallising in the monoclinic crystal system[42]. The structure is composed of two 6-membered C-N rings joined by a common N-C-N bridge. The preferred conformation is 'chair-chair'[43], although with bulky substituents a 'boat-chair' conformation is adopted[44].

I.1.E.(3). **1,3,5-Triacetylhexahydro-s-triazine (TRAT)**



TRAT was first prepared by Gradsten and Pollock[45] and later prepared by Gilbert and co-workers in 63% yield[40]. **TRAT** is a white, crystalline solid whose structural conformation depends on the bulkiness of the groups attached to nitrogen[46,47].

I.1.E.(4). **1,3,5,7-Tetraacetyloctahydro-1,3,5,7-tetrazocine (TAT)**



Gilbert and coworkers stated that the preparation of **TAT** was first cited in an unpublished government report of 1943 (declassified in 1956), which involved the reflux of **DAPT** with acetic anhydride and a trace of acetyl chloride to give a yield of 20-35%[20]. This yield was subsequently improved by the authors to 70% by heating **DAPT** with pure acetic anhydride for 3 hours at 110°C and further increased to 75-90% by Siele[48]. A further proceedure for the synthesis of **TAT** was reported by Coon[49] from the reaction of paraformaldehyde with methylene-bis-acetamide. This method would have been potentially a useful alternative route to **TAT** except for the low yield of 17%, as methylene-bis-acetamide is easily made from formaldehyde and acetamide[50], [1.5].

$$2(AcNH)_2CH_2 + 2CH_2O \longrightarrow TAT + H_2O \qquad [1.5]$$

was found that tetrafluoroethylene reacts in a similar manner to give imidyl fluorides which may be isolated as the α,α-difluoroacetamides by the addition of borax (to supply water)[73]. Secondary amines add to chlorotrifluoroethene[74] and this reaction was extended to other aliphatic and alicyclic secondary amines and to other fluoroolefins. The reactions are very exothermic and in some cases requires moderating with solvent[73] (Table 1.3).

Table 1.3

Nucleophilic Addition of Fluorocarbon Alkenes to Primary and Secondary Amines

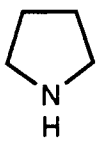
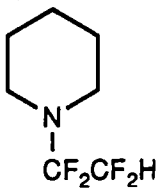
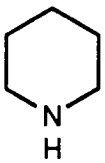
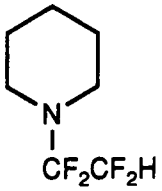
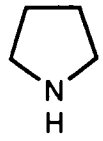
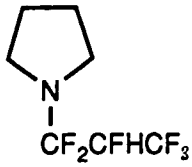
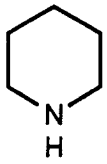
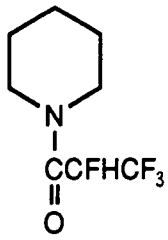
Amine	Alkene	Products	% Yield	Reference
Aliphatic				
$(C_2H_5)_2NH$	$CF_2=CF_2$	$HCF_2CF_2N(C_2H_5)_2$	77	73
$(C_2H_5)_2NH$	$CF_2=CFCl$	$HCFClCF_2N(C_2H_5)_2$	70	73
Cyclic				
	$CF_2=CF_2$		60	73
	$CF_2=CF_2$		85	73

Table 1.3 (cont.)

Amine	Alkene	Product	% Yield	Reference
	CF_2=$CFCF_3$		34	73
	CF_2=$CFCF_3$ / H_2O			56

I.2.C.(3) Addition to Cyclic Fluoroalkenes

There is an extensive literature concerning the addition of fluorinated cyclic olefins with primary[72,75,76,77] and with secondary[75,78,79,80] amines. In the case of primary amines the reaction products are iminoamines, secondary amines reacting to give monosubstitution in a vinylic position (Table 1.4).

Table 1.4

Nucleophilic Addition of Cyclic Fluoroalkenes to Primary and Secondary Amines

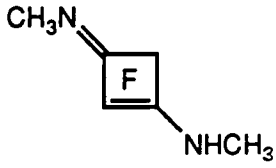
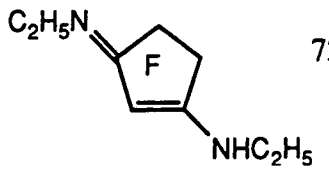
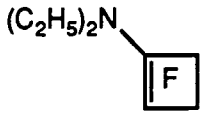
Amine	Alkene	Product	% Yield	Reference
CH_3NH_2			58	77
$C_2H_5NH_2$			72	77

Table1.4(cont.)

Amine	Alkene	Product	% Yield	Reference
$(C_2H_5)_2NH$			59	72

I.2.D. Tertiary Amines

I.2.D.(1). Addition to Fluoroalkenes

Despite the large number of nucleophilic reactions between amines and fluoroolefins, a number of free radical additions of aliphatic tertiary amines[56,57,58,81,82,83] and tertiary di-amines[84] are known (Table 1.5).

Table 1.5

Free Radical Addition of Fluoroalkenes to Tertiary Amines

Amine	Alkene	Initiation	Products	Reference
Me_3N	CF_2=CFCl	γ	$R_fCH_2NMe_2$, $(R_fCH_2)_2NMe$, $ClCHFCONMe_2$, $(R_f)_2CHNMe_2$ R_f= CF_2CFHCl	82
Et_3N	CF_2=CFCl	γ	$R_fCH(CH_3)NEt_2$, $(FCH_2CF_2CHMe)_2NEt$, $FCH_2CF_2CHMeNEt_2$, $R_fCFClCF_2CHMeNEt_2$, $(R_fCHMe)_2NEt$, $R_fCHFCF_2CHMeNEt_2$, $FCH_2CF_2CHMeN(Et)R_f$ R_f= CF_2CFHCl	82

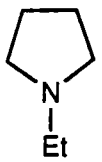
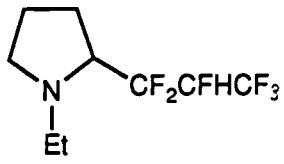
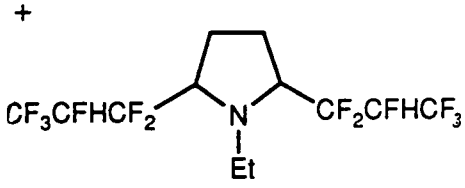
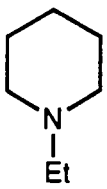
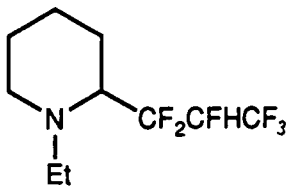
Table1.5(cont.)

Amine	Alkene	Initiation	Products	Reference
Me_2CHNMe_2	CF_2=CFCl	UV or γ	$R_fCH_2NMeCHMe_2$, $R_fCMe_2NMe_2$, $R_fCMe_2NMeCH_2R_f$ R_f= CF_2CFHCl	83
$Me_2N(CH_2)_2NMe_2$	CF_2=CF_2	UV	$R_fCH_2(Me)N(CH_2)_2NMe_2$, $Me_2NCH(R_f)CH_2NMe_2$, $R_fCH_2(Me)N(CH_2)_2N(Me)CH_2R_f$ R_f= CF_2CF_2H	84

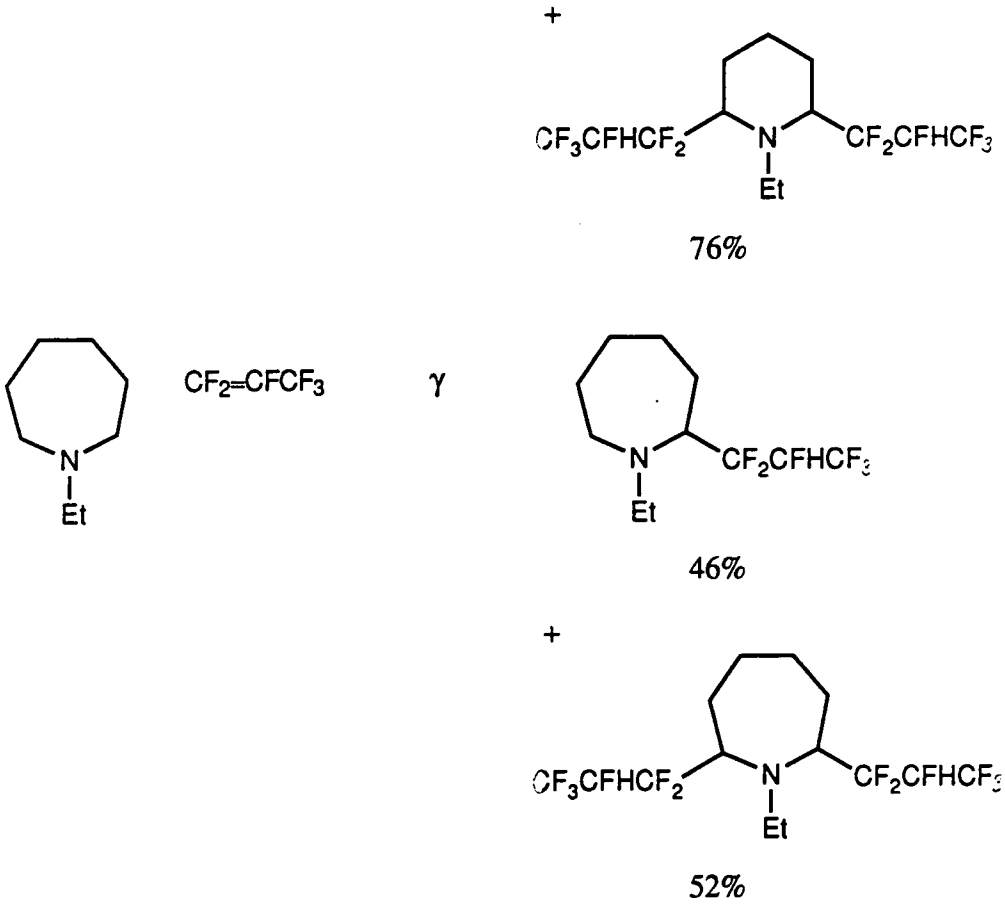
A series of cyclic tertiary amines has also been investigated[57] (Table 1.6).

Table 1.6

Free Radical Addition of Fluoroalkenes to Cyclic Tertiary Amines[57]

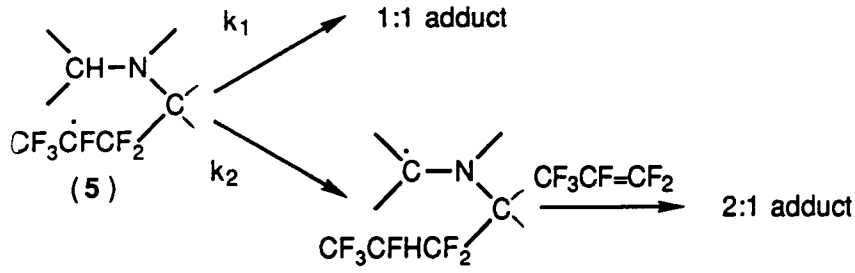
Amine	Alkene	Initiation	Products
	CF_2=$CFCF_3$	γ	 75% +  21%
	CF_2=$CFCF_3$	γ	 19%

Amine	Alkene	Initiation	Products



The variation in the distribution of mono- and di-adducts in the reactions of cyclic *N*-ethyl amines with hexafluoropropene (Table 1.6) demonstrates the presence of a stereoelectronic effect, which has previously been demonstrated for the analogous cyclic ethers[85,86]. Indeed the presence of a stereoelectronic effect has already been observed in amines from the rate of hydrogen abstraction by butoxy[87] and carbonate radicals[88].

The ratio of mono- and di-adducts produced will be related to a competition between (i) the intermediate radical (**5**) reacts to give mono-adduct (k_1) and (ii) an intramolecular [1,5] hydrogen shift occurs leading to a di-adduct (k_2)[89],(Scheme 1.1).



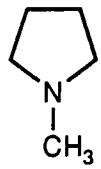
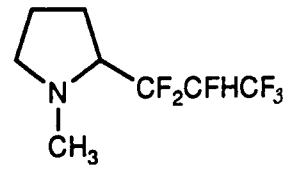
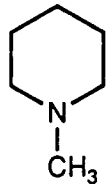
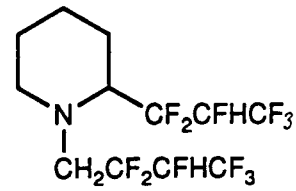
Scheme 1.1

It was proposed by Jones[57] that the rate of intramolecular [1,5] shift varies little within an analogous cyclic series, providing that the hydrogen being abstracted was not sterically hindered. The ratio of products, therefore, will be mainly influenced by the ease of hydrogen abstraction from the substrate by the adduct radical, a high proportion of mono-adduct resulting from a highly reactive cyclic amine.

This is illustrated in the reactions of *N*-methylpyrrolidine and *N*-methylpiperidine with hexafluoropropene (Table 1.7).

Table 1.7

Free Radical Addition of Hexafluoropropene to Cyclic Tertiary Amines[57]

Amine	Initiation	Products
	γ	 95%
	γ	 81%

In *N*-methylpyrrolidine it was proposed[57] that the stereoelectronic effect results in very easy abstraction of a hydrogen atom from the substrate molecule, and this is

reflected in the formation of a mono-adduct. The slow abstraction rate in the case of *N*-methylpiperidine results in a [1,5] intramolecular shift and the production of a di-adduct. From an observance of the percentage of mono-adduct formation an order of reactivity was found to be 5 > 7 > 6 as observed for ethers[85].

The order of reactivity reflects an increase in the value of the dihedral angle δ between the lone pair on nitrogen and the breaking C-H bond during the hydrogen abstraction process. If δ is small then effective overlap is possible creating a more stable radical intermediate[89].

I.2.D.(2). Addition to Cyclic Fluoroalkenes

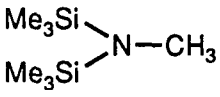
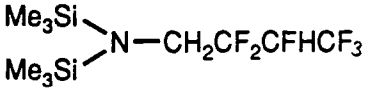
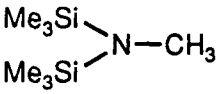
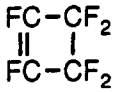
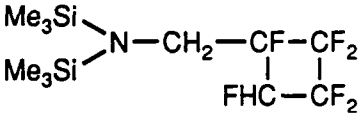
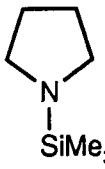
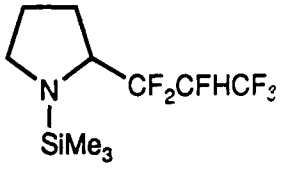
Tertiary amines react with cyclic fluoroalkenes by nucleophilic addition to form ylides[90] which may be isolated as the hydrolysed salts[91]. The addition of *N*-methyl-pyrrolidine to perfluorocyclobutene and perfluorocyclopentene gave unidentified products of nucleophilic attack, but with perfluorocyclohexene gave a free radical mono-adduct. The driving force for the nucleophilic reactions is the relief of ring strain in the 4-membered ring enhanced by eclipsing fluorine atoms. In the 6-membered ring the ring strain is substantially reduced in comparison with the 4-membered ring, and the free radical reaction is the preferred pathway.

I.2.E. Introduction of a Silyl Group into Primary and Secondary Amines

The ability of tertiary amines to react with fluoroalkenes by free radical addition reactions was explained by Swales[58] in terms of the increased crowding around nitrogen compared to primary and secondary amines. The author proposed that the use of a trimethylsilyl protecting group would give compounds structurally similar to tertiary amines and that the ease of removal of tthe trimethylsilyl group would give a simple synthetic route to primary and secondary fluorocarbon amines. There are several papers available on the use of the trimethylsilyl moiety as a protecting group[92,93], and examples of free radical adducts using this protecting group have been prepared (Table 1.8).

Table 1.8

Addition of Fluoroalkenes and Cyclic Fluoroalkenes to Primary and Secondary Amines Protected with Silyl Groups[58]

Amine	Alkene	Initiation	Product
Primary			
	$CF_2=CFCF_3$	γ	 86% (by GLC)
		γ	 90% (by GLC)
Secondary			
	$CF_2=CFCF_3$	γ	 62%

I.3. Amides

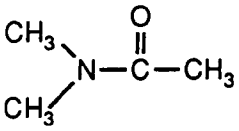
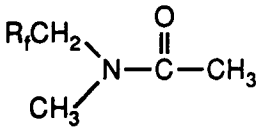
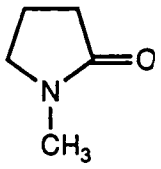
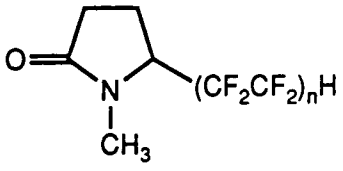
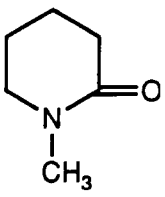
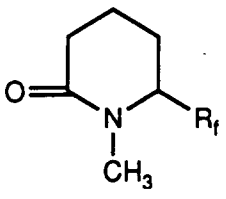
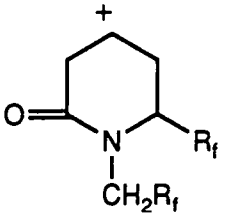
I.3.A. Introduction

The lower basicity of amides[57] in comparison to amines reduces the possibility of nucleophilic reaction with fluoroalkenes, although this must be contrasted with the lower availability of the lone pair of electrons on nitrogen for stabilisation of an intermediate radical in reaction with electrophilic alkenes.

Despite the problems mentioned above, amide additions are known from the literature with a range of fluoroalkenes (Table 1.9).

Table 1.9

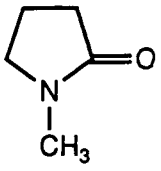
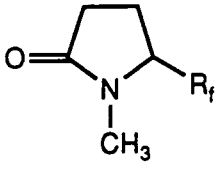
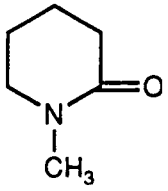
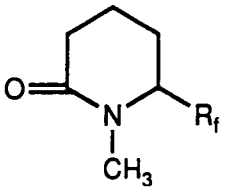
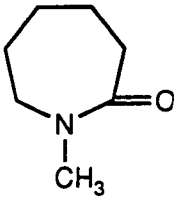
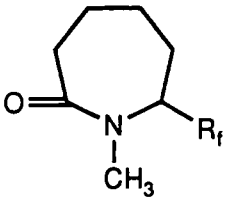
Free Radical Addition of Fluoroalkenes to Tertiary Amides

Amide	Alkene	Initiation	Products	Reference
	$CF_2=CFCF_3$	γ	 $R_f = CF_2CFHCF_3$	56,94
	$CF_2=CF_2$	$(tBuO)_2$		95
	$CF_2=CFCl$	UV/acetone	 +  $R_f = CF_2CFHCF_3$	96

I.3.B. Addition of Fluoroalkenes to Tertiary Amides

Jones[57] studied a series of cyclic amides, and found that in contrast to the reactions of esters[56], a high yield of adducts was observed (Table 1.10).

Table 1.10

Amide	Alkene	Initiation	Product	% conversion (from recovered alkene)
	$CF_2=CFCF_3$	γ		98
	$CF_2=CFCF_3$	γ		84
	$CF_2=CFCF_3$	γ		60

$R_f = CF_2CFHCF_3$

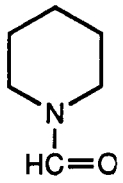
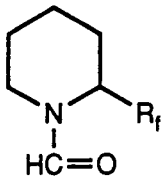
The additions of cyclic tertiary amides with hexafluoropropene in which the carbonyl group was incorporated in the ring gave only mono-adducts, in contrast to the cyclic amines[57]. In all cases reaction occured exclusively at the ring CH_2 so that the stereoelectronic effect could be determined directly from the amount of product produced, the yields indicating that even with an electron withdrawing carbonyl group the nitrogen atom is still effective at stabilising a radical centre. It was found that the reactivity order decreased in the order 5 > 6 > 7 which was different to amines[57] and ethers[85], and this series was confirmed by a series of competition experiments[57].

It appears that the conformation of the ring is affected by the presence of the sp^2 hybridised carbon atom, and that this effect is more pronounced for the 6-membered ring.

The introduction of a formyl group on nitrogen allows for the possibility of further adduct formation (Table 1.11).

Table 1.11

Free Radical Addition of Fluoroalkenes to Formyl Derivatives of Tertiary Amides

Amide	Alkene	Initiation	Product	Reference
$HCON(CH_3)_2$	$CF_2{=}CFCl$	UV/ acetone	$R_fCH_2\diagdown\diagup NCOR_f$ (with CH_3) + $(CH_3)_2NCOR_f$ + telomers; $R_f = CF_2CFHCl$	97
$HCON(CH_3)_2$	$CF_2{=}CFCF_3$	γ	$R_fCH_2\diagdown\diagup NCHO$ (with CH_3) + $(CH_3)_2NCOR_f$	56
			$R_fCH_2\diagdown\diagup NCOR_f$ (with CH_3) + ; $R_f = CF_2CFHCF_3$	
	$CF_2{=}CFCF_3$	γ	 $R_f = CF_2CFHCF_3$	57

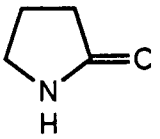
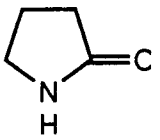
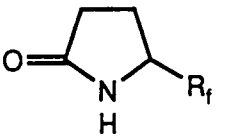
Jones[57] observed only mono-adduct formation in the reactions of cyclic formyl derivatives indicating the greater reactivity of the radical formed in the ring over the formyl radical.

I.3.C. Addition of Fluoroalkenes to Secondary Amides

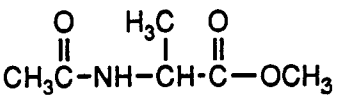
Amines containing a free N-H group readily undergo nucleophilic addition reactions. The presence of a carbonyl group in secondary amides renders the N-H group less basic and allows for the free radical reaction to compete (Table 1.12).

Table 1.12

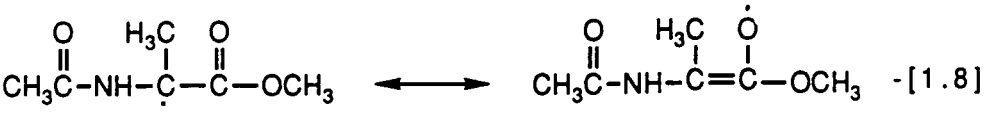
Free Radical Addition of Fluoroalkenes to Secondary Amides

Amide	Alkene	Initiation	Product	Reference
$(CH_3)_2CHNHCHO$	CF_2=$CFCl$	UV /acetone	$(CH_3)_2CHNHCOR_f$ $R_f = CF_2CFHCl$	96
	CF_2=CF_2	$(tBuO)_2$	Mixture of telomers	95
	CF_2=$CFCF_3$	γ	 $R_f = CF_2CFHCF_3$	57

The modification of biologically active compounds by the introduction of fluorine is widely known[98], and the modification of amino acids[99,100] is an area of great chemical interest. Swales[58] investigated the potential for the modification of amino acids by the introduction of a fluoroalkyl group using the amide derivative of alanine shown below.



The author observed that addition was not possible and accounted for the fact by a consideration of the intermediate radical. Delocalisation of the radical onto the carbonyl oxygen is possible and the combination of the increased radical stability together with the decreased nucleophilicity of the intermediate radical would disfavour addition to an electrophilic fluoroalkene, [1.8].



-[1.8]

CHAPTER TWO

FREE RADICAL REACTIONS OF NITROGEN CONTAINING SUBSTRATES

CHAPTER TWO

FREE RADICAL REACTIONS OF NITROGEN CONTAINING SUBSTRATES

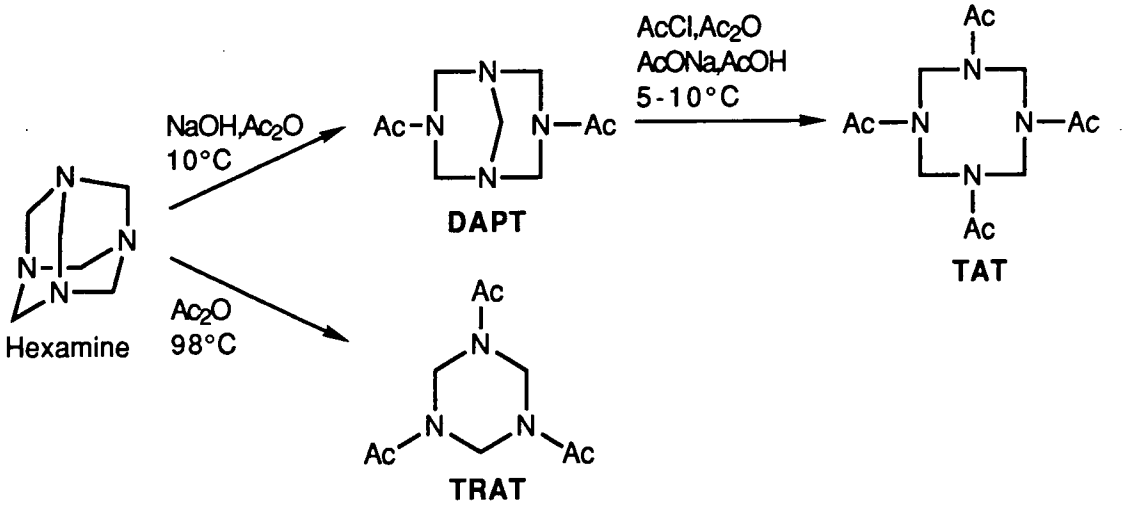
II.1. Introduction

Free radical reactions of amines and amides are of continuing interest in these laboratories, and several studies have been undertaken by previous workers[55,56,57,58]. This study aimed to continue this work with the aim of using the C-H bond as a functional group in the synthesis of fluorocarbon derivatives of amines and amides. The work described in this thesis was funded by the Ministry of Defence with the overall aim of modifying the non-explosive amide analogues of military high explosives, with specific reference to the explosives **RDX** and **HMX**.

II.2. Derivatives of High Explosives

Amide analogues of **RDX** and **HMX** used in this study were prepared from hexamine and acetic anhydride using conditions which lead exclusively to the formation of each derivative, Scheme 2.1.

Hexamine as a Starting Material in Amide Derivative Synthesis

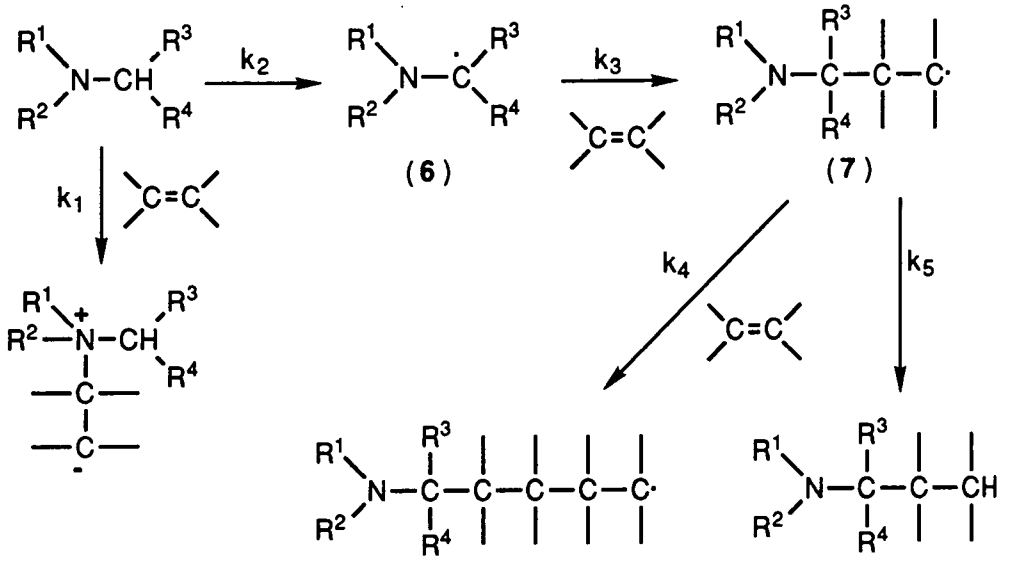


Scheme 2.1

Reaction of hexamine with electrophiles may involve either (i) selective cleavage of hexamine bonds or (ii) the total cleavage of hexamine to smaller fragments which may then recombine (section I.1.C.). Acetolysis under mild conditions results in selective bond cleavage which results in the preferential formation of **DAPT** and **TAT**, whilst more forcing conditions result in the total cleavage of hexamine to smaller fragments which recombine to give **TRAT**, Scheme 2.1.

II.3. Addition of Nitrogen Containing Substrates to Fluoroalkenes

II.3.A. Introduction



Scheme 2.2

Reaction of nitrogen containing substrates with alkenes is a competition between the rate of the nucleophilic addition process (k_1) and the rate of the free radical reaction (k_2), (section I.2). This study was concerned with the addition of nitrogen containing substrates to fluorinated alkenes, with the aim of producing fluorinated amine derivatives. Radicals formed adjacent to nitrogen are nucleophilic in character (section I.2.B.), and are ideally suited to react with electrophilic fluorinated alkenes. This is illustrated by the propagation step (k_3) in Scheme 2.2 involving the addition of radical (**6**) to a molecule of alkene with the formation of a new bond and the generation of adduct radical (**7**). This intermediate radical (**7**) may then either (i) abstract a hydrogen atom from the substrate

molecule to regenerate the initial radical (**6**) in a chain-transfer step (k_5), or alternatively (ii) add to another molecule of alkene (k_4). This alkene addition step could, in principle, continue leading to a range of telomeric adducts. Relative rates of (k_4) and (k_5) are dependent upon the ability of the alkene to telomerise, easily telomerisable alkenes such as tetrafluoroethene, vinylidene fluoride and chlorotrifluoroethene resulting in (k_4) being the preferred pathway, whilst alkenes which are not prone to telomerise such as hexafluoropropene result in (k_5) being the predominant pathway.

In this study the free radical reactions of a range of nitrogen containing substrates has been investigated using a variety of fluoroalkenes.

Free radical addition of amide derivatives (Scheme 2.1) was initially investigated using hexafluoropropene, which should lead to the chain transfer step (k_5) being the preferred reaction pathway. A solvent was used in order to improve contact between the substrate and the alkene, and the generation of radicals (**6**) was initiated using high energy (γ-rays) (at room temperature unless otherwise stated), thermal initiation (peroxides) and photochemical initiation (UV irradiation).

The results of this study are tabulated in Table 2.1.

Table 2.1

II.3.B. **Attempted Addition of Hexafluoropropene to Model Compounds for Explosives**

Substrate	Solvent	Initiation			Product
		Peroxide	γ-ray	UV/ Acetone	
Hexamine	CF_3CH_2OH	80°C			×
	CF_3CH_2OH	140°C			×
	CF_3CH_2OH		√		×
	CF_3CH_2OH			√	*a*
DAPT	CF_3CH_2OH	80°C			×
	CF_3CH_2OH	140°C			×
	CF_3CH_2OH		√		×
	Me_2CO		√		×
TRAT	Me_2CO	80°C			×
	Me_2CO	140°C			×
	Me_2CO		√		×
	Me_2CO			√	*b*
TAT	CF_3CH_2OH	80°C			×
	Me_2CO		√		×

a. UV/ acetone initiated reaction produced rapid darkening of the solution over a period of 2-3 hours resulting in the formation of an unidentified brown/black tar. No hexafluoropropene was recovered or starting material isolated.

b.UV/ acetone initiated reaction produced a very slight conversion to a mixture of mono- and di- adducts identified by mass spectrometry.

As the initial systems investigated above were unsuccessful, it was therefore decided to conduct a much more fundamental study into the reactions of nitrogen containing substrates, with the possibility that a better fundamental understanding might lead to

successful modification of the reactions described in Table 2.1, leading to the synthesis of fluorinated derivatives.

Substituent effects on radical (**6**), (Scheme 2.2), have been considered as sub-divided below. We have attempted to address each of these points experimentally in an effort to analyse the factors affecting reactivity.

1. The effect of varying substituents on nitrogen on ease of generation of radicals or their reactivity.
2. The effect of oxygen as a neighbouring heteroatom on the stability or reactivity of a radical.
3. The effect of nitrogen as a neighbouring heteroatom on the stability or reactivity of a radical.

Each of these effects will be considered to form an overall picture of the factors affecting reactivity.

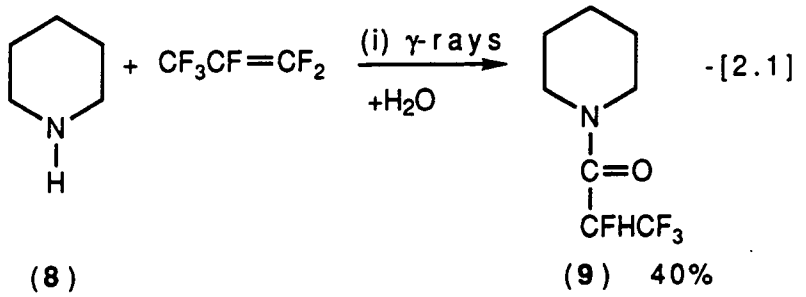
II.3.C. Reactions of Amine Derivatives with Hexafluoropropene

II.3.C.(1). Effect of Varying Substituents on Reactivity of Nitrogen Derivatives

II.3.C.(1).a. Introduction

The addition of both primary and secondary amines to fluoroalkenes is well known (section I.2.C.), the high base strength resulting in the nucleophilic addition process (k_1), Scheme 2.2, being the preferred reaction pathway.

This is illustrated by the reaction of piperidine (**8**) with hexafluoropropene[56], which gave the product of nucleophilic attack (**9**), [2.1].



(**8**) (**9**) 40% -[2.1]

Aliphatic secondary amines react in a nucleophilic reaction with fluoroalkenes, *e.g.* *N,N*-dimethylamine (**10**) was found to react in a previous study with hexafluoropropene to give tar formation, [2.2][58].

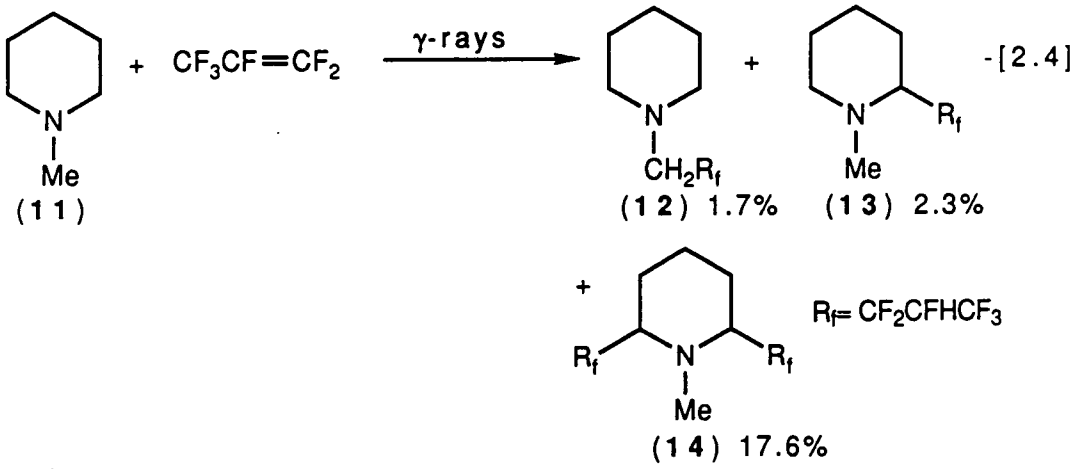
$$\underset{(10)}{Me_2NH} + CF_3CF{=}CF_2 \xrightarrow{\gamma\text{-rays}} \text{Tar formation} \quad -[2.2]$$

II.3.C.(1).b. **Tertiary Amines**

Addition of tertiary amines to hexafluoropropene, however, leads to products of free radical addition. It was found that triethylamine reacted in a previous study with hexafluoropropene to give several adducts[57], [2.3].

$$Et_3N + CF_3CF{=}CF_2 \xrightarrow{\gamma\text{-rays}} CH_3CH{=}NCH(CH_3)CF_2CFHCF_3\ 19\% \quad -[2.3]$$
$$+\ EtN(CH(CH_3)CF_2CFHCF_3)_2\ 67\%$$
$$+\ N(CH(CH_3)CF_2CFHCF_3)_3\ 14\%$$

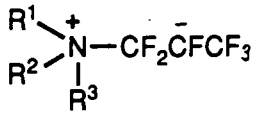
and *N*-methylpiperidine (**11**) reacted with hexafluoropropene to give the mono-adducts (**12**) and (**13**), and a di-adduct (**14**)[56], [2.4]. It was also noted by the author that nucleophilic attack had occured, from the formation of oligomers of hexafluoropropene.



Therefore,in the case of tertiary amines it would appear that the rate of the free radical reaction (k_2), Scheme 2.2, is able to compete successfully with the rate of the nucleophilic reaction (k_1) leading to the corresponding products of free radical addition.

A possible explanation for this may be a result of either:-

1. The larger steric requirement of a tertiary amine hinders nucleophilic attack on a fluoroalkene or results in a crowded transition state in vinylic substitution.
2. The product of nucleophilic addition, zwitterion (**15**), has a longer lifetime.

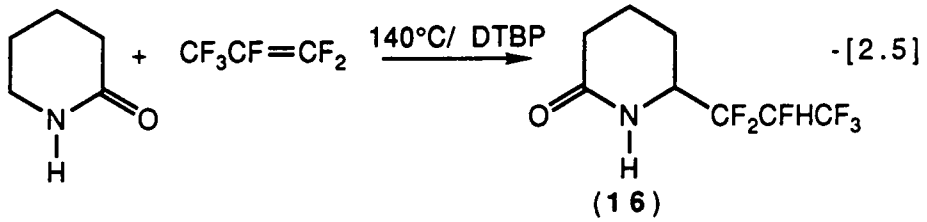


(15)

II.3.C.(1).c. **Cyclic Amides**

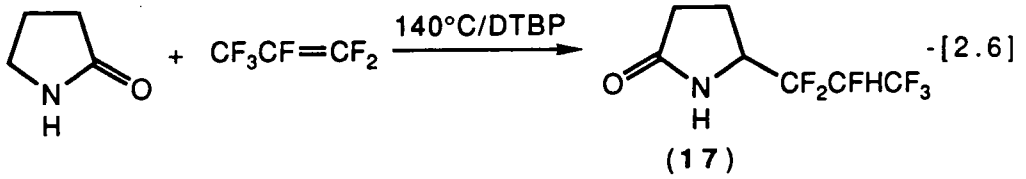
As the nucleophilic reaction of amines is promoted by the availability of the lone pair of electrons on nitrogen, then it may be possible to bring about a reduction in the availability of this lone pair for reaction by modifying primary and secondary amines.

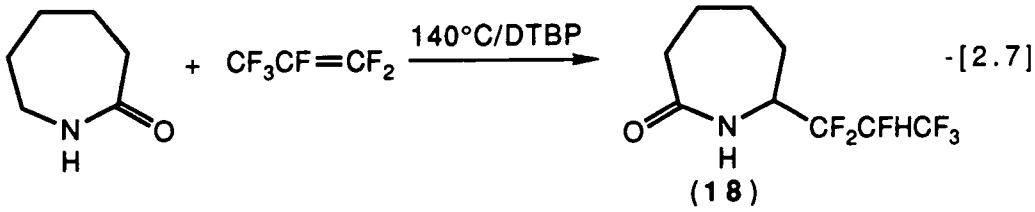
Introduction of a carbonyl group adjacent to the N-H of (**8**) leads to successful free radical reaction with hexafluoropropene[95] giving the mono-adduct (**16**), [2.5],



(16)

and this reaction may be extended to cover other cyclic amides, *e.g.* the reaction of 2-pyrrolidinone with hexafluoropropene gave the mono-adduct (**17**), [2.6], and the reaction of ε-caprolactam gave (**18**)[95], [2.7].

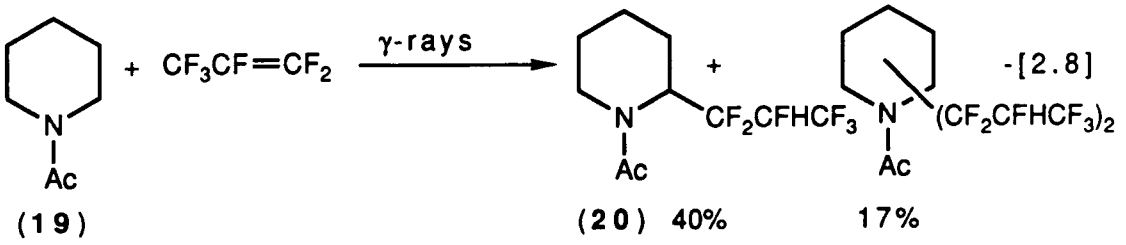




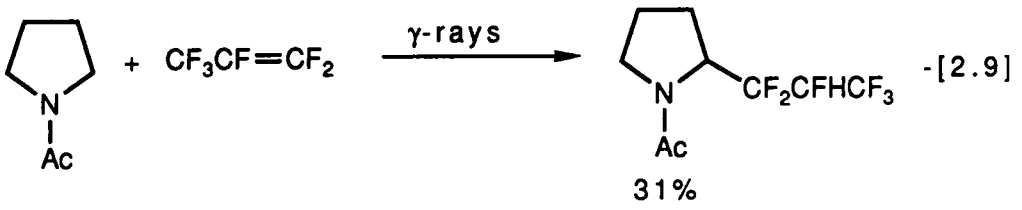
The presence of an electron withdrawing group adjacent to nitrogen results in a reduction in the availability of the lone pair of electrons for radical stabilisation, and this results in suppression of the rate of the nucleophilic addition process (k_1). However an electron withdrawing carbonyl group probably also leads to a reduction in the stability (less interaction between the radical centre and the lone pair on nitrogen), and nucleophilic character of radicals formed adjacent to nitrogen, hence the rate of the free radical reaction (k_2) will also be reduced, but the effect of the electron withdrawing group is clearly more pronounced on the rate of the nucleophilic reaction, allowing the free radical reaction to compete. Thus reactions [2.5]. [2.6] and [2.7] gave products of free radical addition, exclusively.

II.3.C.(1).d. Acyl Derivatives of Amines

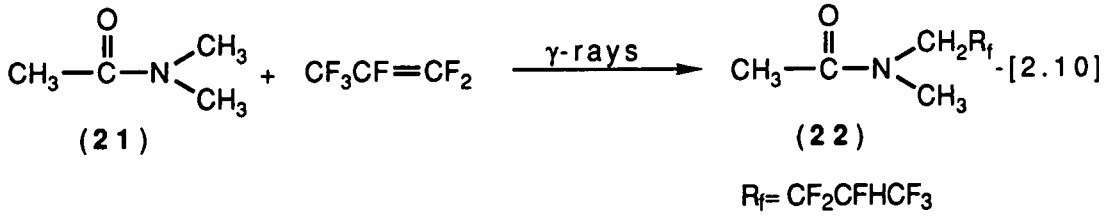
If the carbonyl group is placed outside the ring, then products of free radical reaction would also be expected to be observed, and this is indeed found to be the case. In a previous study *N*-acetylpiperidine (**19**) reacted with hexafluoropropene to give a mixture of the mono-adduct (**20**) and an unassigned mixture of di-adducts[56], [2.8]. Again the absence of hexafluoropropene oligomers indicates that the free radical process is able to compete effectively.



Similarly *N*-acetylpyrrolidine was found to react with hexafluoropropene to give the mono-adduct[57], [2.9].

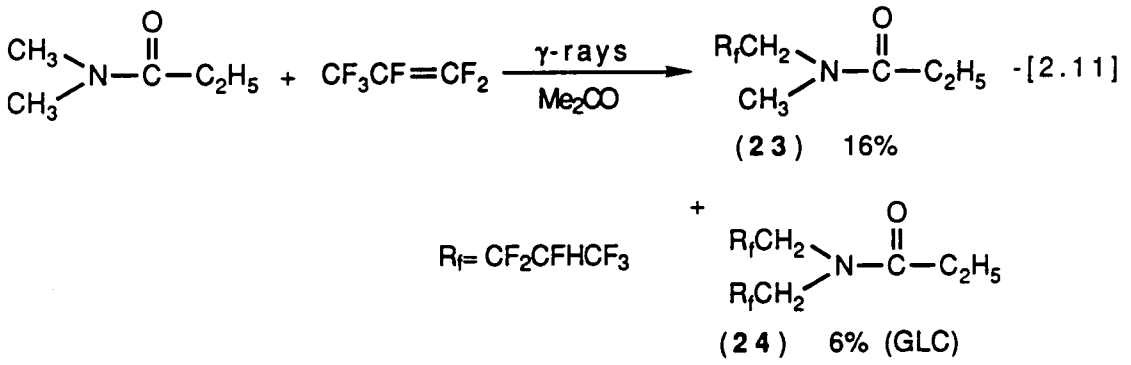


The same methodology used in the modification of the cyclic secondary amines may also be used for the modification of aliphatic secondary amines via the introduction of an acetyl group. Introduction of an acetyl group in (**10**) gives *N,N*-dimethylacetamide (**21**) which was found in a previous study to react with hexafluoropropene giving the mono-adduct (**22**)[56], [2.10].



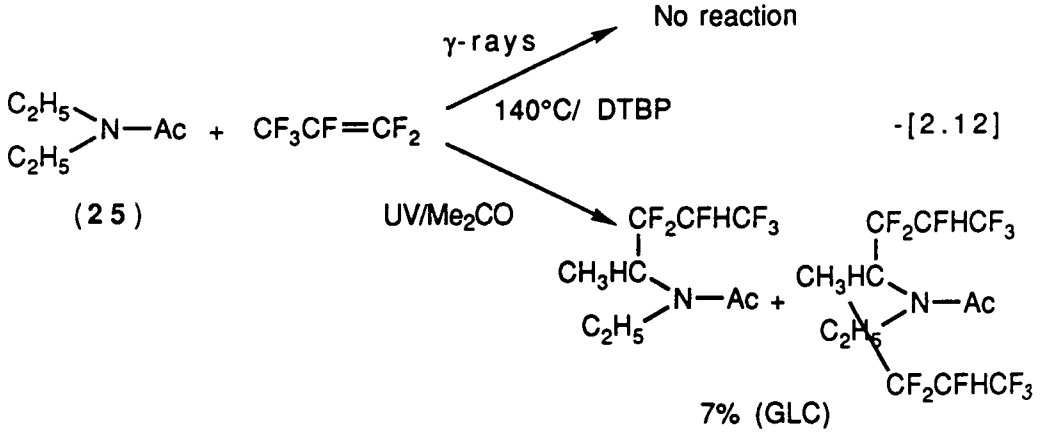
The nucleophilicity of a radical formed from compound (**22**) would be greatly reduced by the combined electron withdrawing effects of both the acetyl and fluoroalkyl groups, and consequently further reactivity with an electrophilic radical would not be expected.

In an analogous reaction the introduction of an ethanoyl moiety to give *N,N*-dimethylpropionamide gave the mono-adduct (**23**) on reaction with hexafluoropropene, together with a low conversion to di-adduct (**24**), identified by G.C. mass spectrometry, [2.11].



-[2.11]

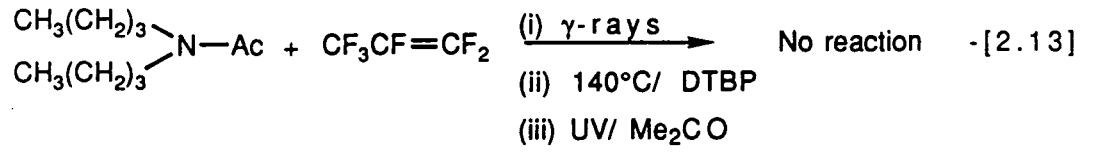
Surprisingly, introduction of an acetyl group into the homologous *N,N*-diethylamine results in no addition to hexafluoropropene using either γ-ray or peroxide initiation. UV initiation with acetone as photosensitizer results in a very low conversion to a mixture of mono- and di-adducts (from G.C. mass spectrometry), [2.12]. The site of addition of the second molecule of alkene is uncertain and this is illustrated in [2.12] by a bond drawn to the centre of the product.



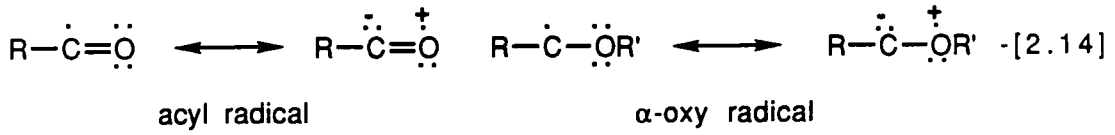
-[2.12]

The only reasonable explanation of this result would seem to be in (**25**) adopting an unfavourable stereochemistry which prevents good orbital overlap between the lone pair on nitrogen and the breaking C-H bond of the radical, or, alternatively, steric inhibition of the addition step. A further illustration of this effect may be observed on comparing the free radical yields of [2.15] and [2.16].

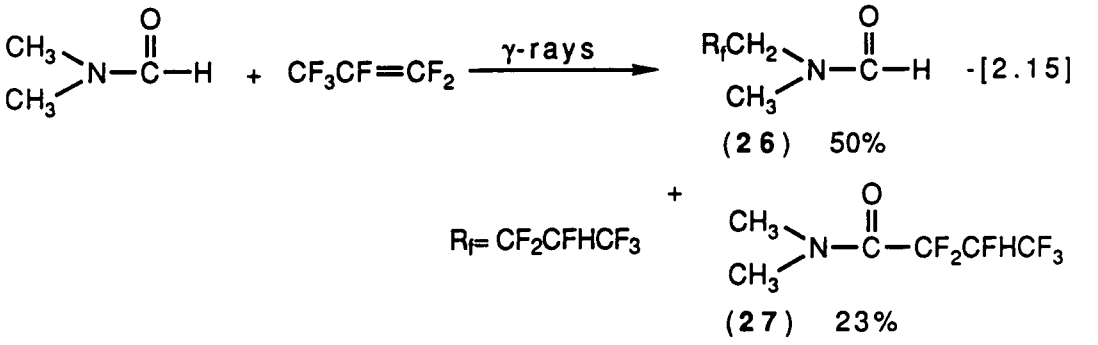
Steric constraints observed in the reaction of (**25**) with hexafluoropropene seem to be enhanced in the reaction of *N,N*-dibutylacetamide, which does not react with hexafluoropropene even with UV initiation, [2.13].



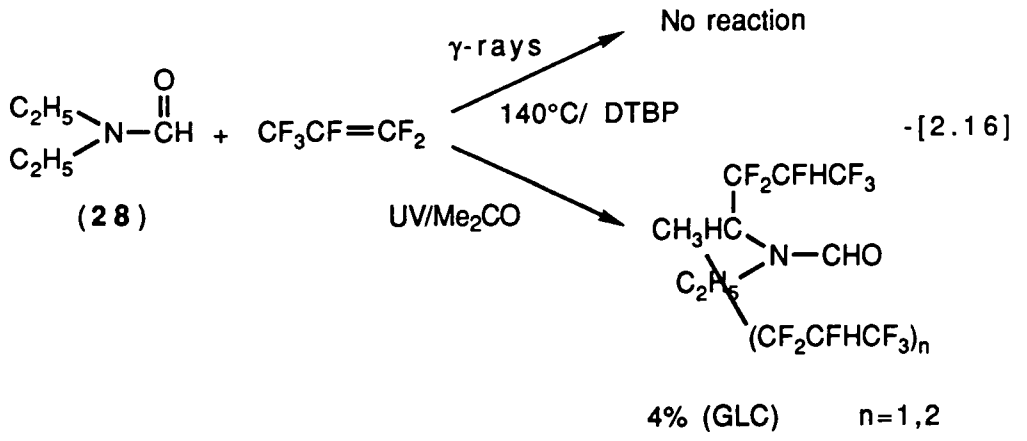
If the acetyl protecting group is replaced by a formyl group then the possibility of alternative reaction at this group exists, the stabilisation of an acyl group being analogous to the stabilisation encountered in the α-oxy radical of an ether, [2.14].



This type of process was observed in a previous study where *N*,*N*-dimethylformamide reacted with hexafluoropropene to give the methyl substituted adduct (**26**) and the formyl substituted adduct (**27**)[56] in a reasonable yield, [2.15].



The corresponding reaction of the higher amide homologue *N*,*N*-diethylformamide (**28**) gave no adduct formation with hexafluoropropene using either γ-ray or peroxide initiation, but with photochemical initiation very low conversion to a mixture of di- and tri-adducts was observed (G.C. mass spectrometry), [2.16].



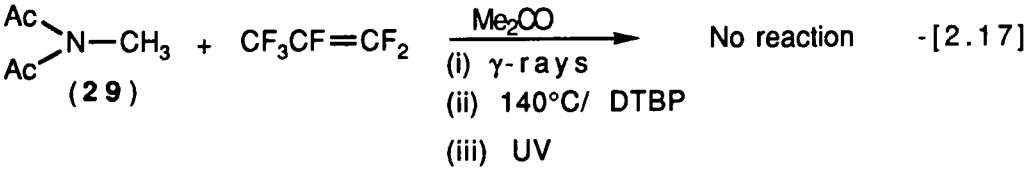
(28) -[2.16]

The site of addition of the second and third molecules of fluoroalkene is uncertain and this is illustrated in [2.16] by a bond drawn to the centre of the product.

A surprisingly low yield in the reaction of (**28**) with hexafluoropropene in comparison with reaction [2.15] illustrates *a remarkable sensitivity of reactivity towards comparatively small changes in steric requirements of the system.*

Having successsfully achieved competitive free radical reactions of secondary amines via the introduction of a carbonyl group, it was possible that the reactivity of primary amines could be modified in a similar way.

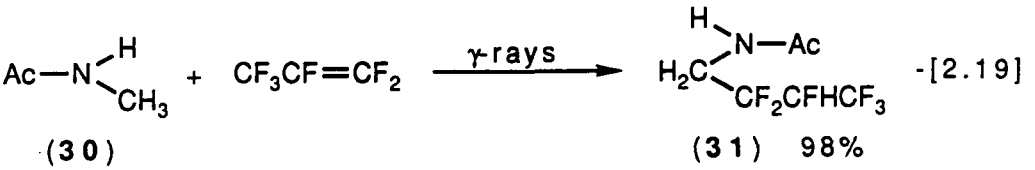
Methylamine may be protected by the introduction of two acetyl groups to give *N,N*-methyldiacetamide (**29**). However reaction of (**29**) with hexafluoropropene gave no products of free radical addition using either γ-ray, peroxide or photochemical initiation, [2.17].



(29) -[2.17]

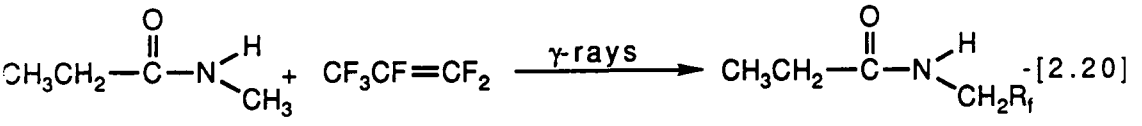
Thus, although we have eliminated competing nucleophilic attack, the presence of the two electron withdrawing acetyl groups has inhibited the ability of nitrogen to stabilise an adjacent radical centre, [2.18], and this leads to reduced nucleophilicity of the radical resulting in a lower reactivity with electrophilic alkenes.

Subsequently, it was found that only one carbonyl protecting group need be present in order to sufficiently suppress the nucleophilic reaction and to allow the free radical reaction to occur. In a previous study *N*-methylacetamide (**30**) reacted readily with hexafluoropropene to give the product of mono-addition (**31**)[57], [2.19].



(**30**) (**31**) 98% -[2.19]

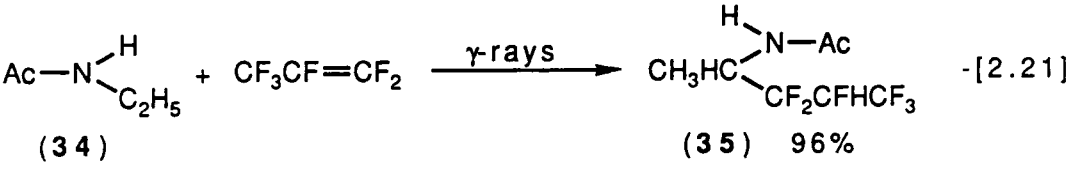
Again, however, the system is very sensitive to steric effects because the ethanoyl derivative (**32**), [2.20], gave a very much reduced yield in comparison with [2.19].



(**32**) (**33**) 9.5% -[2.20]

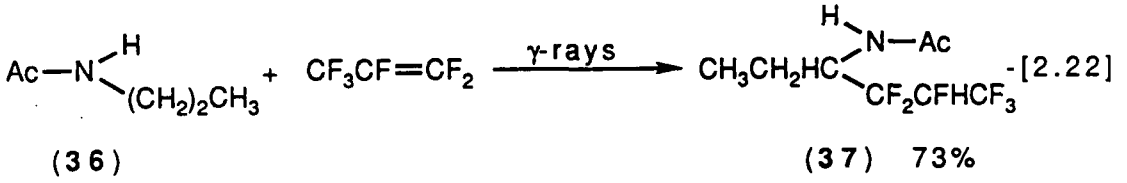
R_f= CF_2CFHCF_3

These steric effects are, however, remarkably subtle because N-ethylacetamide (**34**) gave an almost quantitiative conversion to the mono-adduct (**35**) on reaction with hexafluoropropene, [2.21]. It is extremely difficult to explain the difference in reactivity between (**32**) and (**34**).



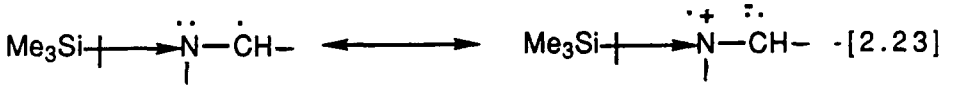
(**34**) (**35**) 96% -[2.21]

N-(^{n}propyl)acetamide (**36**) also reacted with hexafluoropropene to give the corresponding mono-adduct (**37**) in high conversion, [2.22].



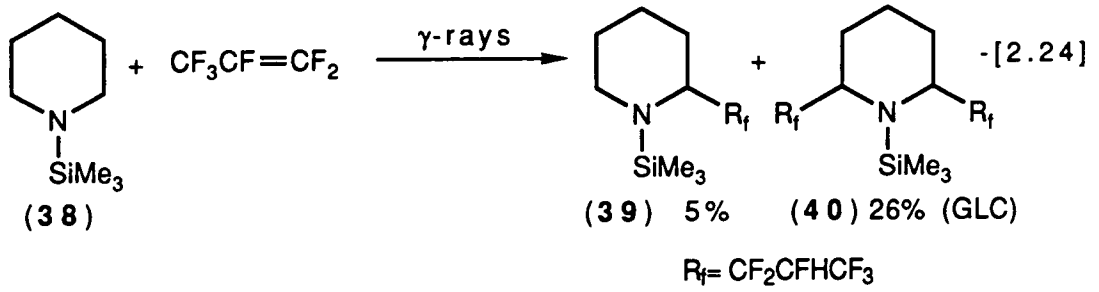
(36) (37) 73%

Obviously, introduction of the acetyl group has been partly successful in promoting the reactions of the secondary amides [2.9], and (**25**), [2.12], but the lower availability of the lone pair of electrons on nitrogen, necessary for inhibiting the ionic process, also seems to reduce stabilisation of a radical. The question then posed is: is it possible to produce protected secondary amine derivatives with the same ability to hinder nucleophilic addition as an acetyl group but which will not reduce the availability of the lone pair for radical stabilisation? Introduction of a trimethylsilyl group could be the answer as the substantial steric requirements of this group would be able to hinder the nucleophilic reaction whilst not reducing the availability of the electron pair. Additionally, the trimethylsilyl group is easily introduced and removed (there are several review articles available on this subject[92,93]), and is able to stabilise an adjacent radical centre by electron donation, [2.23], and provided that this group does not interfere with the free radical reaction then such derivatives could in principle be a particularly useful synthetic procedure.



II.3.C.(1).e. **Trimethylsilyl Derivatives Of Amines**

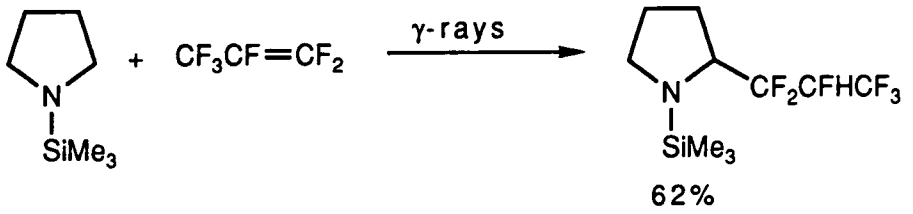
Piperidine (**8**) was converted to the trimethylsilyl derivative *N*-trimethylsilylpiperidine (**38**), which did, indeed, react with hexafluoropropene to give a mono-adduct (**39**), isolated by distillation, together with a di-adduct (**40**) which could not be separated (identified by G.C. mass spectrometry), [2.23].



-[2.24]

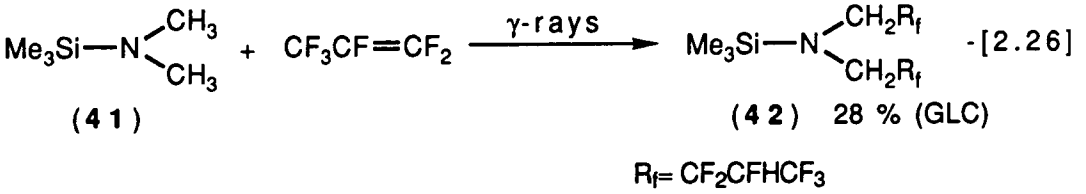
The overall yield of (**38**) with hexafluoropropene is comparable to the yield of (**19**), [2.8], although the production of mainly di-adduct (**40**) in the case of reaction [2.24] clearly indicates enhanced reactivity in the trimethylsilyl derivative.

Using a deficiency of hexafluoropropene, previous studies have shown an even more marked difference in reactivity between *N*-trimethylsilylpyrrolidine[58], [2.25], and the corresponding acetyl protected substituent[57], [2.9].



-[2.25]

Using a trimethylsilyl group for protection with aliphatic secondary amines is also found to be beneficial. *N,N*-dimethyltrimethylsilylamine (**41**) gave exclusively the di-adduct (**42**) on reaction with hexafluoropropene, [2.26].

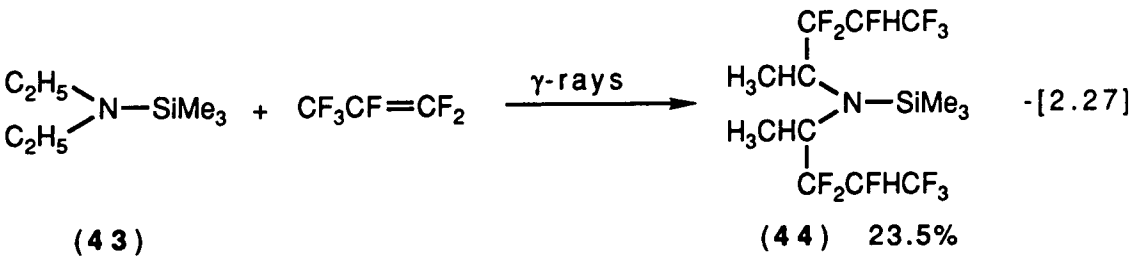


-[2.26]

This is in contrast to the reaction of (**21**) with hexafluoropropene which gave only the mono-adduct (**22**), [2.10]. The nucleophilicity of a radical produced from the initially formed mono-adduct in the reaction of (**41**) with hexafluoropropene would only be reduced by the presence of the fluoroalkyl group, and it is possible that intramolecular

hydrogen atom abstraction would lead to further radical formation leading to the di-adduct (**42**).

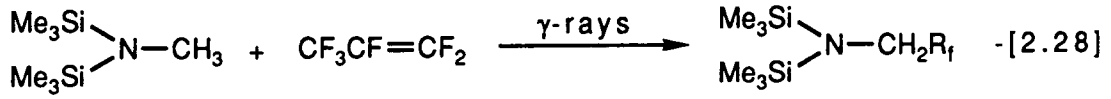
Similarly *N*,*N*-diethyltrimethylsilylamine (**43**) reacted with hexafluoropropene to form the di-adduct (**44**), [2.27].



(**43**) (**44**) 23.5%

Although steric effects may still be important (the yield in [2.27] is relatively low), there is however a marked increase in the reactivity of (**43**) in comparison with (**25**) in [2.12]. Production of the di-adduct (**44**) would seem to indicate that the lone pair on nitrogen is readily available for stabilisation of a free radical, and that the trimethylsilyl group is a good chain transfer agent.

This same methodology may be extended to cover primary amines. Introduction of two trimethylsilyl groups allows methylamine to be protected as *N*,*N*-bis(trimethylsilyl)methylamine (**45**). Reaction of (**45**) with hexafluoropropene was found in a previous study to give the mono-adduct (**46**) in high yield[58], [2.28].



(**45**) (**46**) 86% (GLC)

R_f= CF_2CFHCF_3

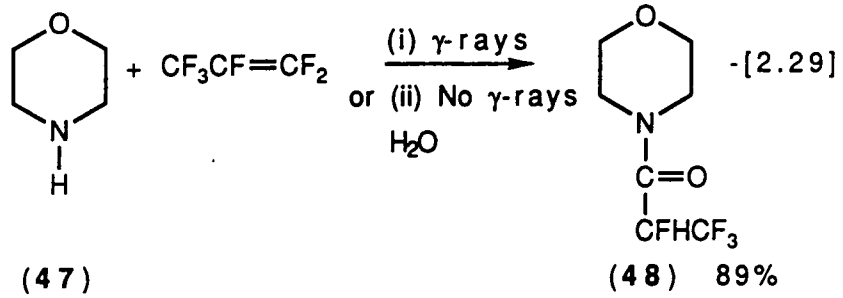
This reaction may be compared to the di-acetyl derivative (**29**), [2.17], which failed to react with hexafluoropropene, confirming that the trimethylsilyl groups are able to sterically hinder the nucleophilic reaction without reducing the nucleophilicity of a radical formed α- to nitrogen.

It would therefore appear that the introduction of a trimethylsilyl group is beneficial over an acetyl group in promoting free radical reactions.

II.3.C.(2). Effect Of Introducing An Oxygen Atom On The Reactivity Of Nitrogen Derivatives

The question which must now be addressed is whether the introduction of a second heteroatom will affect this general order of reactivity. It was possible that the introduction of an oxygen atom into a cyclic secondary amine may have a strong enough inductive electron withdrawing effect to lower the availability of the nitrogen lone pair, thus reducing the rate of the nucleophilic reaction (k_1) and allowing the free radical reaction (k_2) to compete.

Morpholine (**47**) however reacted via a nucleophilic addition process with hexafluoropropene to give (**48**), [2.29].

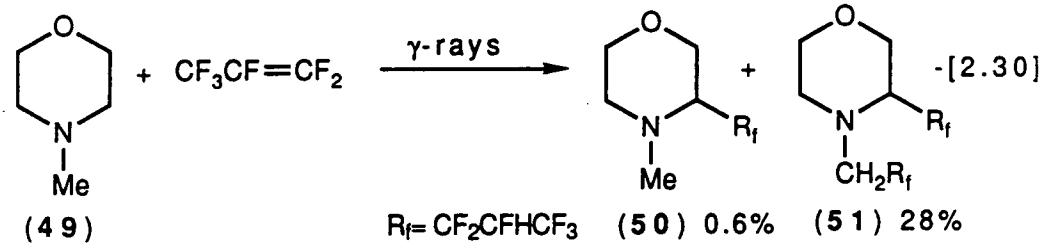


(**47**) (**48**) 89%

Clearly, the amine nitrogen of (**47**) is sufficiently basic to allow the nucleophilic reaction to proceed leading to adduct (**48**).

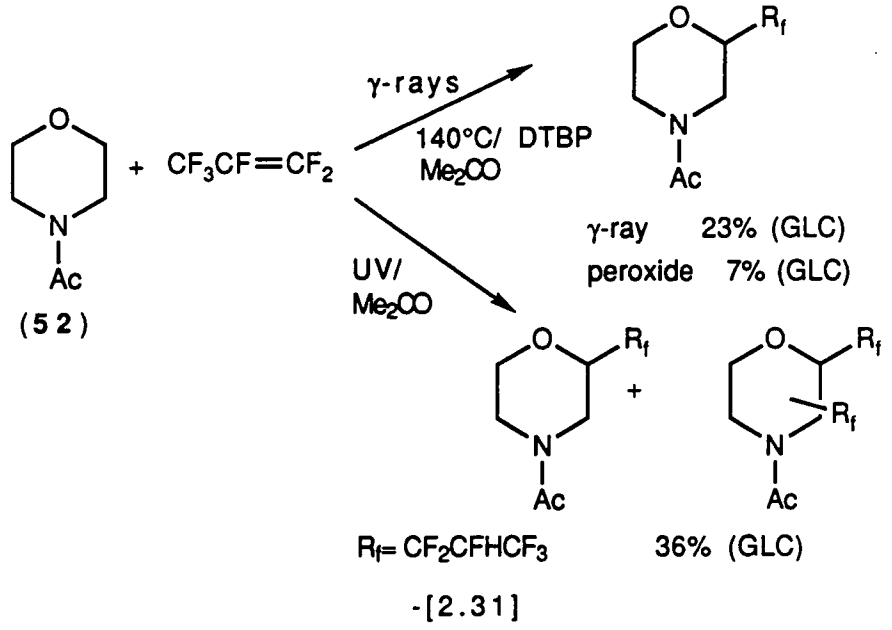
II.3.C.(2).a. Oxygen Containing Tertiary Amines

Addition of tertiary amines to hexafluoropropene however seem to result in predominently the products of free radical reaction. *N*-methylmorpholine (**49**) had previously been found to react with hexafluoropropene[56] to give a trace of mono-adduct (**50**) together with a di-adduct (**51**), [2.30], and it was noted that some nucleophilic reaction had also occured from the formation of oligomers of hexafluoropropene. It was also noted that adducts (**50**) and (**51**) were produced mainly adjacent to the nitrogen atom.



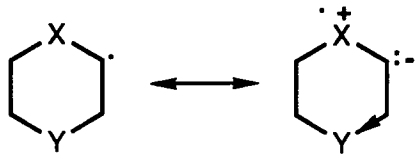
II.3.C.(2).b. **Oxygen Containing Acyl Derivatives**

Protecting (**47**) as the acetyl derivative should lead to products of free radical addition, as was observed for (**19**) in [2.8]. *N*-acetylmorpholine (**52**) was found in a previous study to give a low yield of a mixture of mono-adducts which could not be separated, on reaction with hexafluoropropene[56], [2.31].



In our study the use of peroxide initiation resulted in an even lower yield of a mixture of mono-adducts, but in comparison, the use of photochemical initiation gave a greatly improved yield together with the identification of di-adducts. Separation of the mixture was precluded due to the similar GLC retention times of the products, and identification of the adducts was only possible from ^{19}F NMR and G.C. mass spectrometry. For reasons which will be discussed later, it is assumed that addition occurred next to the oxygen atom.

The lower reactivity of (**52**) with hexafluoropropene may be contrasted with the reactivity of (**19**), [2.8]. Introducing an oxygen atom separated from the first heteroatom by two or more methylene units can only give rise to an electron withdrawing inductive effect; and this would result in two effects illustrated in the generalised system, [2.32], (i) the rate of addition step (k_3) would be lowered as a result of a reduction in the nucleophilicity of the substrate radical (**6**),

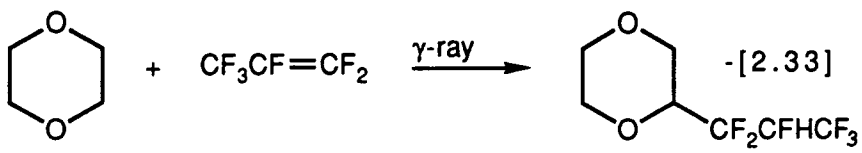


-[2.32]

and also (ii) have an effect on the chain-transfer step (k_5) (Scheme 2.2), because the radical (**7**) is derived from hexafluoropropene, and would therefore be quite electrophilic. The additional heteroatom in the substrate would therefore make the hydrogen atom abstraction process,(k_5), less favourable. Thus the combined effect of a less nucleophilic substrate radical together with the lower rate of hydrogen atom abstraction from the substrate by an electrophilic adduct radical is to reduce the reactivity of (**52**) with fluoroalkenes.

An analogous effect was illustrated in a competition experiment carried out by Grievson[56] from the greater reactivity of oxane compared to p-dioxane (**53**) for a deficiency of perfluorocyclobutene and perfluorocyclopentene.

However with hexafluoropropene (**53**) was still found to react well giving a high conversion to mono-adduct (**54**)[56], and this is, at first sight, puzzling, [2.33].

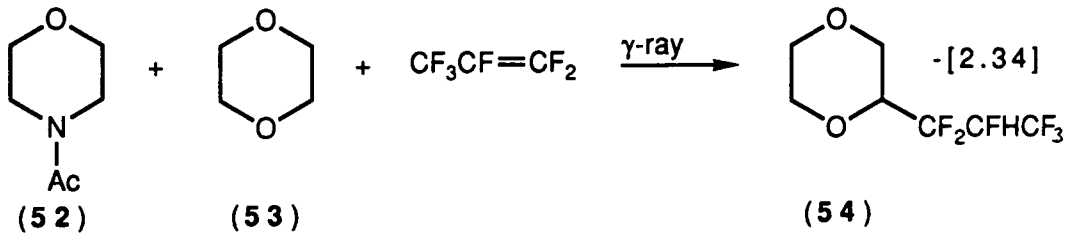


-[2.33]

(**53**) (**54**)

However a competition reaction between (**52**) and (**53**) for a deficiency of hexafluoropropene gave addition of the fluoroalkene exclusively on (**53**) following γ-ray

initiation, confirming the greater activating influence of oxygen than a substituted nitrogen atom, [2.34].



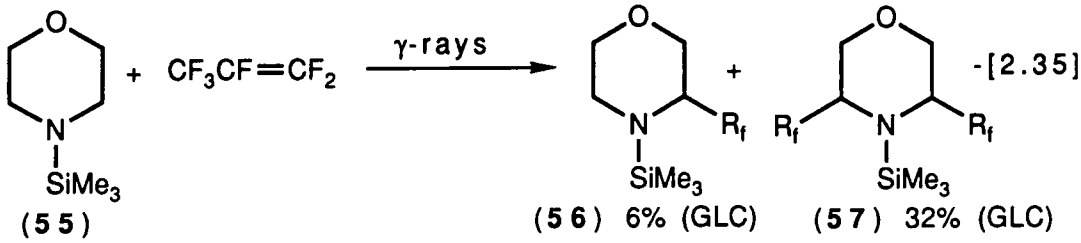
(52) (53) (54)

It therefore seems likely that the reaction of (**52**) with hexafluoropropene leads to addition principally next to the oxygen atom.

Since we have established that a trimethylsilyl group is known to be beneficial over an acetyl group, then the introduction of a trimethylsilyl group as a protecting group for (**47**) should in principle lead to enhanced free radical reactivity.

II.3.C.(2).c. Oxygen Containing Trimethylsilyl Derivatives

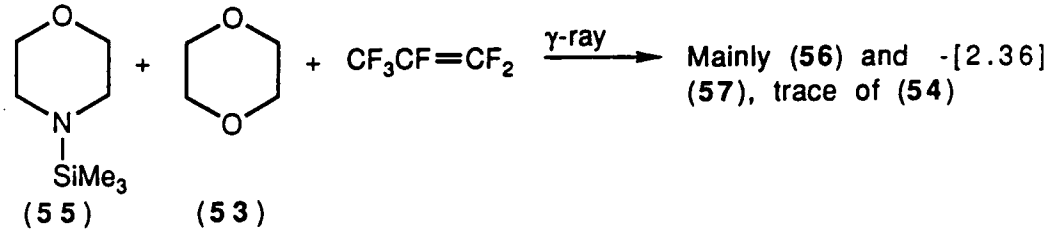
This was indeed observed to be the case. *N*-trimethylsilylmorpholine (**55**) reacted with hexafluoropropene to give the mono-adduct (**56**) and a di-adduct (**57**), although it was only possible to separate and characterise the di-adduct (**57**), [2.35].



(55) (56) 6% (GLC) (57) 32% (GLC)

$R_f = CF_2CFHCF_3$

That addition occured next to nitrogen was found from a competition reaction between (**55**) and (**53**) for a deficiency of hexafluoropropene. Addition of the fluoroalkene mainly on (**55**) following γ-ray initiation confirmed the greater activating influence of the trimethylsilyl substituted nitrogen atom over the oxygen atom, [2.36].



(55) (53)

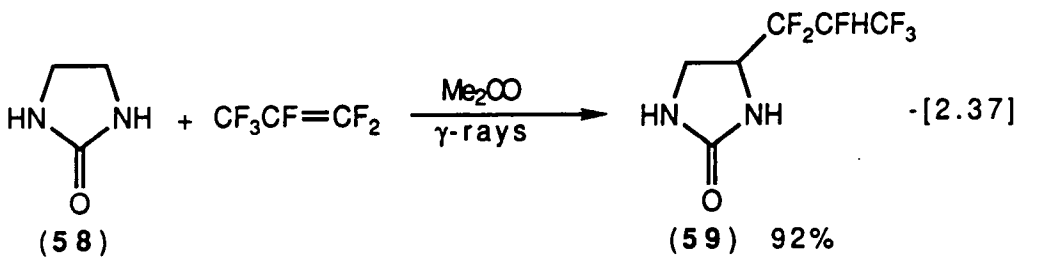
Again the absence of oligomers of hexafluoropropene is indicative of the greater steric crowding.

In conclusion the introduction of a second heteroatom has an associated inductive effect which acts to reduce the nucleophilicity and stability of the initially formed substrate radical together with the ability of the intermediate adduct radical (**7**) to abstract a hydrogen atom from a second molecule of substrate in the chain-transfer step (k_5). Additionally, the effect of an electron withdrawing substituent on nitrogen (*i.e.* an acetyl group) acts to destabilise the radical, resulting in the low reactivity of (**52**), [2.31]. The introduction of a trimethylsilyl group to some extent counters the inductive effect of the oxygen atom and consequently a higher degree of reactivity is observed.

What then is the effect of the introduction of a second nitrogen atom into cyclic systems?

II.3.C.(3). Effect Of Introducing A Second Nitrogen Atom- Diamine Derivatives

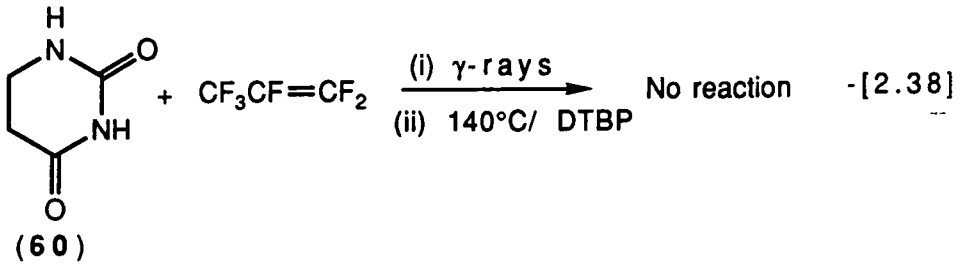
A second nitrogen atom within a ring also requires protection. As was discussed for monoamine systems, introduction of a carbonyl group is able to reduce the availability of the lone pair of electrons on nitrogen for participation in nucleophilic addition, thus allowing the free radical reaction to compete. Consequently, we have established that reaction of the cyclic urea 2-Imidazolidinone (**58**) with hexafluoropropene using acetone as solvent, gave the mono-adduct (**59**) in very high yield, [2.37].



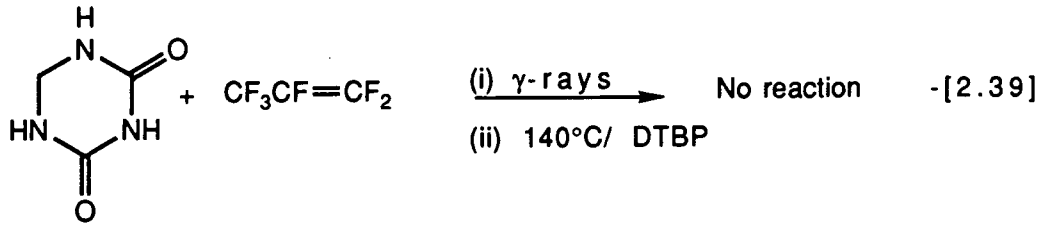
(58) (59) 92%

Adduct (**59**) is potentially useful because hydrolysis would lead to a fluoroalkyl derivative of 1,2-diaminoethane, which may be useful as a polymer precursor.

With the successful reaction of (**58**) , the scope of these reactions was explored to cover related compounds such as 5,6-dihydrouracil (**60**), [2.38], and 2,4-dioxohexahydro-s-triazine (**61**), [2.39].

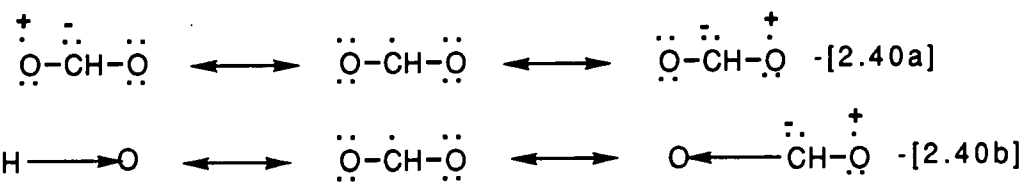


(**60**)



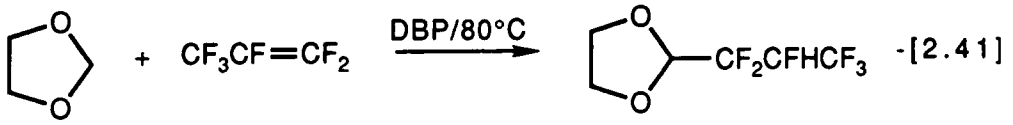
(**61**)

In both [2.38] and [2.39] no addition was observed to hexafluoropropene. It seems that the inductive effect of a second carbonyl group in (**60**) further reduces the nucleophilicity of a radical formed adjacent to nitrogen, resulting in the observed lack of reactivity with an electrophilic alkene. In the case of compound (**61**), the nucleophilicity of a radical formed α- to both nitrogens should not be reduced to the same extent as heteroatoms in a 1,4-relationship. And consequently heteroatoms which are separated by one methylene unit are able to stabilise a radical formed α- to both heteroatoms owing to the ability of forming an additional valence stabilised structure with the second heteroatom, and this is illustrated for oxygen,[2.40a].



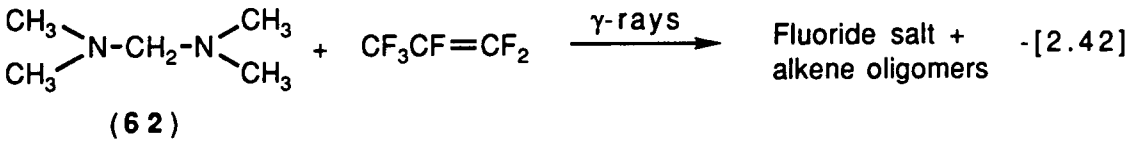
In contrast the second heteroatom also acts to offset the nucleophilic character of the radical [2.40b], and this will tend to reduce the reactivity of the substrate towards electrophilic alkenes, so that the overall reactivity will be a combination of both a stabilising and a destabilising effect.

That the overall effect is stabilising is found to be the case in the reaction of 1,3-dioxolane with hexafluoropropene[101], where addition occurs at the site between the oxygen atoms, [2.41].



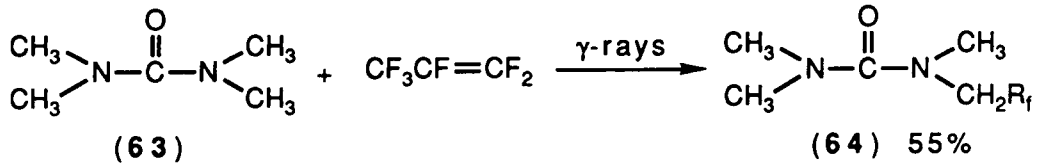
Failure of (**61**) to react with hexafluoropropene, [2.39], may simply be due to a phase problem, as the substrate was found to be insoluble in all the standard solvents used in free radical reactions.

Aliphatic di-amines may also be modified to encourage free radical reaction. In a previous study *N,N,N',N'*-tetramethyldiaminomethane (**62**) reacted with hexafluoropropene to form a fluoride salt together withn extensive oligomerisation of the alkene, showing that a nucleophilic reaction had taken place[56], [2.42].



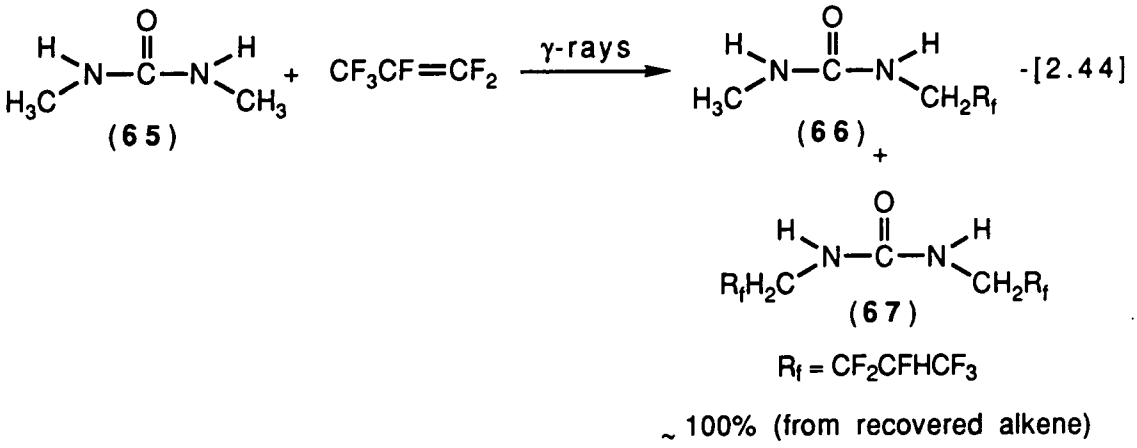
(**62**)

However, introduction of a carbonyl group reduced the rate of the nucleophilic reaction (k_1), allowing the free radical reaction (k_2) to compete. In a previous study *N,N,N',N'*-tetramethylurea (**63**) gave a moderate yield of the mono-adduct (**64**) on reaction with hexafluoropropene[56], [2.43].



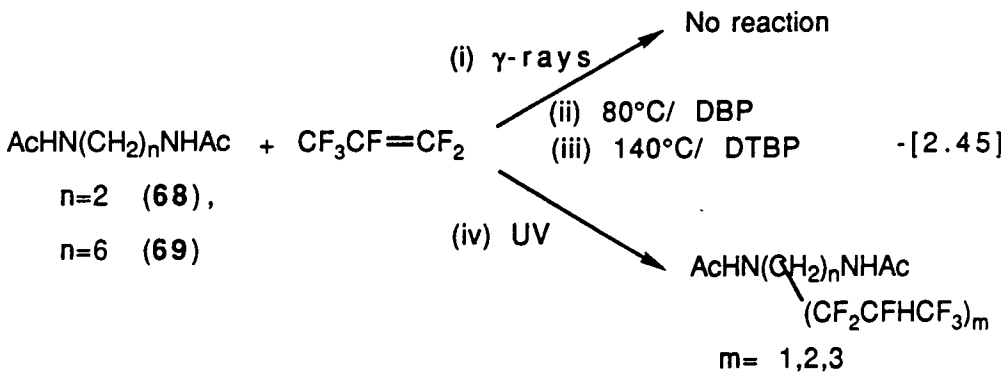
-[2.43]

In this study the aliphatic secondary amide *N,N'*-dimethylurea (**65**) reacted quantitatively with hexafluoropropene using acetone as a solvent to give a mixture of the mono-adduct (**66**) and a di-adduct (**67**) which were identified by mass spectrometry. Attempts to separate (**66**) and (**67**) by chromatography proved to be unsuccessful, and it was found that (**66**) could not be produced exclusively even using a vast excess of the urea. The mixture of (**66**) and (**67**) was therefore reacted with excess hexafluoropropene in order to convert the mixture to (**67**) which could then be purified, [2.44].



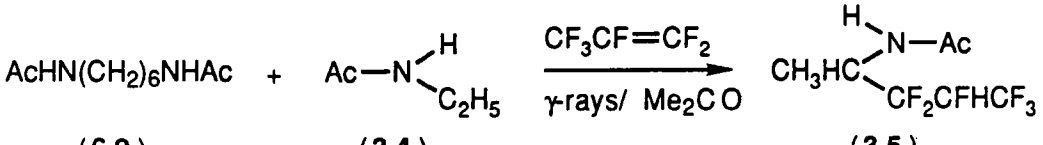
-[2.44]

Success in the reactivity of the alkyl acetamides to free radical reactions with hexafluoropropene prompted an investigation in order to determine the distance over which an inductive effect may be operating using a series of diacetyl derivatives of aliphatic di-amines, [2.45].



-[2.45]

In the case where n=2 and 6 no reaction was observed using either γ-ray or peroxide initiation with acetone as solvent. Photochemical initiation gave a trace of material identified by mass spectrometry as a mixture of adducts, but owing to the very low yields these adducts were not investigated further. The site of addition of the fluoroalkyl groups is uncertain and this is represented by a bond drawn to the centre of the product. Although the alkylacetamides reacted well with hexafluoropropene, the lack of reactivity of the aliphatic diacetyl derivatives, [2.45], was very surprising. Stereoelectronic effects are unlikely to be important as the C-C bonds are able to freely rotate and consequently could readily adopt the required conformation for good orbital overlap. With *N,N'*-diacetyl-1,2-ethanediamine (**68**) the inductive effect of the two heteroatoms separated by only two methylene units may be important, and this, coupled with the steric constraints of the two acetyl substituents in close proximity may account for the lack of reactivity. With *N,N'*-diacetyl-1,6-hexanediamine (**69**) the lack of reactivity is more difficult to explain. The inductive effect between two heteroatoms separated by six methylene units would be expected to be small, and the steric arguments proposed for (**68**) would not apply as the acetyl substituents are no longer in close proximity. It could have been possible that a radical inhibitor was present as (**69**) was used as received from the supplier. An inhibition experiment with a mixture of (**69**) and (**34**) gave the mono-adduct (**35**) in high yield, [2.46], so that inhibition may be discounted.

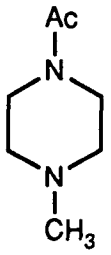


(**69**) (**34**) (**35**) -[2.46]

This only leaves the possibility that the steric requirements of a radical derived from (**69**) results in low reactivity in free radical reactions.

II.3.C.(3).a. **Acyl Derivatives**

The introduction of a carbonyl protecting group outside the ring in the form of an acetyl group may also leads to free radical reactivity in di-amine systems. Reaction of *N*-acetyl,*N'*-methylpiperazine (**70**) with hexafluoropropene, surprisingly however, gave only products of nucleophilic attack, [2.47].



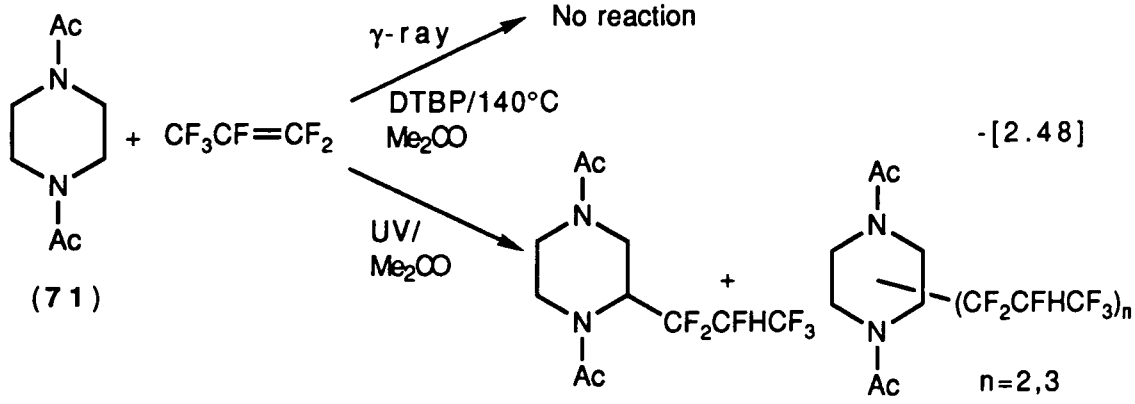
(**70**)

$$+\ CF_3CF{=}CF_2 \xrightarrow[\text{or (ii) No } \gamma\text{-rays}]{\text{(i) } \gamma\text{-rays}} \text{Starting material and oligomers of hexafluoropropene} \qquad -[2.47]$$

Nucleophilic attack of (**70**) on hexafluoropropene is unexpected on the basis that tertiary amines tend to react preferentially via a free radical reaction, [2.4], [2.30]. It was noted, however, that reaction of both (**11**), [2.4], and (**49**), [2.30], in addition to producing products of free radical addition also gave some oligomerisation of hexafluoropropene, indicating that the rate of the nucleophilic reaction (k_1) was still competing, to some extent, with the rate of the free radical addition process (k_2). In reaction [2.42], (**62**) reacted with hexafluoropropene to give entirely the products of nucleophilic attack. It would seem that the presence of the strong inductive effect of the second heteroatom, enhanced by the presence of an electron withdrawing acetyl substituent, is further reducing the rates of both the free radical and the nucleophilic reaction to a greater extent, and hence allowing the nucleophilic reaction to compete.

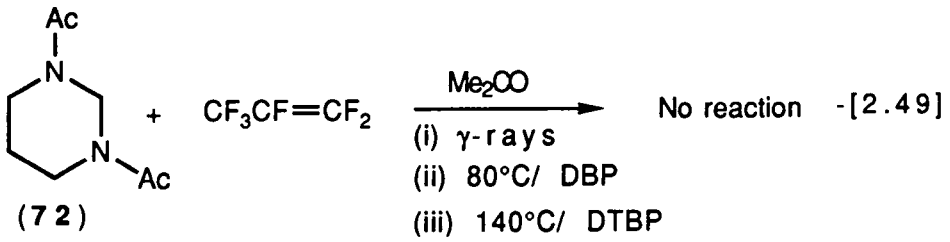
Introducing a second acetyl moiety reduces reactivity even further. *N*,*N'*-diacetylpiperazine (**71**), prepared from the reaction of piperazine with acetic anhydride, failed to react with hexafluoropropene using either γ-ray or peroxide initiation. Using photochemical initiation with acetone as a photosensitizer, together with a solvent to

improve contact between reagents, a very low conversion to products was observed, which were analysed by mass spectrometry to be a mixture of mono- and di-adducts together with higher order adducts which could not be assigned. Prolonged irradiation failed to increase this yield, [2.48].



The low reactivity of (**71**) may be rationalised in terms of the very strong inductive effect of the second heteroatom, enhanced by the electron withdrawing effect of the acetyl substituent, on the nucleophilicity of a radical formed adjacent to the first heteroatom.

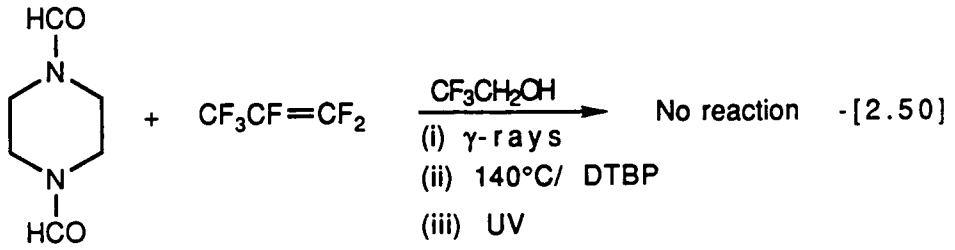
N,N'-diacetylhexahydropyrimidine (**72**), prepared from the reaction of 1,3-diaminopropane with formaldehyde[102], followed by acetylation using acetic anhydride, gave no adduct formation on reaction with hexafluoropropene using acetone as solvent, [2.49].



This result was unexpected on the basis that it is known that a fluoroalkene is able to add adjacent to two heteroatoms, [2.41].

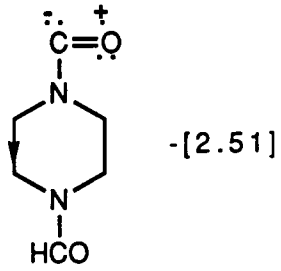
Surprisingly, the inductive effect of a second heteroatom is even able to influence side chain reactivity. Replacement of the acetyl protecting group on the nitrogen atom with a formyl group allows for the additional possibility of reaction at this group (see [2.14]).

N,N'-diformylpiperazine (**73**), however, failed to react with hexafluoropropene using either γ-ray, peroxide or photochemical initiation, with 2,2,2-trifluoroethanol as solvent, [2.50].



(**73**)

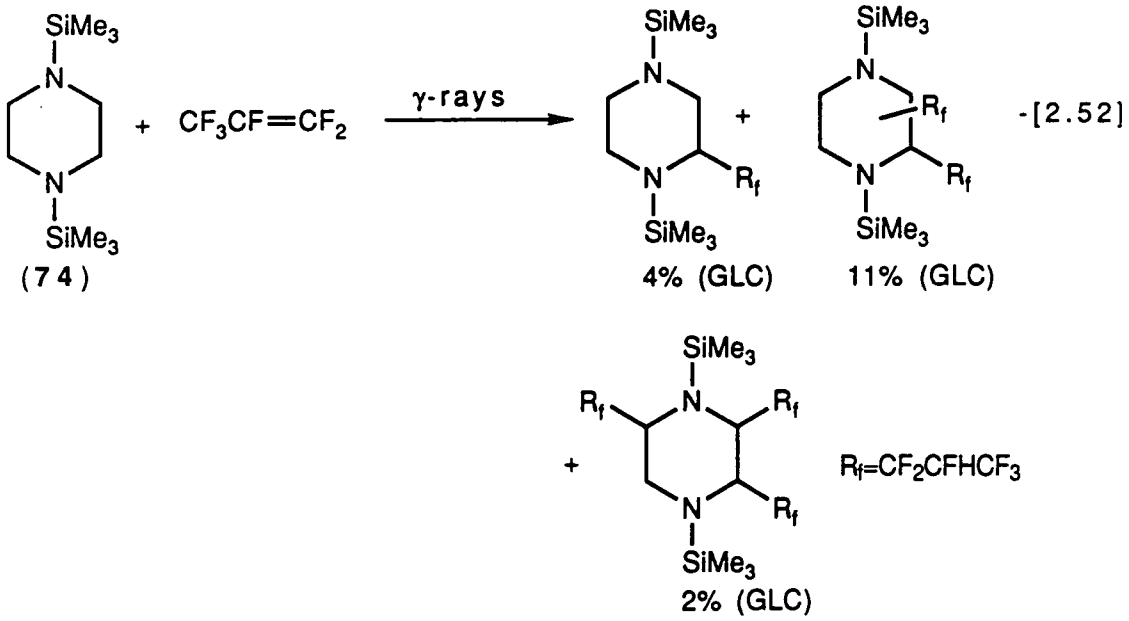
The apparent explanation for the lack of reactivity observed at the formyl groups of (**73**) is the reduction in the nucleophilicity of the substrate acyl radical as a direct result of the inductive electron withdrawing effect of the second nitrogen atom, [2.51], but it is unlikely that we would have predicted this result.



-[2.51]

II.3.C.(3).b. **Trimethylsilyl Derivatives**

Since we have demonstrated that introducing a trimethylsilyl group is beneficial, *N,N'*-di(trimethylsilyl)piperazine (**74**) was prepared by the reaction of piperazine with chlorotrimethylsilane, and reacted with a deficiency of hexafluoropropene. A complex mixture of mono-, di- and tri-adducts was obtained which were identified by ^{19}F NMR and G.C. mass spectrometry, but were not separated, [2.54].



Introduction of trimethylsilyl groups in (**74**) has lead to some enhanced reactivity in comparison with electron withdrawing groups in (**71**), [2.48], and (**72**), [2.49], but the inductive effect of the second heteroatom is still important however, and this is reflected in the low yield in [2.52].

As a general conclusion, introduction of a trimethylsilyl moiety over acetyl enhances free radical reaction, but the introduction of a second heteroatom has a negative effect on reactivity, arising from inductive electron withdrawal.

Having examined the reactivity of a range of nitrogen containing systems with hexafluoropropene, this study was extended in order to investigate the effects on reactivity with different fluoroalkenes.

II.3.D. Reactions of Amine Derivatives with Chlorotrifluoroethene

II.3.D.(1). Effect of Varying Substituents on Reactivity of Nitrogen Derivatives

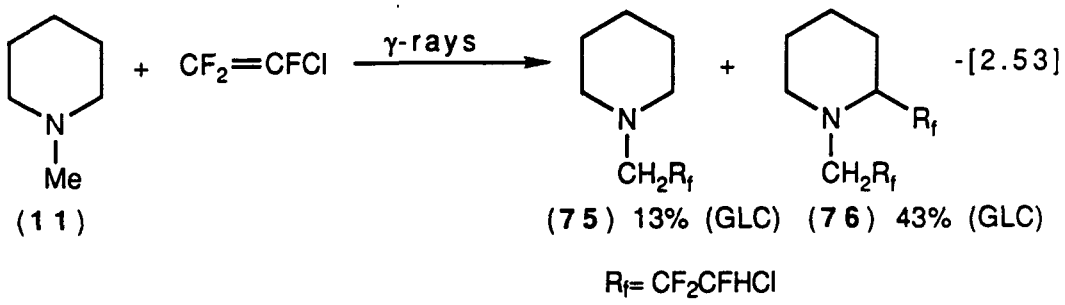
II.3.D.(1).a. Introduction

An intermediate radical (**7**) in Scheme 2.2 is able to undergo two reactions, (i) the abstraction of a hydrogen atom from the substrate molecule to regenerate the initial radical (**6**) in a chain transfer step (k_5), or alternatively (ii) addition to another molecule of alkene (k_4), a step which may continue leading to a range of telomeric adducts. The relative

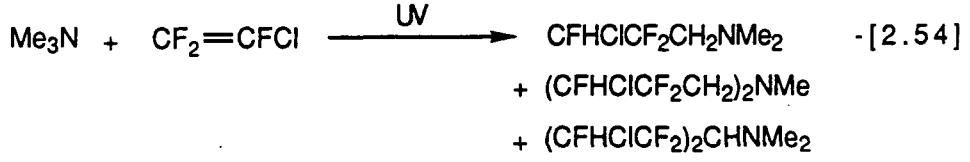
rates of (k_4) and (k_5) are dependent upon the ability of the alkene to telomerise. Easily telomerisable alkenes such as tetrafluoroethene, vinylidene fluoride and chlorotrifluoroethene often lead to (k_4) being the preferred pathway.

II.3.D.(1).b. Tertiary Amines

Addition of tertiary amines to chlorotrifluoroethene leads to a similar product distribution to that observed with hexafluoropropene. Compound (**11**) reacted with chlorotrifluoroethene to give predominantly the di-adduct (**76**) together with a small amount of the mono-adduct (**75**), [2.53].



Similarly in a previous study the aliphatic tertiary amine, trimethylamine reacted with chlorotrifluoroethene to give a mixture of adducts, [2.54], as had been observed for the reaction of triethylamine with hexafluoropropene[82], [2.3].

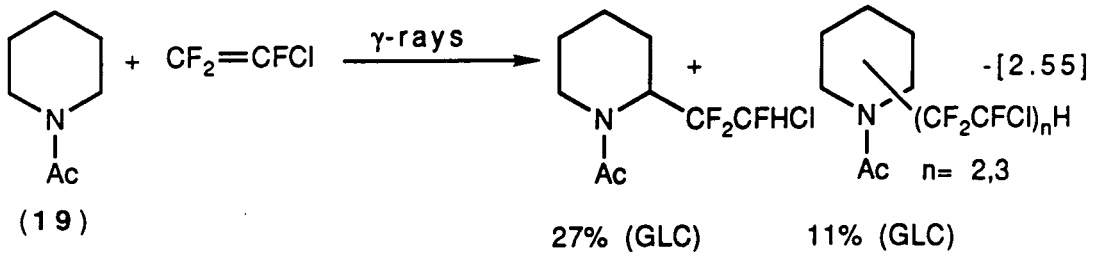


Since few telomers were obtained, these results demonstrate that amines are very effective chain transfer agents with this readily polymerisable alkene.

II.3.D.(1).c. Cyclic Amides

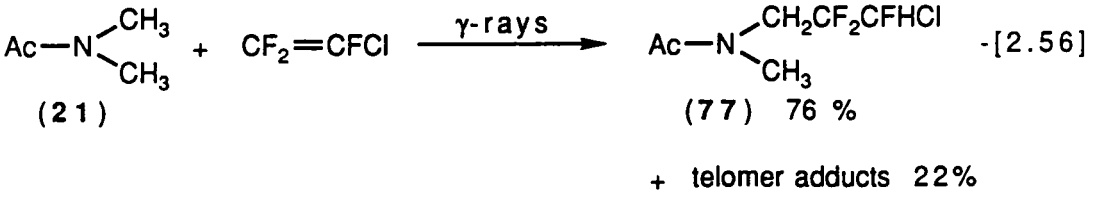
Protecting with an acetyl group allows for the reaction of the cyclic secondary amine piperidine (**8**). Compound (**19**) reacted with chlorotrifluoroethene to give a mixture of mono- and telomeric adducts assigned by ^{19}F NMR and G.C. mass spectrometry.

Although it was possible to separate the starting material from the mixture, it was not possible to separate the mixture of adducts from each other, [2.55].



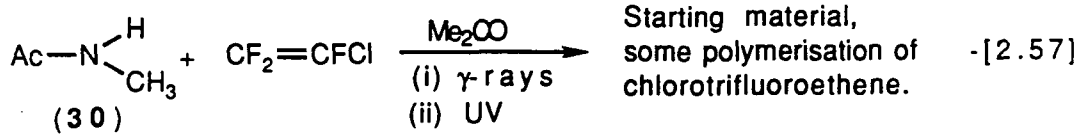
Production of telomers with chlorotrifluoroethene is indicative of the reduced electron density of the α-hetero carbon of the substrate as a result of the inductive effect of the acetyl group, and this in turn reduces the rate of hydrogen atom abstraction by an electrophilic adduct radical (**7**), and hence the rate of the chain transfer step (k_5), allowing the telomerisation step (k_4) to compete favourably.

Similarly, the protected aliphatic secondary amine (**21**) was found in a previous study to react with chlorotrifluoroethene to give the mono-adduct (**77**), but it was noted that telomer adducts were also formed, again reflecting the reduced efficiency of the chain transfer step (k_5), [2.56].



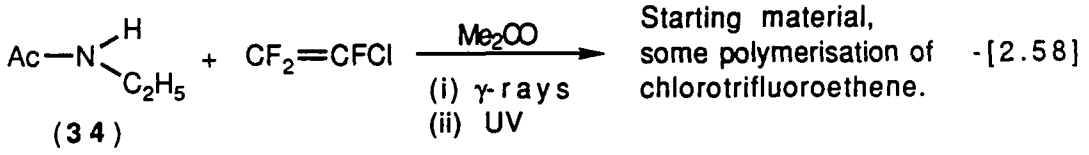
Primary amines, as was noted previously (**30**), [2.19], require only one acetyl group in order to lower the basicity of nitrogen sufficiently for the rate of the free radical reaction (k_2) to compete with the rate of the nucleophilic reaction (k_1) leading to products of free radical addition.

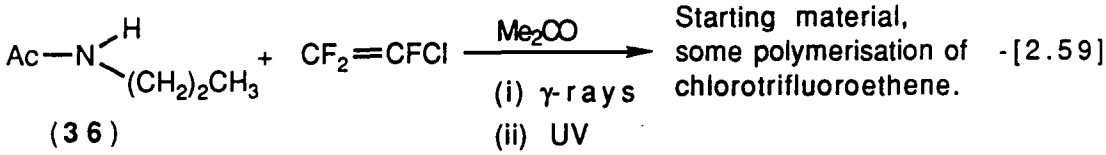
In this study, however, compound (**30**) failed to react with chlorotrifluoroethene using either γ-ray or UV initiation. It was also observed that the alkene was not fully recovered, and there was evidence that polymerisation had taken place, [2.57].



Clearly the rate constant (k_5) for chain transfer is substantially reduced.

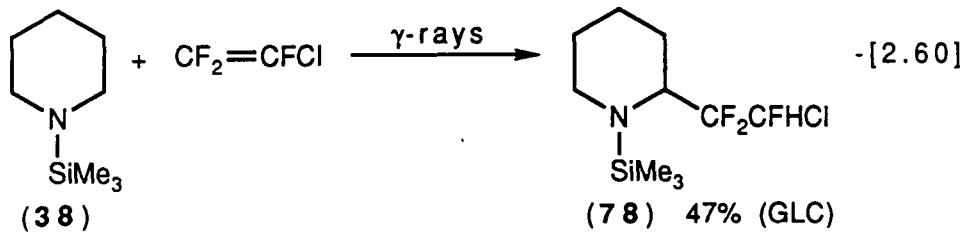
Analogous results were also observed in the reaction of the higher homologues (**34**) and (**36**) which also gave recovery of starting material together with some polymerisation of chlorotrifluoroethene, [2.58] and [2.59].





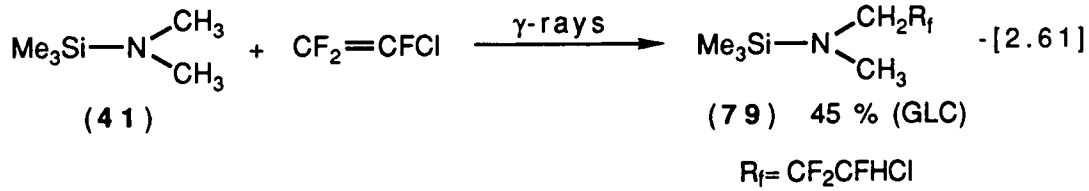
II.3.D.(1).d. **Trimethylsilyl Derivatives of Amines**

Introduction of a trimethylsilyl group leads to the production solely of the mono-adduct (**78**) on reaction of (**38**) with chlorotrifluoroethene, [2.60], and it is clear that

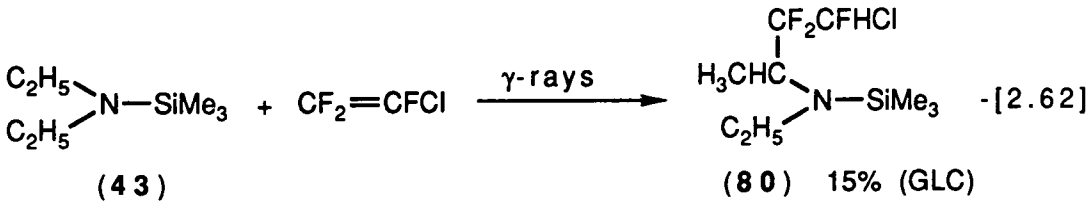


trimethylsilyl increases the rate of the chain transfer step (k_5) preventing the telomerisation step (k_4) from competing.

Trimethylsilyl in aliphatic secondary amines is also beneficial in eliminating the formation of telomeric adducts. Compound (**41**) reacted with chlorotrifluoroethene to give the mono-adduct (**79**), [2.61].



Compound (**43**) also reacted with chlorotrifluoroethene to give the product of free radical addition (**80**), [2.62], although in low yield.

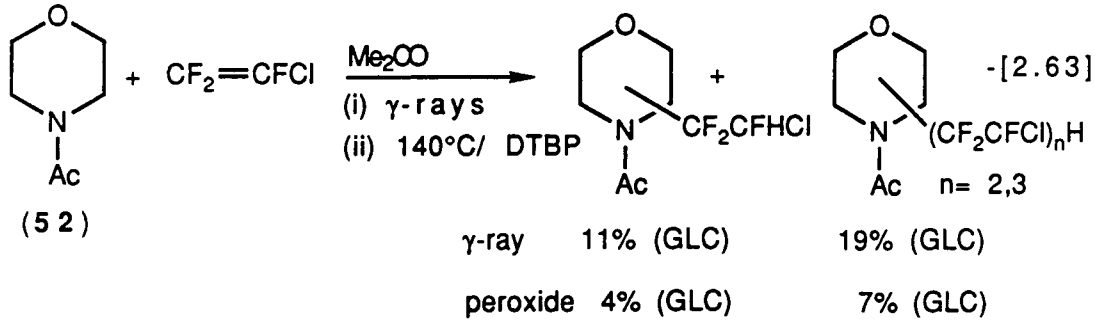


The low yield in the reaction of (**43**) with chlorotrifluoroethene probably results from the steric effects noted for [2.12].

II.3.D.(2). Effect of Introducing an Oxygen Atom on the Reactivity of Nitrogen Derivatives

II.3.D.(2).a. Oxygen Containing Acyl Derivatives

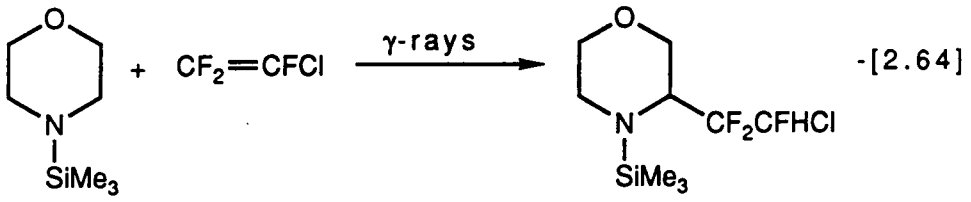
Introduction of an electron withdrawing oxygen atom leads to a change in the product distribution. Compound (**52**) reacted with chlorotrifluoroethene to give a low yield of a mixture of mono-adduct together with telomeric adducts, which were assigned by ^{19}F NMR and G.C. mass spectrometry. Again it was possible to separate the starting material from the mixture but it was not possible to separate the mixture of adducts from each other, [2.63].



It is notable that there is an increase in the amount of telomeric adducts in comparison with [2.55]. This is a result of the reduced electron density at the α-hetero carbons of (**52**) on introducing an electron withdrawing oxygen atom, and this in turn reduces the rate for hydrogen atom abstraction by an electrophilic adduct radical (**7**), and hence the rate of chain transfer (k_5). As a result of a reduction in (k_5) the telomerisation step (k_4) is able to compete, leading to an increase in telomer adduct production.

II.3.D.(2).b. Oxygen Containing Trimethylsilyl Derivatives

The reduction in electron density at the α-hetero carbons is not as pronounced on the introduction of a trimethylsilyl group and (**55**) gave only the mono-adduct (**81**) on reaction with chlorotrifluoroethene, [2.64].



(55) (81) 48% (GLC) -[2.64]

Clearly, chain transfer in the system (**55**) is enhanced over (**52**), and this is important in demonstrating that the substituent has an effect on the rate of hydrogen atom abstraction (k_5).

Results of amine and amide reactions with chlorotrifluoroethene give support to the advantage in free radical reactions of the introduction of a trimethylsilyl group over the electron withdrawing acetyl substituent, the trimethylsilyl substituents resulting in good yields of free radical product with no telomeric side products.

As a final confirmation of these effects attention was switched to the reactions of cyclic fluoroalkenes, in particular to the reactions of perfluorocyclobutene and perfluorocyclopentene.

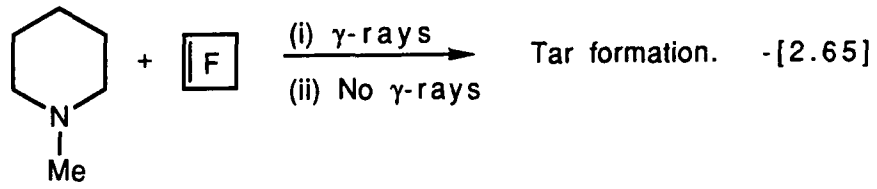
II.3.E. Reactions of Amine Derivatives with Perfluorocyclobutene and Perfluorocyclopentene

The addition of perfluorocyclobutene or perfluorocyclopentene to a radical (**6**) will be dependent upon both steric and polar effects, and this has been discussed in detail by Jones[57]. It was noted by Grievson[56] that increased perfluoroalkyl substitution of the fluoroalkene resulted in a lower adduct yield.

II.3.E.(1). Effect of Varying Substituents on Reactivity of Nitrogen Derivatives

II.3.E.(1).a. Tertiary Amines

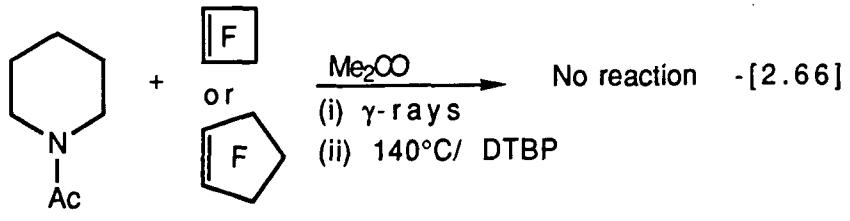
Addition of perfluorocyclobutene to tertiary amines has been reported in the literature[90] to give ylide products (section I.2.D.(2).). This was also found to be the case in the reaction of (**11**) with perfluorocyclobutene, [2.65], which gave a black tar which was not investigated further. It seems likely that the relief of ring strain, enhanced by the presence of eclipsing fluorine atoms is increasing the rate of the nucleophilic addition reaction (k_1) at the expense of the free radical reaction (k_2).



(**11**)

II.3.E.(1).b. Acyl Derivatives of Amines

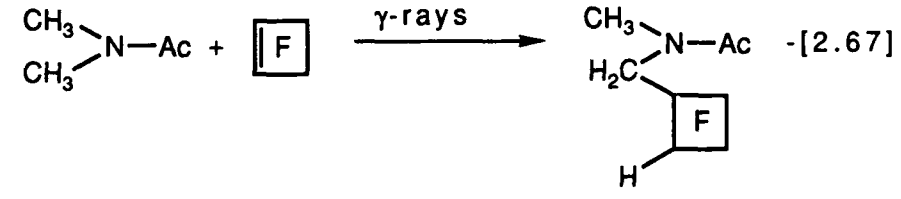
Introduction of an acetyl group results in much reduced reactivity of (**19**) with either perfluorocyclobutene or perfluorocyclopentene, using acetone as solvent, [2.66].



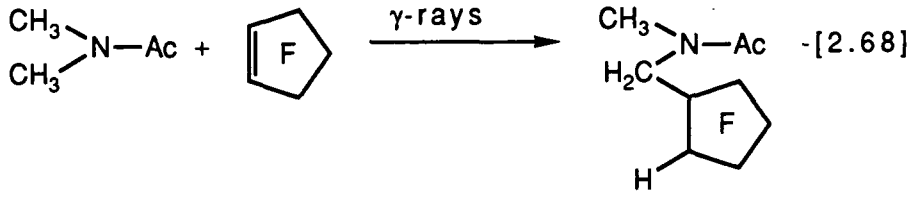
(**19**)

Obviously, the acetyl group suppresses both the ionic but also the radical reaction to too great an extent.

In extending the scope of these reactions to include aliphatic secondary amines, (**21**) was found in a previous study[56] to give the product of free radical addition with both perfluorocyclobutene, [2.67] and perfluorocyclopentene, [2.68].



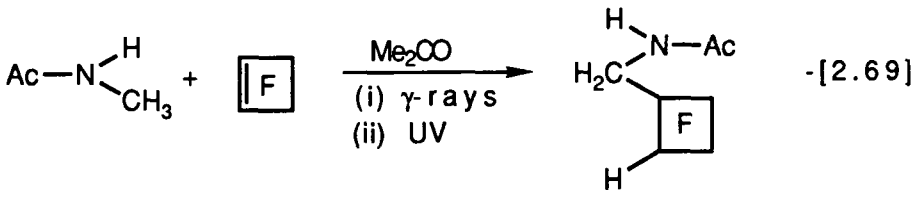
(**21**) 29%



(**21**) 28%

Obviously these effects are finely balanced and changes from rings to aliphatic systems have a major effect on reactivity.

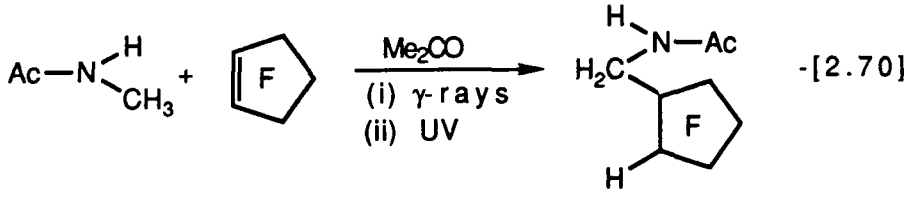
Primary aliphatic amines (protected as the amides) react with perfluorocyclobutene and perfluorocyclopentene to give the products of free radical addition. Compound (**30**) reacted with perfluorocyclobutene to give a low yield of the mono-adduct (**82**) using γ-ray initiation, whereas the use of photochemical initiation improved the yield of (**82**) substantially, allowing the product to be isolated, [2.69].



(**30**) (**82**)

γ-rays 12% (GLC)
UV 39%

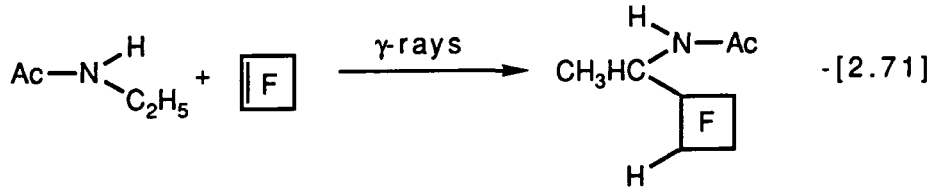
With less strained perfluorocyclopentene (**30**) gave only a trace of the mono-adduct (**83**) using γ-ray initiation, the yield of (**83**) again being improved with photochemical initiation, [2.70].



(**30**) (**83**)

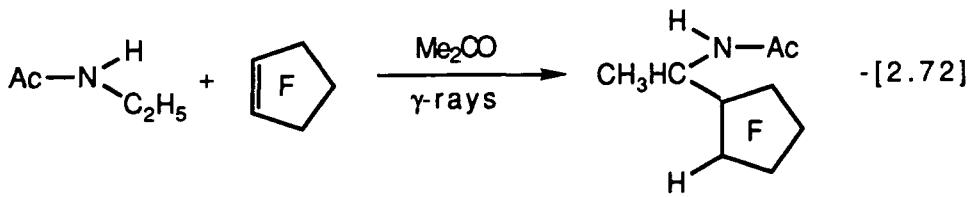
γ-rays	4% (GLC)
UV	15%

The higher homologue (**34**), however, gave a high conversion to the mono-adduct (**84**) on reaction with perfluorocyclobutene, [2.71].



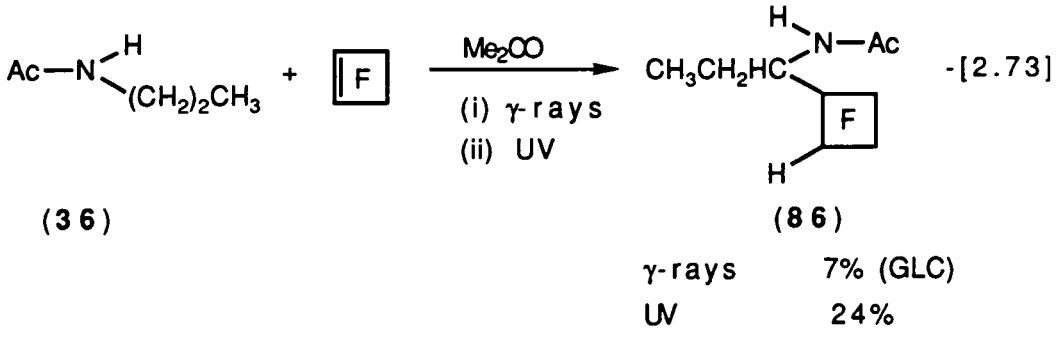
(**34**) (**84**) 78%

Similarly the reaction of (**34**) with perfluorocyclopentene gave mono-adduct (**85**), but in a much reduced yield, [2.72].



(**34**) (**85**) 12%

Continuing this series compound (**36**) gave the corresponding mono-adduct (**86**) on reaction with perfluorocyclobutene in a very low yield using γ-ray initiation, the yield again being improved using photochemical initiation, [2.73].



(36) (86)

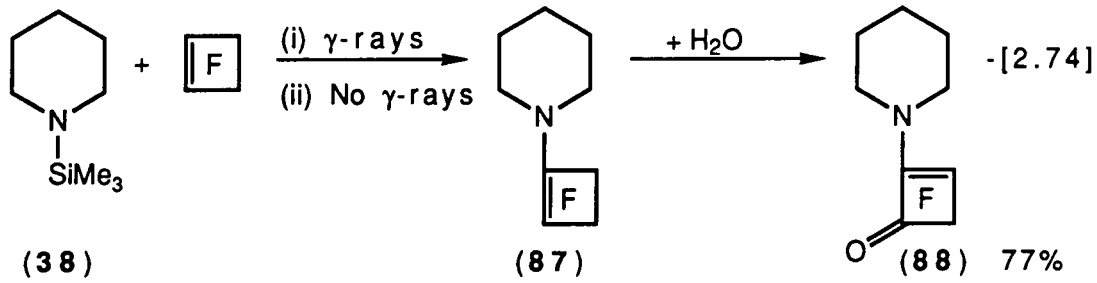
γ-rays 7% (GLC)

UV 24%

Despite the unusually high reactivity of (**34**) with perfluorocyclobutene, [2.71], the yields of the acetamide reactions were generally low, and this reflects the steric constraints of the cyclic alkenes. Nevertheless, we do not understand all of the factors at play since the ethyl derivative (**34**) is more reactive than the methyl derivative (**30**) and at this time, we have no satisfactory explanation for this.

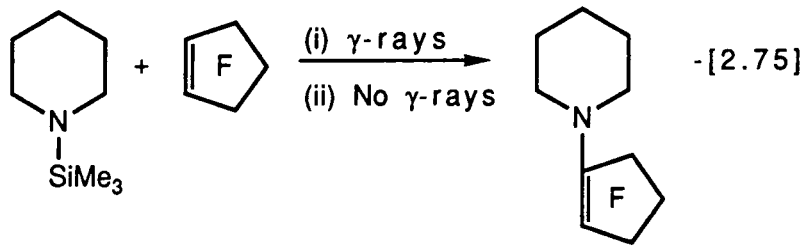
II.3.E.(1).c. Trimethylsilyl Derivatives of Amines

The introduction of a trimethylsilyl group in (**38**) gave a product of nucleophilic addition (**87**), which was found to hydrolyse readily in the air to give (**88**), [2.74].



(38) (87) (88) 77%

A similar product of nucleophilic addition (**89**) was also observed in the reaction of perfluorocyclopentene with (**38**), [2.75], although it may be noted that (**89**) was much less prone to hydrolysis than (**87**), [2.74].

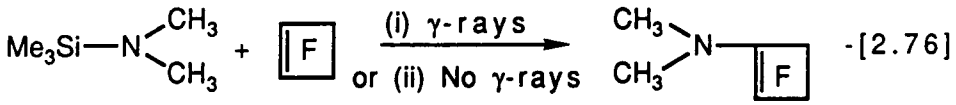


(38) (89) 88%

In order to discount the possibility of either water or hydrogen fluoride in the alkene (which would cause formation of the free amine), the cyclic fluoroalkenes were shaken and stored over molecular sieve and potassium fluoride. Free amine may have catalysed the nucleophilic reaction. In order to eliminate the possibility of free amine in the starting material, (**38**) was distilled under reduced pressure and used immediately, with all apparatus being maintained under an atmostphere of dry nitrogen.

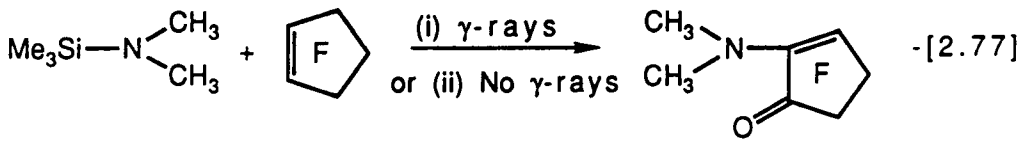
Having taken reasonable precautions against the possibility of free amine catalysing a nucleophilic reaction, it may be postulated that in [2.74] and [2.75] the initially formed ylide is able to eliminate fluoride ion which is then able to cleave the N-Si bond eliminating the trimethylsilyl group as trimethylsilylfluoride to give the nucleophilic products (**87**) and (**89**). Moisture in the air is then able to hydrolyse (**87**) to (**88**).

The trimethylsilyl analogue of (**21**) underwent reaction with both perfluorocyclobutene and perfluorocyclopentene, analogous to [2.74] and [2.75]. Compound (**41**) reacted with perfluorocyclobutene to give the product of nucleophilic addition (**90**), [2.76].



(**41**) (**90**) 90%

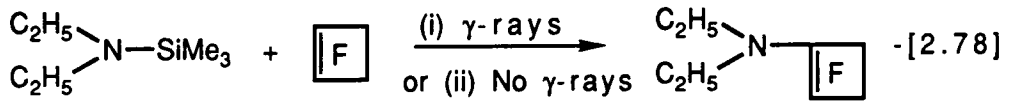
Similarly reaction with perfluorocylopentene gave the nucleophilic product (**91**), [2.77].



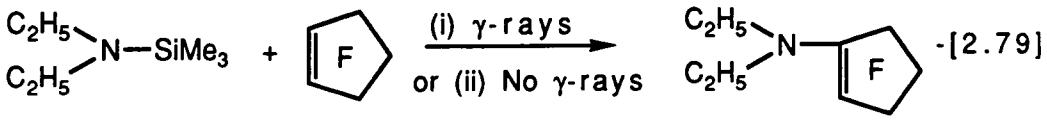
(**41**) (**91**) 79%

As was previously noted for the reactions of [2.74] and [2.75] contamination of the reaction mixture with either free amine, water or hydrogen fluoride has been minimised, so that it seems that the rate of the nucleophilic addition reaction is higher than the corresponding free radical reaction, the driving force being the relief of ring strain.

This is also observed for the higher homologue (**43**) which reacted with perfluorocyclobutene and perfluorocyclopentene to give the corresponding products of nucleophilic addition (**92**), [2.78] and (**93**), [2.79].



(**43**) (**92**) 87% (GLC)



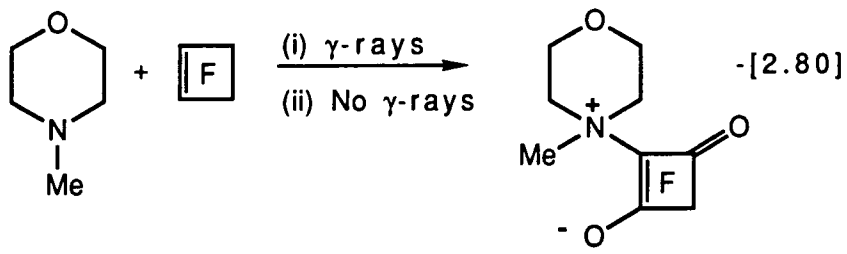
(**43**) (**93**) 94%

These reactions may be developed for the controlled nucleophilic reactions of amines with fluoroalkenes, avoiding possible 'run-away' reactions in base-catalysed procedures.

II.3.E.(2). Effect of Introducing an Oxygen Atom on the Reactivity of Nitrogen Derivatives

II.3.E.(2).a. Oxygen Containing Tertiary Amines

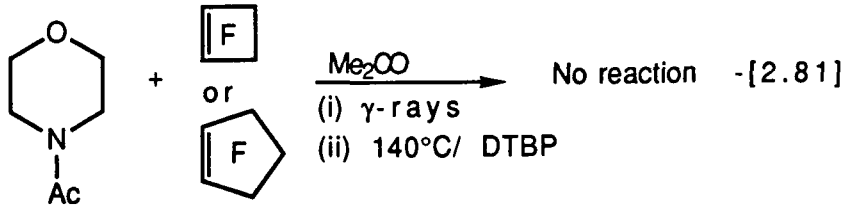
The introduction of an electron withdrawing oxygen atom into a tertiary amine may have a strong enough inductive effect to lower the availability of the nitrogen lone pair which may prohibit ylide formation. This was found not to be the case, with (**49**) reacting to give a product of nucleophilic addition, which was isolated as its salt (**94**), [2.80].



(**49**) (**94**) 73%

II.3.E.(2).b. **Oxygen Containing Acyl Derivatives**

Protection of (**47**) as the acetyl derivative should allow for the reactivity of secondary amines. However compound (**52**) gave no addition on reaction with either perfluorocyclobutene or perfluorocyclopentene, [2.81].

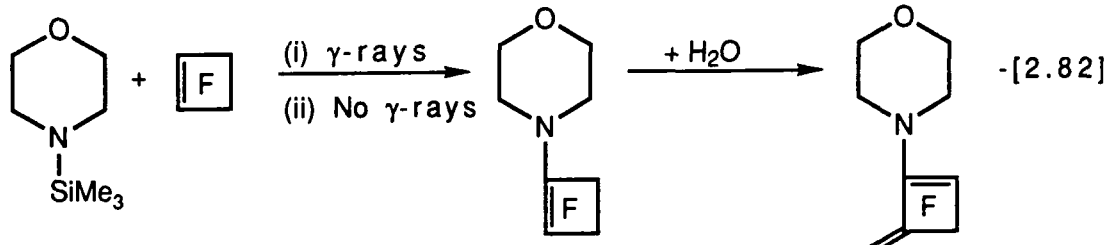


(**52**)

This result is reasonable as (**19**), [2.66], did not react with either cyclic alkene.

II.3.E.(2).c. **Oxygen Containing Trimethylsilyl Derivatives**

Protecting the secondary amine (**47**) as the trimethylsilyl derivative would be expected to compensate for the problems encountered with the acetyl substituent, but the reaction of (**55**) with perfluorocyclobutene again leads to the product of nucleophilic addition (**95**) which hydrolyses to (**96**), [2.82].



(**55**) (**95**) 38% (**96**) 22%

II.4. Reactions of Acetamide Derivatives

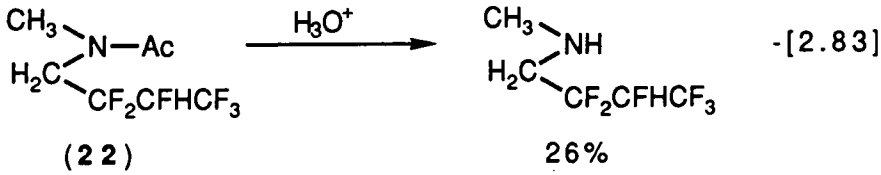
II.4.A. Introduction

The ease of formation of several of the alkylacetamide adducts investigated previously prompted an investigation into further chemistry of these derivatives.

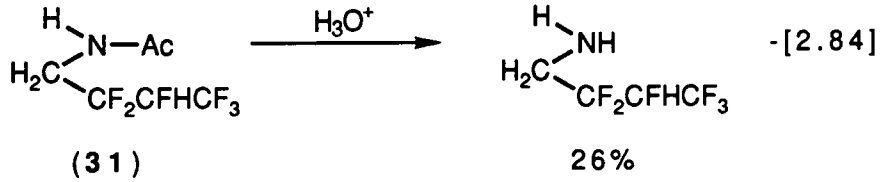
An amide functionality allows for the synthesis of either fluorinated primary or secondary amines, which could not be obtained by direct free radical reactions owing to the competing nucleophilic reaction pathway.

II.4.B. Hydrolysis-Synthesis of Primary Amine Derivatives

It is expected that amides can be hydrolysed using either acid or base to give the corresponding primary amines. It was proposed[57] that the presence of a hexafluoropropyl group may prohibit base catalysed deacylations as dehydrofluorination of the side chain may also occur, and the author went on to show that deacetylation to the corresponding primary amine is indeed possible for the hexafluoropropene adduct (**22**), [2.83] and (**31**), [2.84], using 10% aqueous sulphuric acid, although the isolated yields of these reactions were low.



(**22**) 26% -[2.83]



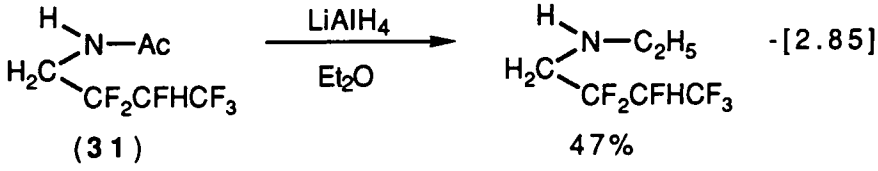
(**31**) 26% -[2.84]

In our study we found that the hexafluoropropene adduct of *N*-ethylacetamide (**35**), [2.21], could not be deacetylated in a similar manner to [2.84]. On adding 10% sulphuric acid the solid failed to dissolve even under prolonged reflux, and would only dissolve in strong acid (~70%). Following reflux and neutralisation with potassium hydroxide no lower fluorocarbon layer separated as had been observed in [2.83] and [2.84]. Continuous extraction using either diethylether or dichloromethane to try to separate any product was unsuccessful, and addition of excess base followed by prolonged reflux and re-extraction separated only a small amount of starting material. By monitoring the reaction on an NMR scale a shift in the N-H absorption to higher field was observed which would be indicative of protonation of (**35**). Following reflux at

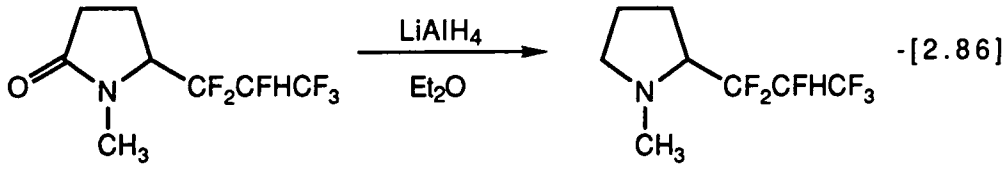
160°C this spectrum did not change. It would seem that although protonation in acid of (**35**) is occuring the subsequent loss of an acetyl group to generate the amine is not.

II.4.C. Reduction-Synthesis of Secondary Amine Derivatives

Reduction of alkylacetamides using lithium aluminium hydride should give the corresponding secondary amines, and this reaction had been used previously[57] to prepare both secondary, [2.85], and tertiary, [2.86], amines from the corresponding perfluoroalkyl amides.

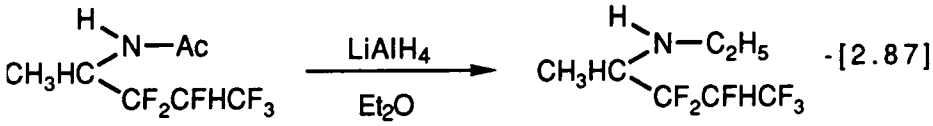


(**31**) 47% -[2.85]



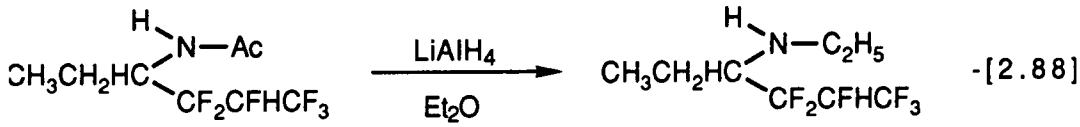
55% -[2.86]

It was possible to reduce the adduct of *N*-ethylacetamide and hexafluoropropene (**35**) to give the corresponding secondary amine (**97**), [2.87].



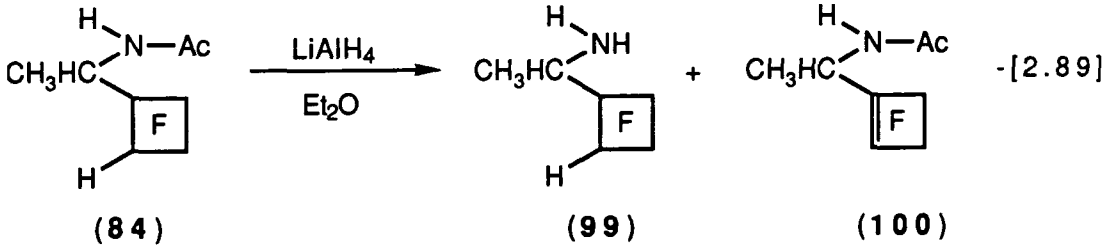
(**35**) (**97**) 28% -[2.87]

A secondary amine (**98**) is also obtained from the reaction of lithium aluminium hydride with the adduct of *N*-propylacetamide and hexafluoropropene (**37**), [2.88].



(**37**) (**98**) 32% -[2.88]

In the reduction of the adduct of *N*-ethylacetamide and perfluorocyclobutene, (**84**), the reaction yielded a mixture of the secondary amine (**99**) and a derivative in which the secondary amine had eliminated hydrogen fluoride (**100**), (identified by ^{19}F NMR and G.C. mass spectrometry), [2.89].



(84) (99) (100) -[2.89]

Derivative (**100**) was prone to hydrolysis, as had been observed with some of the products of nucleophilic addition (e.g. [2.74]), and the complexity of products precluded separation.

II.4.D. Reactions of Secondary Amine Derivatives

In order to examine the effect of the introduction of a perfluoroalkyl group on the nucleophilic reactivity of amines the adducts (**97**) and (**98**) were reacted with several reagents which would be expected to give product formation with the corresponding non-fluorinated amines.

II.4.D.(1). With Methyl Iodide

Methyl iodide is well known for its ability to methylate amines and reacts in a classic S_N2 displacement reaction, e.g. exhaustive methylation[66].

Reaction of (**97**) and (**98**) even following prolonged reflux failed to give products of methylation. Heating adduct (**97**) to 120°C in a sealed tube for 24 hours gave a 15% (by capillary GLC) conversion to the methylated derivative identified by G.C. mass spectrometry. Owing to the low yield of the reaction this adduct was not investigated further.

II.4.D.(2). **With Hexafluoropropene**

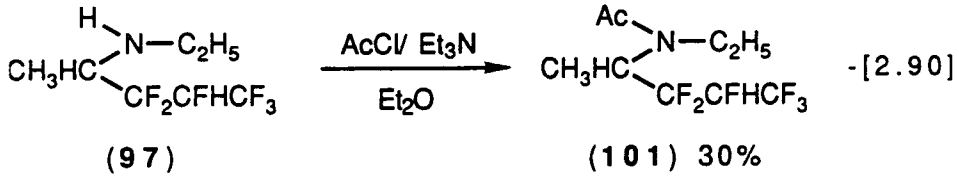
Hexafluoropropene is expected to react with amines via a nucleophilic addition process. Compounds (**97**) and (**98**) failed to react with hexafluoropropene even after several days indicating a drastic reduction in the nucleophilicity of the fluorinated amines in comparison with non-fluorinated amines (section I.2.C.(2).).

II.4.D.(3). **With Phenylisothiocyanate**

Phenylisothiocyanate is known to react readily with amines and is in fact a standard test for both primary and secondary amines owing to the ease with which the thiourea is formed[103]. Reaction of (**97**) and (**98**) with phenylisothiocyanate following reflux and G.C. mass spectrometry revealed only starting materials.

II.4.D.(4). **With Acetyl Chloride**

Addition of acetyl chloride to (**97**) produced immediate reaction to give following micro-distillation the corresponding acetyl derivative (**101**) in reasonable conversion of amine, [2.90].



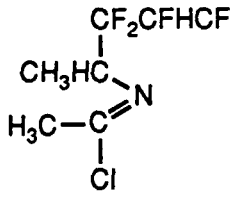
(**97**) (**101**) 30% -[2.90]

This reaction provides a novel route for the preparation of fluoroalkyl derivatives of (**25**), [2.12], as (**25**) is known to react poorly with hexafluoropropene .

These reactions demonstrate a reduction in the reactivity of amines to nucleophilic attack on introduction of a perfluoroalkyl group. This may be as a result of the reduction in the availability of the lone pair on nitrogen for participation in nucleophilic reactions or possibly due to the increased crowding in the transition state of these reactions.

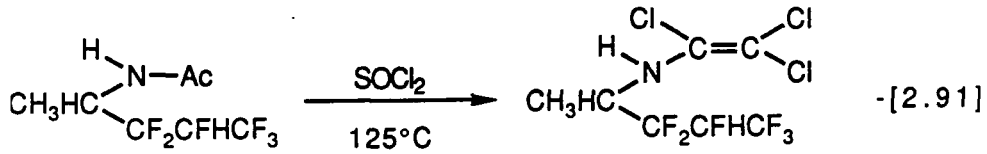
II.4.E. Attempted Synthesis of an Halogenated Imine

It was proposed that the reaction of (**35**) with sulphuryl chloride would produce the halogenated imine (**102**).



(**102**)

Reaction with sulphuryl chloride however produced the new and unexpected derivative (**103**), [2.91].



(**35**) (**103**) 61% -[2.91]

Thionyl chloride and phosphorous oxychloride also gave (**103**) but in reduced yield. Using phosphorous pentachloride no fluorinated material could be isolated from the reaction mixture following work-up.

An attempt was made to produce the analogous derivative of (**84**) and (**37**) with sulphuryl chloride. This reaction, however, resulted in the formation of a complex mixture of adducts which were found to be neither the desired halogenated imine or a derivative similar to (**103**) from G.C. mass spectrometry and owing to the small amount of material produced this reaction was not investigated further.

II.5.A. Rationalisation for the Low Reactivity of RDX and HMX Derivatives

Having completed a detailed survey concerning the reactivity of a wide variety of amine and amide derivatives, it is now possible to draw together some general

conclusions concerning the lack of free radical reactivity of hexamine, **DAPT**, **TRAT** and **TAT** with hexafluoropropene.

In order for a free radical reaction to proceed its rate must necessarily be higher than the rate of the competing nucleophilic reaction. It was found that in order to favour the rate of the free radical reaction it was important to protect the amine. Protection with an acetyl group was found to be beneficial in promoting free radical reaction with fluoroalkenes, but the electron withdrawing effect of the acetyl group was found to reduce the stability of the initially formed substrate radical (**6**), Scheme 2.2. Introduction of a trimethylsilyl group as a protecting group for amines did not reduce the stability or reactivity of the initially formed radical (**6**), and this was reflected in the formation of adducts (compare reactions [2.8] and [2.24], and also reactions [2.17] and [2.28]).

A second heteroatom further reduces the availabilty of the lone pair for stabilisation of an adjacent radical due to the presence of a strong inductive effect, and the combination of this effect together with the electron withdrawing effect of an acetyl group further reduces reactivity (compare reaction [2.8] with [2.31]). Introduction of a trimethylsilyl group (which is not electron withdrawing) allows for some reactivity in systems which with acetyl protecting groups failed to react at all (compare the reactivity of [2.48] with [2.52]).

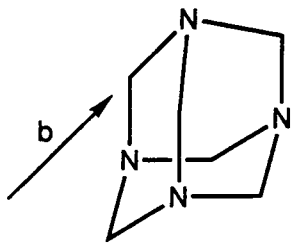
Steric effects and stereoelectronic effects are also important, the inability of hexafluoropropene to add between the nitrogen atoms of (**72**), a situation which is known to be stabilising, [2.41], is almost certainly due , at least in part, to the bulkiness of the acetyl protecting groups on nitrogen. The stereochemistry of a substrate affects its ability to undergo free radical reactions. This is observed in the addition of various substituted methyl radicals to ethene[104], where it was observed that as the size of the radical increased the rate of addition decreased. In the limiting case where the radicals are large enough they may become persistent and the reactivity is reduced to zero, e.g. in the case of the *tert*-butyl and perfluoroisopropyl radicals.

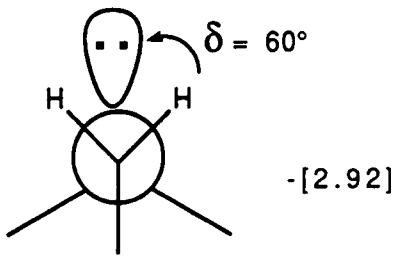
Effects of stereochemistry on free radical reactions were investigated by Grievson[56] who reacted a series of cyclic ethers with hexafluoropropene and found from competition experiments that there was a preferential order of reactivity, 5 > 7 > 6. Steric effects

were discounted on the basis that the smallest and largest ring systems were the most reactive whilst the intermediate ring system was less reactive. The author concluded from this that the conformation of the intermediate radical must be important, and proposed that a stereoelectronic effect in which the degree of reactivity was dependent upon the dihedral angle between the breaking C-H bond and the lone pair on the heteroatom was in operation, and this has also been discussed in the analogous nitrogen containing substrates (section I.2.D.(1).).

Applying the principles discussed above to the unreactive derivatives shown in Table 2.1 allows for a possible explanation for the lack of reactivity observed in free radical reactions.

Hexamine has a tetra-aza-adamantane structure which has a fixed conformation, and may be regarded as four fused 6-membered heterocycles adopting a chair conformation, [2.92].





-[2.92]

Viewing along bond (b)

Viewing along bond (b) gives a dihedral angle of 60°. This high value for the dihedral angle results in less orbital overlap between a developing singly occupied radical orbital and the lone pair orbital of nitrogen, and consequently the radical is less stabilised resulting in a higher dissociation energy for the C-H bond and this is reflected in the lack of reactivity.

The structure of **DAPT** has been found by various studies to adopt a 'chair-chair' conformation[42,43,44] the presence of the two acetyl groups being insufficiently bulky to cause deformation to a 'boat-chair' conformation. This conformation again leads to a dihedral angle of 60° and poor orbital overlap. Similarly the chair conformation of **TRAT** also leads to a dihedral angle of 60°, and poor overlap would again be expected.

In the case of TAT the dihedral angle is 60° between two of the lone pairs on nitrogen and the adjacent C-H bonds and 120° between the remaining two , and although TAT is able to distort its conformation, the distortion required for good orbital overlap would bring the lone pair of electrons on N-1 and N-5 together with their associated acetyl groups into close proximity.

II.5.B. Acetone/ *tert*-butanol Ratios

A measure of the reactivity of various substrates may be obtained from a measurement of the ease of hydrogen abstraction. This was based on the thermal decomposition of di-*tert*-butylperoxide with the substrate as solvent. In the case of the solids the substrate was dissolved in 2,2,2-trifluoroethanol and a Carbowax column used to separate the solvents following reaction.

A *tert*-butoxyl radical can either abstract a hydrogen atom from the substrate giving *tert*-butanol, [2.93a], or alternatively decompose giving acetone and a methyl radical, [2.93b], Scheme 2.3.

$$(CH_3)_3CO^{\cdot} + R\text{-}H \xrightarrow{k_a} (CH_3)_3COH + R^{\cdot} \qquad \text{-[2.93a]}$$

$$(CH_3)_3CO^{\cdot} \xrightarrow{k_b} CH_3^{\cdot} + CH_3COCH_3 \qquad \text{-[2.93b]}$$

$$\frac{k_a}{k_b} \propto \frac{\%\, CH_3COCH_3}{\%\, (CH_3)_3COH} \qquad \text{-[2.93c]}$$

Scheme 2.3

At a given temperature k_b is independent of the substrate whereas k_a is dependent on the ease of hydrogen atom abstraction. The ratio of acetone to *tert*-butanol will therefore be a measure of the ease of hydrogen atom abstraction,[2.93c]. A large number of these experiments were run previously[56] and the author proposed that an acetone/ *tert*-butanol ratio below ~0.4 would lead to good reaction with hexafluoropropene at room temperature and that despite the limitations e.g. solvent effects, good correlation between reactivity and the acetone/ *tert*-butanol ratios were observed.

In this study a number of acetone/ *tert*-butanol ratios were obtained and the results are given in Table 2.2.

Table 2.2

Acetone/ *tert*-Butanol Ratios for the Thermal Decomposition of Di-t-Butyl Peroxide with a Variety of Substrates

Substrate	Ratio	Substrate	Ratio
N,*N*-Dimethylacetamide (**21**)	0.14	*N*-Methylpiperidine (**11**)	*a*
N,*N*-Diethylacetamide (**25**)	0.26	*N*-Methylmorpholine (**49**)	0.02
N-Acetylpiperidine (**19**)	0.41	$AcHN(CH_2)_2NHAc$ (**68**)	0.35
N-Acetylmorpholine (**52**)	0.23	$AcHN(CH_2)_6NHAc$ (**69**)	0.25
TRAT	2.19	Hexamine	2.48
DAPT	1.97		

a No acetone was detected.

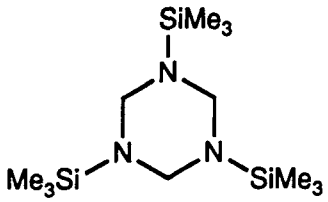
The high values of the acetone/ *tert*-butanol ratios for **TRAT**, **DAPT**, and hexamine are consistent with the stereochemical arguments outlined previously. Compounds (**19**), (**21**), (**52**), (**11**) and (**49**) all have low values for the acetone/ *tert*-butanol ratio and are all reactive to hexafluoropropene as would be predicted. The di-acetyl derivatives (**68**) and (**69**), however, all have low ratios and would be expected to react well with heaxafluoropropene, so that clearly there is more to be considered in these cases than simply initial radical formation indicating that a conformational argument may be significant.

Combining the factors discussed above the lack of reactivity of the acetyl derivatives of **RDX** and **HMX** may be rationalised in terms of:-

1. An acetyl substituent reduces the stability and reactivity of radical (**6**), (Scheme 2.2).
2. The inductive effect of a second heteroatom further reduces the reactivity of radical (**6**), together with a reduction in the electron density at carbon. This results in a reduction in the rate of hydrogen atom abstraction by an electrophilic adduct radical (**7**), (k_5).
3. Steric or stereoelectronic effects are also important in preventing free radical addition to fluoroalkenes.

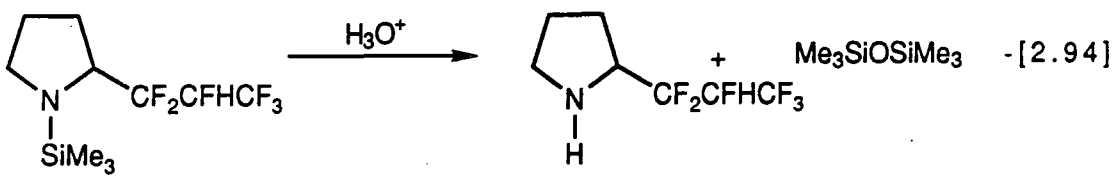
It is now understandable that the acetyl derivatives of **RDX** and **HMX** are unreactive with hexafluoropropene. From our studies, we concluded that the only means of raising the potential for reactivity is the introduction of trimethylsilyl groups as protection for nitrogen. With a view to investigating this an attempt was made to synthesis the trimethylsilyl analogue of **TRAT**, 1,3,5-tris(trimethylsilyl)hexahydro-s-triazine (**104**).

II.6. Attempted Synthesis of 1,3,5-Tris(trimethylsilyl)hexahydro-s-triazine (104)



(**104**)

Introduction of trimethylsilyl groups into the hexahydro-s-triazine ring should not only lead to greater reactivity with fluoroalkenes but should also allow for easy transformation into the **RDX** analogue as the trimethylsilyl group is easily cleaved under mild acid conditions to yield the free amine[58], [2.94], which may then be nitrated. Alternatively it may be possible to displace the trimethylsilyl group directly by a nitro group.

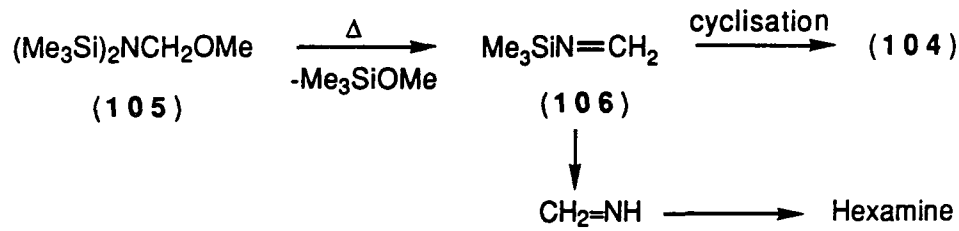


-[2.94]

53%

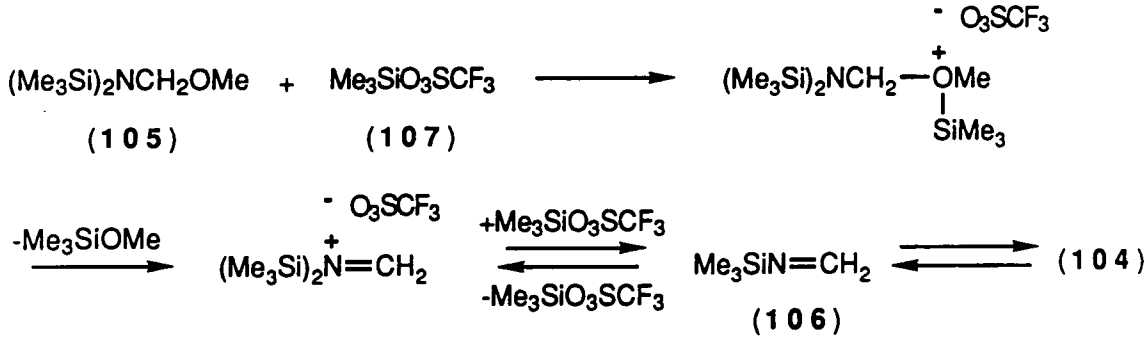
Compounds of the type R^1NHCH_2OMe where (R^1= aryl, alkyl) are known to eliminate methanol to yield an intermediate imine which is then able to cyclise to give a perhydrotriazine[105]. It was possible that elimination of methoxytrimethylsilane could occur from a compound of the type $R^1R^2NCH_2OMe$ (**105**) where (R^1, R^2= trimethylsilyl) to generate an intermediate trimethylsilylimine which could then be capable of cyclisation to (**104**).

Synthesis of (**105**) involved the addition of chloromethylmethylether to lithium bis(trimethylsilyl)amide using hexamethyldisilazane as solvent in a Grignard type reaction[106]. Compound (**105**) was produced in a low yield (~5%) although this yield was subsequently improved by carrying out the addition at -10°C and using tetrahydrofuran as solvent (~35%)[107]. Compound (**105**) was heated in a Carius tube under vacuum but no reaction was observed on gradually increasing the temperature until 100°C when a white solid was observed to form, which was subsequently identified as hexamine. It seems possible that instead of producing the desired trimethylsilylimine intermediate (**106**) an imine intermediate of the type CH_2=NH is being formed, Scheme 2.4. This imine is a proposed intermediate in the mechanism of the reaction of formaldehyde and ammonia which leads ultimately to hexamine[37].



Scheme 2.4

It has been proposed that (**104**) may be produced in equilibrium with trimethylsilylimine (**106**) during the decomposition of *N*,*N*-bis(trimethylsilyl)-methoxymethylamine[108] (**105**) induced catalytically by trimethylsilyl trifluoromethane-sulphonate (**107**), Scheme 2.5, and this claim needs to be investigated further.


(Me3Si)2NCH2OMe
(105)
Me3SiO3SCF3
(107)
- O3SCF3
(Me3Si)2NCH2—OMe
SiMe3
-Me3SiOMe
- O3SCF3
(Me3Si)2N=CH2
+Me3SiO3SCF3
-Me3SiO3SCF3
Me3SiN=CH2
(106)
(104)

Scheme 2.5

CHAPTER THREE

THE SYNTHESIS OF FLUORINATED HETEROCYCLES FROM FLUORINATED ALDEHYDES AND AMMONIA

CHAPTER THREE

THE SYNTHESIS OF FLUORINATED HETEROCYCLES FROM FLUORINATED ALDEHYDES AND AMMONIA

III.1. Introduction

In the previous chapter an investigation was undertaken with the aim of introducing fluoroalkyl groups into the 2,4 and 6 positions of the hexahydro-s-triazine ring via the free radical modification of **TRAT** (section II.3.B.). It was concluded that a combination of an unfavourable stereochemistry together with the presence of an electron withdrawing group on nitrogen was responsible for the subsequent lack of reactivity.

An alternative approach would be to synthesise the s-triazine ring directly from fluorinated precursors. There are essentially two routes to s-triazines which may be adopted.

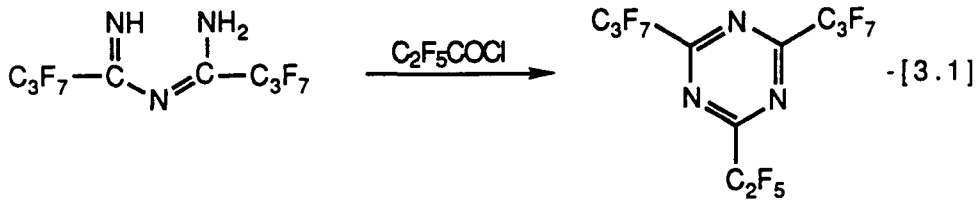
III.2. Synthesis of s-Triazine Derivatives

III.2.A. The Synthesis of Unsaturated s-Triazine Derivatives

Unsaturated s-triazine heterocycles have been known since the mid 19th century and a text book is available on the subject[34]. Synthesis of haloalkyl s-triazines, however, is a more recent topic with the preparation of the first perhalomethyl-s-triazine in 1940 from the acid catalysed cyclisation of 2,2,2-trichloroacetonitrile at about 55 atmostpheres[109]. In 1947 the first fluorine containing perhaloalkyl-s-triazine was prepared from the fluorination using hydrogen fluoride and antimony pentachloride of the trichloro-acetonitrile trimer[110], and later work made possible the synthesis of a wide range of α-haloperfluoromethyl-s-triazines by the reaction of the corresponding α-haloperfluoro-methylnitriles with ammonia[111].

Synthesis of an s-triazine ring in which the perfluoroalkyl groups may be varied on the 2,4 and 6 positions was achieved from the reaction of *N'*-(perfluoroacylimidoyl)-perfluoroalkylamidines with a perfluoroacylanhydride or chloride[112]. This is illustrated for the reaction of *N'*-(perfluorobutyrimidoyl)perfluorobutyramidine (**108**) with

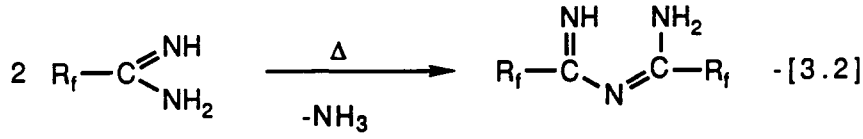
perfluoropropionylchloride, giving 2-(perfluoroethyl)-4,6-bis(perfluoropropyl)-s-triazine (**109**), [3.1].



-[3.1]

(**108**) (**109**)

The formation of the *N'*-(perfluoroacylimidoyl)perfluoralkylamidine was achieved by the deammonation of perfluoroalkylamidines[113] (**110**), [3.2].



-[3.2]

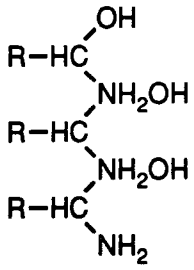
(**110**) R_f = perflouroalkyl

It has also been demonstrated recently that perfluoroalkyl-s-triazines, in which the perfluoroalkyl groups on the 2,4 and 6 positions are the same, may be prepared directly from the trimerisation of perfluoroalkylnitriles at pressures ≥ 400MPa (~ 3950 atm.) and ~125°C using teflon ampoules[114].

III.2.B. The Synthesis of Saturated s-Triazine Derivatives

Attempts to directly synthesise 2,4,6-hexahydro-s-triazine derivatives has received relatively little attention in the literature, with most preparations concentrating on the synthesis of the 1,3,5-hexahydro-s-triazines. Towards the end of the last century it was claimed that the reaction of acetaldehyde and ammonia at low temperature gave 2,4,6-trimethylhexahydro-s-triazine, known in the literature as 'aldehyde-ammonia'[115]. A claim was also made for the synthesis of 2,4,6-tris(trichloromethyl)-hexahydro-s-triazine from an analogous reaction of trichloroacetaldehyde (chloral) with ammonia[116]. The production of these hexahydro-s-triazines was however questioned, and it was suggested

that the products of these reactions were in fact linear trimers (**111**) which decomposed over several days to linear dimers[117].



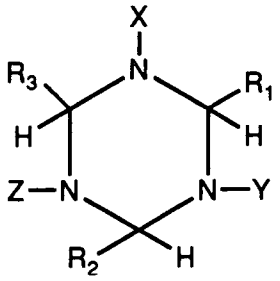
R= CH_3, CCl_3

(**111**)

The cyclic structure of 'aldehyde-ammonia' was, however, later confirmed from the results of X-ray data[118], which was supported by a more detailed Infra-red study[119].

III.3. The Synthesis of Trifluoroacetaldehyde Derivatives

In 1971 it was claimed that trifluoroacetaldehyde (fluoral) reacted with ammonia at low temperature (-50°C)[33], with the initial adduct eliminating water to give a monomeric imine. This was analogous to the reaction observed previously with hexafluoroacetone and ammonia[120], but whereas the imine formed from hexafluoroacetone and ammonia did not react further, the imine formed from trifluoroacetaldehyde and ammonia was claimed to cyclise to give the trimer 2,4,6-tris(trifluoromethyl)-hexahydro-s-triazine (**112**), [3.3].



(**112**) X=Y=Z=H, $R_1=R_2=R_3=CF_3$
(**113**) X=Y=Z=NO, $R_1=R_2=R_3=CF_3$ -[3.3]
(**114**) X=Y=Z=NO_2, $R_1=R_2=R_3=CF_3$
(**115**) X=Y=Z=NO, $R_1=R_2=R_3=H$

In the same paper further reactions of (**112**) were reported with dinitrogen tetroxide to give the trinitroso derivative (**113**). It was not possible to oxidise (**113**) to the trinitro derivative (**114**) using the same method used to oxidise (**115**) to **RDX**[34], but it was

found possible to prepare (**114**) by treating (**113**) with a mixture of 100% nitric acid and trifluoroacetic anhydride.

III.3.A. Results and Discussion

III.3.A.(1). Introduction

It appeared then from the literature[33] that the desired fluoroalkyl-hexahydro-s-triazine derivatives of **RDX** could be synthesised from the reaction of a fluorinated aldehyde and ammonia, although it seemed surprising that only the trimer was formed. It was therefore decided to investigate the literature claim by reacting trifluoroacetaldehyde and heptafluorobutyraldehyde with ammonia.

III.3.A.(2). The Synthesis of Trifluoroacetaldehyde

Trifluoroacetaldehyde may be prepared from the reduction of acid chlorides (the Rosenmund reaction)[121], from the reduction of nitriles[122] or the oxidative nitration of 1,1,1-trifluoropropane[123]. Problems which are associated with these methods are in the relatively low yields of aldehyde in comparison with the inverse addition of lithium aluminium hydride to the perfluoroacid at low temperature (-5 to 0°C)[124], which gives > 75% yield of the aldehyde. The aldehyde is produced as its hydrate, a discussion of which is given in the literature[125], free aldehyde being obtained from the dehydration of the hydrate using phosphorous pentoxide and concentrated sulphuric acid[124]. Formation of trifluoroacetaldehyde is confirmed from its gas cell Infra-red spectrum[121,126].

III.3.A.(3). The Synthesis of Fluorinated Heterocycles

III.3.A.(3).a. The Reaction of Trifluoroacetaldehyde and Ammonia

Following the method given in the literature[33], trifluoroacetaldehyde was added as a gas below the surface of a solution of liquid ammonia in dry diethylether at -50°C. After refluxing the mixture for a short time (Dry Ice condenser), the mixture was allowed to warm to room temperature and excess ammonia and solvent removed by distillation. Water of reaction was removed azeotropically using toluene, and the semi-crystalline residue remaining was purified by sublimation *in vacuo* at 60°C. Only a small amount of

fluorocarbon residue remained following reaction, indicating that very little trifluoroacetaldehyde had reacted.

The yield of the reaction was only 1.7% of the theoretical yield (assuming that a trimer is obtained), based on trifluoroacetaldehyde, and compares to a yield of 36% for the literature synthesis[33]. An elemental analysis of the crystalline product was comparable with the value obtained in the literature, which is consistent with a trimer, Table 3.1.

Table 3.1

	C (%)	H (%)	N (%)
Calculated for $C_6H_6F_9N_3$	24.8	2.1	14.4
literature value[13]	25.1	2.3	14.2
Obtained	25.0	1.9	14.0

The melting point found (79-81°C) compared reasonably with the literature value (83-84°C[33]). Similarly in the IR spectrum an N-H stretch was observed at 3390cm^{-1}, except that an additional absorption at 1700cm^{-1} was also observed (carbonyl or imine stretch) which was not seen in the literature[31].

GLC (packed column) analysis of the solid (dissolved in analar acetone) showed the presence of four components with similar retention times. G.C. mass spectrometric analysis (chemical ionisation mode CI^+) gave a different highest mass and breakdown for each component, which would seem to rule out the possibility of isomers being present, *m/z* varying from 575 to 426. The base peak for each component however was the same, *m/z* 91 (*c.f* 97 for $CF_3CH{=}NH$). Values obtained from mass spectrometric analysis were quite different to the molecular weight quoted in the literature (301, ebullioscopic in benzene), which is close to a value corresponding to a trimer (291). Fast atom bombardment mass spectrometry (FB^+ and FB^-) proved to be confusing in that a large range of masses was observed with a highest mass at *m/z* 882.

A ^{19}F NMR spectrum of the solid exhibited two groups of lines in the approximate ratio of 3:1 centred at 60ppm and 70ppm respectively, indicative of CF_3 in two different

environments. A ^{13}C NMR spectrum (broad band decoupled) gave two overlapping sets of quartets centred at 122ppm ($^{1}J_{C-F}$ = 280Hz) indicative of CF_3 again in two different environments and three sets of quartets in the approximate ratio of 4:4:1 centred at 62ppm, 65ppm ($^{2}J_{C-F}$ = 33.5Hz) and 70ppm respectively ($^{2}J_{C-F}$ = 36.9Hz) indicative of the carbon atom attached to CF_3 being in three different enviroments. Owing to the small amount of product obtained from this reaction (0.21g) the method was not pursued further.

In a different approach, the reaction was repeated using an autoclave, which was charged with trifluoroacetaldehyde, ammonia and diethylether and rocked overnight. Following the azeotropic removal of water with toluene and sublimation *in vacuo* at 60°C, a crystalline solid was obtained (25%) (assuming the formation of a trimer). Elemental analysis of the solid was comparable with the values obtained in the literature, Table 3.2.

Table 3.2

	C (%)	H (%)	N (%)
Calculated for $C_6H_6F_9N_3$	24.8	2.1	14.4
literature value[13]	25.1	2.3	14.2
Obtained	24.45	2.1	14.3

The melting point found (78-80°C) also compared reasonably with the literature value (83-84°C[33]). An IR spectrum showed the expected N-H stretch at 3340cm^{-1} and 3315cm^{-1}, but no absorption was observed at 1700cm^{-1} as had been observed previously. GLC (packed column) analysis of the solid (dissolved in analar acetone) showed, in this case, the presence of three components with similar retention times. G.C. mass spectrometric analysis (chemical ionisation mode CI^+) gave a different highest mass and breakdown for each component, *m/z* varying from 573 to 421. The base peak for each component however was the same as observed previously, *m/z* 91 (*c.f.* 97 for $CF_3CH{=}NH$). Thin layer chromatography also indicated the presence of three main

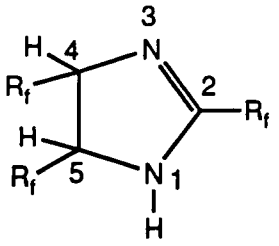
components, although a degree of tailing of each component was observed. Column chromatography and flash column chromatography[127] were used to attempt to resolve these components, but this was found to be unsuccessful, and so it was impossible to obtain a detailed analysis of the products of this reaction.

A ^{19}F NMR spectrum gave two CF_3 lines in the approximate ratio of 1:14 at 64ppm and 69ppm respectively which was different to the spectrum observed previously. A ^{13}C NMR spectrum (broad band decoupled) was similar in the observance of two overlapping sets of quartets centred at 122ppm ($^1J_{C-F}$ =226Hz), but only two sets of quartets centred at 64ppm and 69ppm ($^2J_{C-F}$ =33Hz).

As was suspected the situation for the reaction of trifluoroacetaldehyde and ammonia is much more complex than was reported[33]. It would seem that oligomers are being formed, which cannot be separated, and that the literature report is clearly incorrect in claiming the exclusive formation of the trimer.

III.3.A.(3).b. The Reaction of Heptafluorobutyraldehyde and Ammonia

Reaction of heptafluorobutyraldehyde with ammonia was also investigated for comparison with the reaction of trifluoroacetaldehyde. Heptafluorobutyraldehyde was obtained as a commercial hydrate which was dehydrated to give the free aldehyde[125] (confirmed by gas-cell Infra-red spectrum[122]). A mixture of aldehyde, diethylether and a slight excess of ammonia was charged to an autoclave and rocked at 100°C overnight. Following reaction and azeotropic removal of water a small amount of a viscous oil remained. Analysis (GLC/ packed column) showed the oil to be composed of three components in the ratio 10:1:1. Preparative scale GLC separated the major component as an easily subliming white crystalline solid, which was found to be 2,4,5-tris(heptafluoropropyl)-4,5-dihydroimidazole (**116**).



$R_f = CF_2CF_2CF_3$

(116)

III.4.A. **Identification of the Product**

Elemental analysis gave the combining ratio as $C_{12}H_3N_2$. It is known from the starting material that there are seven fluorine atoms associated with every four carbon atoms, so that the molecular formula $C_{12}H_3N_2F_{21}$ may be postulated for the product. Evidence for the molecular formula was obtained from the mass spectrum (EI^+, *m/z* 555 (M-F, 4%), 405 (M-$CF_2CF_2CF_3$, 100%)). A ^1H NMR spectrum gave three proton signals in a 1:1:1 ratio, a singlet at 5.61ppm (N-H) and two doublets of doublets centred at 4.78 and 5.15ppm respectively. The doublets of doublets were produced from the coupling of the protons at C-4 and C-5 with the inequivalent fluorine atoms of the neighbouring difluoromethylene unit. A signal for a proton attached to carbon next to an NH_2 or NR_2 would be expected to occur around 3ppm, whereas a C-H next to N=C would be expected to occur around 4.9ppm. The similarity observed for the two C-H signals is indicative of tautomerism of the double bond in (**116**). The presence of N-H and C=N is seen from the Infra-red spectrum (3460cm^{-1} , N-H and 1665cm^{-1}, C=N). A ^{13}C NMR spectrum gives a doublet of doublets centred at 59.9 and 69ppm indicative of C-4 and C-5 deshielded by the neighbouring perfluoroalkyl groups, and a triplet centred at 156ppm indicative of C-2. It would appear that the fluorine atoms of the difluoromethylene unit are splitting the C-2 signal in an equivalent manner, and this would again support the tautomerism of the double bond. A complex series of lines appears between 112-121ppm indicative of the highly coupled -$CF_2CF_2CF_3$ unit. A ^{19}F NMR spectrum gave a complex series of lines between 113-127ppm indicative of the highly coupled -CF_2 units and two CF_3 signals at 80.2 and 80.45ppm. This evidence points to the new compound (**116**) as the only reasonable interpretation of this data.

III.4.B. **Confirmation of the Product Structure from the Literature**

That (**116**) is formed is supported by the fact that in general it is known that aromatic aldehydes react to give hydroamides[128], [3.4].

$$3ArCHO + 2NH_3 \longrightarrow ArCH(N{=}CHAr)_2 + 3H_2O \quad -[3.4]$$

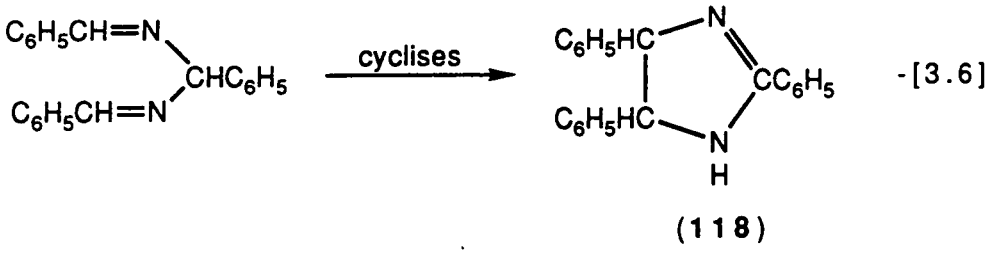
In the case of benzaldehyde an intermediate (**117**) has been isolated which gives the hydroamide on heating[129], [3.5].

$$2C_6H_5CHO + NH_3 \longrightarrow (C_6H_5CHOH)_2NH$$

(**117**) -[3.5]

$$2(C_6H_5CHOH)_2NH \xrightarrow{\Delta} C_6H_5CH(N{=}CHC_6H_5)_2 + C_6H_5CHO + 3H_2O$$

Certain hydroamides on heating further cyclise to give 2,4,5-triaryldihydro-imidazoles, *e.g.* benzaldehyde may be converted into 2,4,5-tribenzyldihydroimidazole (**118**)[130], [3.6].

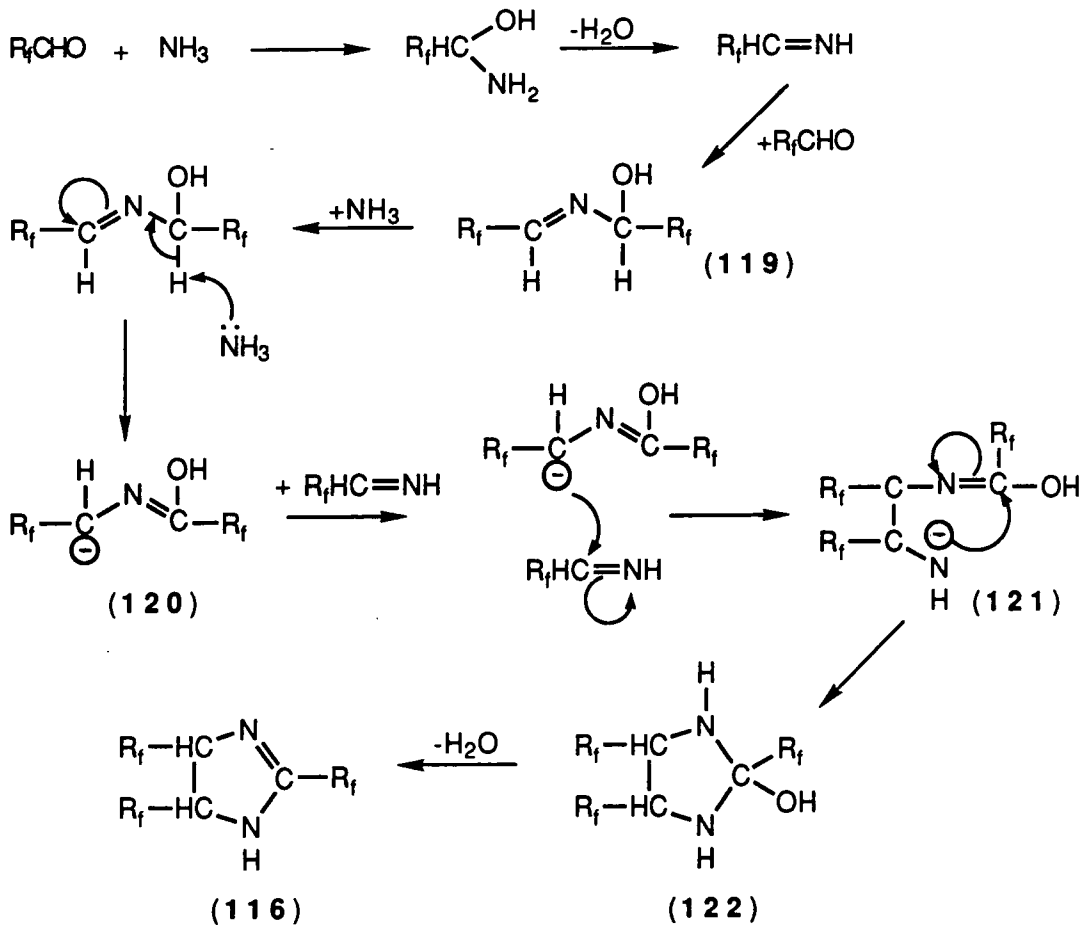


-[3.6]

(**118**)

III.4.C. **The Mechanism for the Formation of (116)**

A mechanism may be proposed to explain the formation of (**116**) from heptafluorobutyraldehyde and ammonia, Scheme 3.1.



Scheme 3.1

In Scheme 3.1 heptafluorobutyraldehyde and ammonia react to give, following the subsequent loss of water, an imine. This imine is then able to react further with aldehyde to give (**119**). Carbanion (**120**), formed from the abstraction of a proton from (**119**) by base, reacts further with imine to give the carbanion (**121**). Internal cyclisation of (**121**) to give (**122**), followed by loss of water, gives the dihydroimidazole derivative (**116**). Formation of (**122**) from (**121**), however, involves a disfavoured 5-*Endo-Trig* cyclisation[131].

III.5. Conclusion

In this study fluorinated aldehydes have been found to react with ammonia, in the case of heptafluorobutyraldehyde reaction leading to the formation of an interesting dihydroimidazole derivative (**116**). Reaction of trifluoroacetaldehyde with ammonia gave a mixture of products, which could not be separated, and clearly for both aldehydes reaction is much more complex than the simple cyclisation of an imine[33].

CHAPTER FOUR

THE DIRECT FLUORINATION OF AMIDES

CHAPTER FOUR

THE DIRECT FLUORINATION OF AMIDES

IV.1. Introduction

Until the early 1960's, fluorination of organic substrates using elemental fluorine had been regarded as being too reactive and dangerous to be of any real practical value[132]. This is easy to understand in that fluorine is such a strong oxidising agent that it will react exothemically with almost any organic compound. Indeed it has been stated that 'the action of fluorine on a carbon compound can be likened to a combustion process where the products are carbon tetrafluoride and hydrogen fluoride'[133]. The exothermic nature of the reaction of an organic compound with fluorine is illustrated in Scheme 4.1.

			ΔG_{298K}/kcalmol^{-1}
Initiation	$F_2 \longrightarrow 2F^{\cdot}$	-(1)	+29.55
Propagation	$R\text{-}H + F^{\cdot} \longrightarrow R^{\cdot} + HF$	-(2)	-36.215
	$R^{\cdot} + F_2 \longrightarrow R\text{-}F + F^{\cdot}$	-(3)	-68.1
Termination	$R^{\cdot} + F^{\cdot} \longrightarrow R\text{-}F$	-(4)	-97.5
	$R^{\cdot} + R^{\cdot} \longrightarrow R\text{-}R$	-(5)	-70.3
Overall reaction	$R\text{-}H + F_2 \longrightarrow R\text{-}F + HF$		-103.4

Scheme 4.1

The overall reaction is exothermic enough to break carbon-carbon bonds (C-C - 86kcal/mol^{-1}). Coupled with this the low solubility of fluorine results in reaction occuring at the 'gas-liquid' interface and this allows for the formation of localised 'hot-spots' which can promote unwanted side reactions.

Problems associated with direct fluorination involve a consideration of both kinetic and themodynamic effects[133].

IV.2. Kinetic Effects

In the early stages of fluorination the probability of there being more than one reaction site on the same molecule needs to be reduced, preventing the production of too much localised energy which would lead to fragmentation. Having only one reaction site per molecule in the initial stages of fluorination allows both thermal conduction and molecular vibration to redistribute the energy allowing smooth fluorination. This problem was solved initially by diluting the fluorine with nitrogen or helium and by the use of silver and gold pellets as heat sinks[134]. In the initial stages of fluorination, when fragmentation is most likely to occur, even a ratio of fluorine to nitrogen of 1:10 may be too high for the smooth fluorination of many organic compounds. Use of a cryogenic reactor, developed by Lagow and Margrave[133], solved this problem by gradually bleeding fluorine into a system maintained under an atmosphere of helium or nitrogen. A very low initial concentration of fluorine in the system greatly decreased the probability of fluorine collisions occuring simultaneously on the same molecule, hence fragmentation is reduced. As the reaction proceeds the concentration of fluorine may be gradually increased allowing further fluorination to take place.

IV.3. Thermodynamic Effects

From a thermodynamic standpoint the only step of the reaction illustrated in Scheme 4.1 sufficiently high in energy to break a carbon-carbon bond is step 4, the termination step (-97.5kcalmol^{-1}). Any steps which reduce the concentration of fluorine atoms would reduce the likelihood of fragmentation and side reactions. It is found that the easiest way in which the population of fluorine atoms may be lowered is simply to reduce the temperature at which the fluorination is carried out[133]. The cryogenic reactor mentioned previously utilises a series of reaction zones of progressively lower temperature which condenses the fluorinated material to allow for further fluorination, and this system has been utilised for the fluorination of a wide variety of both heterocyclic and branched amines for use as potential blood substitutes[135,136,137].

A combination of dilute fluorine together with a low temperature of reaction has enabled a wide range of organic compounds to be fluorinated, and a review of this subject is now available[132].

IV.4. Fluorination of Amides

IV.4.A. Introduction

Direct fluorination of amides is a subject which has received only a limited treatment in the literature. Initial studies were directed towards the fluorination of acetamide and *N*-methylacetamide. Fluorination of an aqueous solution of acetamide using a ratio of fluorine to nitrogen of 1:10 produced only acetic acid, carbon dioxide, nitrous acid and a trace of tetrafluorohydrazine. The corresponding fluorination of *N*-methylacetamide was reported to give acetic acid, carbon dioxide and difluoraminomethane (7%) as the only products of fluorination[138].

Subsequently an investigation was undertaken into the fluorination of a series of secondary amides using a solution or suspension of the amide in either water or acetonitrile[139], Table 4.1.

Table 4.1

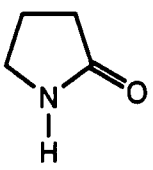
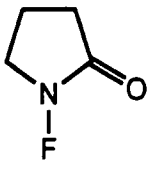
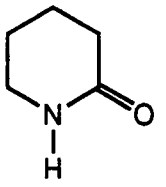
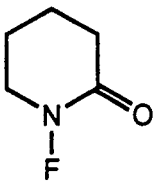
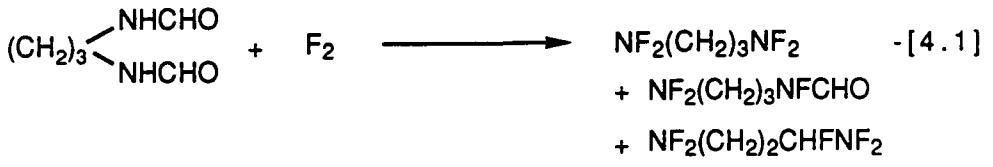
Starting material	Product	% Yield
CH_3NHCHO	CH_3NFCHO	31%
	CH_3NF_2	
C_2H_5NHCHO	C_2H_5NFCHO	5.5%
	$C_2H_5NF_2$	
$CH_3CONHCH_2CH_2CO_2H$	$NF_2CH_2CH_2CO_2H$	36%
		16.5%
	$NF_2(CH_2)_3CO_2H$	11%
	$NF_2(CH_2)_3COF$	

Table 4.1(cont.)

Starting material	Product	% Yield
		20%

Results of this study showed that the reactions of both aliphatic and cyclic secondary amides proceeded by the fluorination of N-H followed by the subsequent fluorinolysis of the acyl group leading to difluoraminoalkanes, analogous to the reactions of carbamates[140,141].

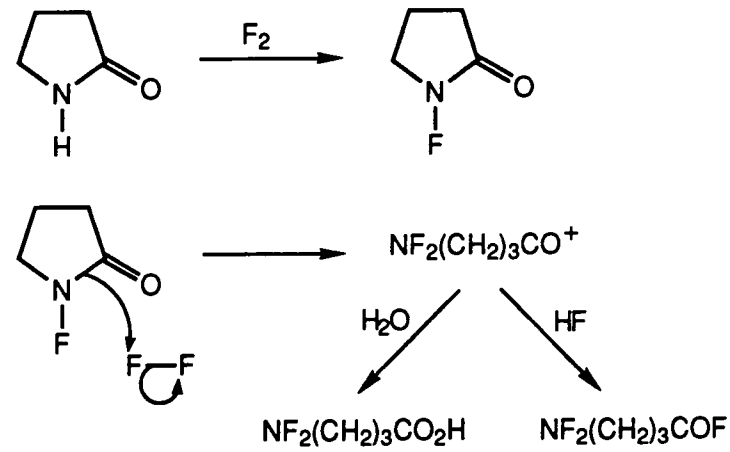
Fluorination of *N,N'* -diformyl-1,3-diaminopropane (a difunctional amide) using a large excess of fluorine gave, in addition to 1,3-bis(difluoramino)-propane and *N,N,N'*-trifluoro-*N'*-formyl-1,3-diaminopropane, a trace of 1,3-bis(difluoramino)-1-fluoropropane, [4.1].



-[4.1]

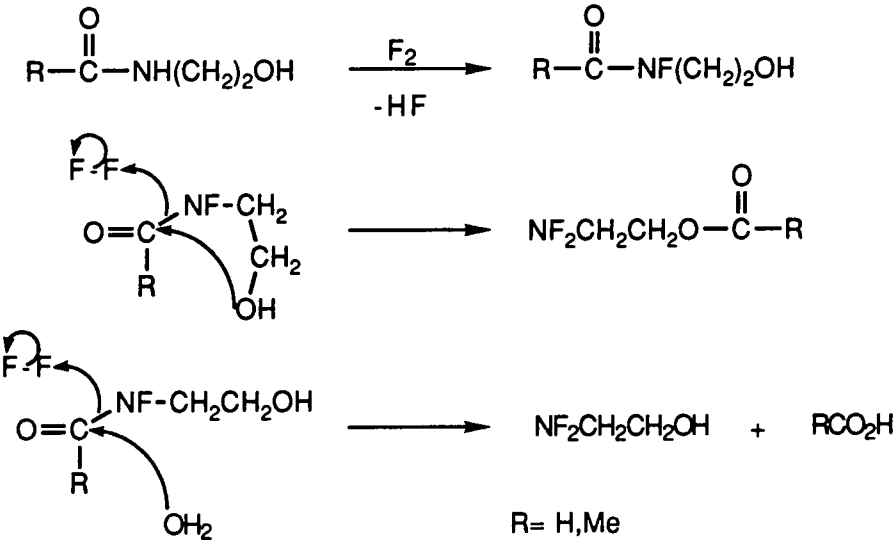
This reaction illustrates the preferential reaction of N-H over C-H, fluorination of C-H occuring only at high fluorine concentrations.

The fluorinolysis of the acyl group encountered in the fluorination of secondary amides was rationalised as an electrophilic displacement of acylium ions by fluorine[139]. In the case of the lactams the acyl fragment is retained and converted to a carboxylic acid in an aqueous medium, and to an acyl fluoride in a non-aqueous medium. This is illustrated for 2-pyrrolidinone which gave 4-difluoraminobutyric acid in water and 4-difluoroaminobutyryl fluoride in the case where no solvent was used, Scheme 4.2.



Scheme 4.2

Further evidence in support of this mechanism was obtained from the fluorination of *N*-acylethanolamines[139]. Fluorination of both the formyl and acetyl derivatives in aqueous solution gave 2-difluoraminoethanol together with a mixture of esters, Scheme 4.3.

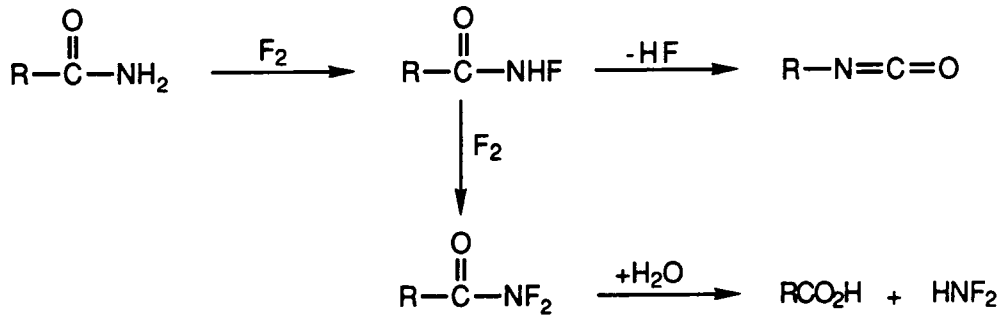


Scheme 4.3

This demonstrated that the alcohol was competing with the solvent for the acylium ion.

The same authors fluorinated cyclohexanecarboxamide (a primary amide) and observed the formation of cyclohexylisocyanate and cyclohexanecarboxylic acid. Starting material was found not to be hydrolysed by hydrogen fluoride in a control experiment, and it was suggested that a difluoroamide was being formed as a precursor to the acid. It

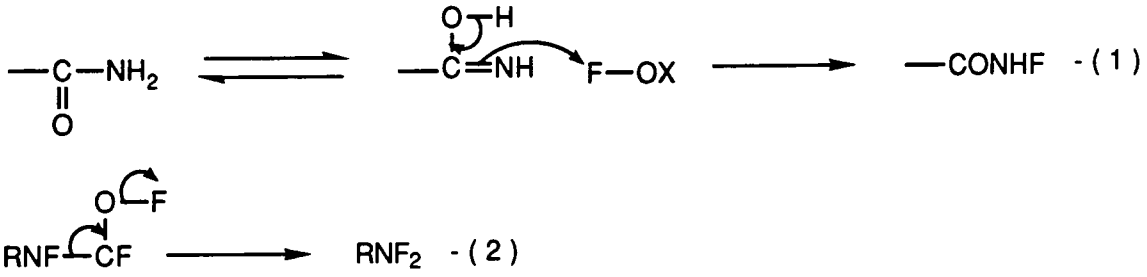
was postulated that the precursor to the isocyanate was an *N*-monofluoroamide which formed the isocyanate via a Hoffmann rearrangement, Scheme 4.4.



Scheme 4.4

Further evidence for the formation of a difluoroamide in the fluorination of primary amides was obtained from the isolation of tetrafluorohydrazine from the chromic acid oxidation of the mixture obtained from the fluorination of acetamide[139]. This indicated the presence in the reaction mixture of either *N,N*-difluoroacetamide or its hydrolysis product difluoramine.

It had previously been proposed that fluorination of amides occured by the reaction of the enol form of the amide with either oxygen difluoride or hypofluorous acid[138]. Fluorine then adds across the carbonyl group of the fluorinated amide and an intramolecular rearrangement leads to the difluoroamine, Scheme 4.5.

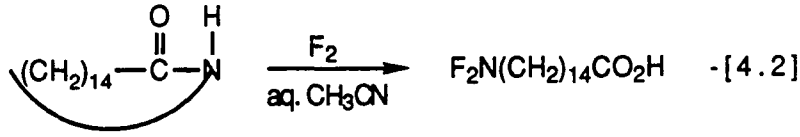


Scheme 4.5

The fact that these reactions lead to the same products using acetonitrile as solvent, together with the fact that simple amines can be fluorinated in buffered aqueous solution[142] would seem to rule out step 1 in Scheme 4.5, and the lack of evidence for the

addition of fluorine to the carbonyl group of simple esters[143] would also seem to rule out step 2. It was proposed that the only simple mechanism which would account for the experimental observations is the electrophilic displacement of hydrogen and acylium ions by molecular fluorine discussed previously[139].

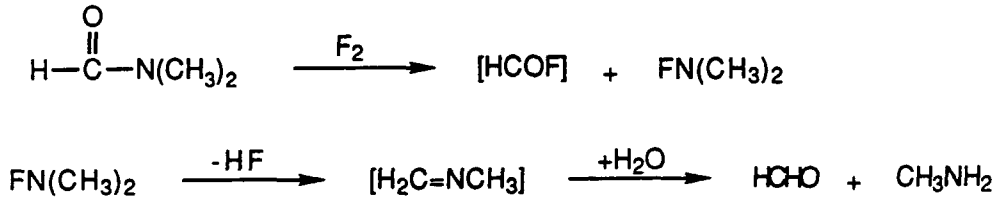
Fluorination of N-H followed by fluorinolysis has been utilised in the preparation of difluoraminocarboxylic acids by the treatment of the corresponding lactam with fluorine in aqueous acetonitrile, illustrated for the preparation of 15-(difluoramino)-pentadecanoic acid, [4.2].



-[4.2]

The $-NF_2$ group is an isostere for $-CH_3$ allowing the formation of radio-labelled long chain fatty acid analogues for use in cardiac imaging[144].

The study of the fluorination of tertiary amides has been limited to *N,N*-dimethylformamide[145] which initially gave a solution stable only at -20°C. Raising the temperature, or the addition of water to this solution, resulted in the formation of methylamine as one of the products. It was proposed that fluorination of *N,N*-dimethylformamide followed by fluorinolysis would be expected to give dimethylfluoramine, which could subsequently eliminate hydrogen fluoride to give methylamine, as illustrated in Scheme 4.6.

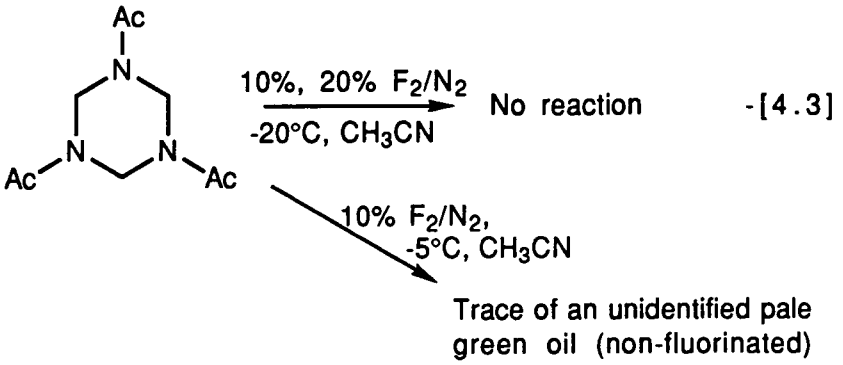


Scheme 4.6

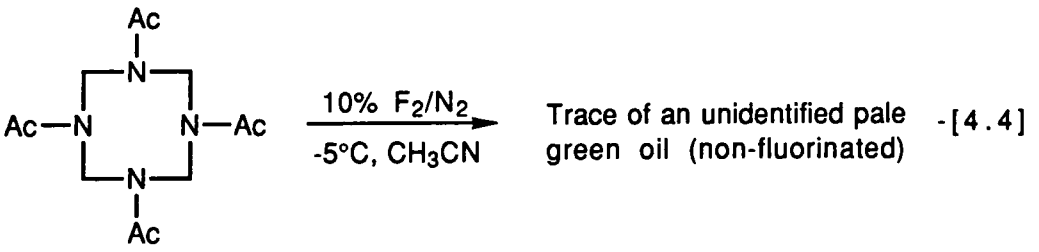
IV.4.B. **Discussion**

The aim of this study was to introduce fluorine into the tertiary amides **TRAT** and **TAT**.

A sample of **TRAT** (in dry acetonitrile) was fluorinated at low temperature (-20°C), (to minimise the heat of reaction), using a 10% mixture of fluorine in nitrogen. Following reaction the mixture was found to contain starting material and no fluorinated products. Subsequently a 20% mixture of fluorine in nitrogen was also found to give no fluorinated material following reaction. Increasing the temperature of reaction to -5°C, and using a 10% mixture of fluorine in nitrogen resulted in the formation of hydrogen fluoride, which would seem to indicate that reaction had occured. Removal of solvent under reduced pressure gave a small quantity of a non-fluorinated pale green oil, which could not be identified, [4.3].



A similar observation was also found on fluorination of **TAT** under comparable conditions, [4.4].



The inability to isolate fluorinated material from the direct fluorination of **TRAT** and **TAT** may be a result of the decomposition of the starting material and any fluorinated

product in the hydrogen fluoride produced during the reaction. Acid-base studies of **TRAT** and **TAT** suggest that a high molar concentration of acid (>6M) would be required for protonation and subsequent decomposition, as both **TRAT** and **TAT** are extremely weak bases, as a result of the cumulative effect of the electron withdrawing acetyl groups[146]. This effect would therefore only be expected to be significant with high concentrations of hydrogen fluoride.

In order to discount this possibility, however, **TRAT** was fluorinated in pyridine (which would form a complex with hydrogen fluoride) and in sodium carbonate solution (which would precipitate sodium fluoride from the reaction mixture). In pyridine, fluorination at -30°C with a 20% mixture of fluorine in nitrogen resulted in a darkening of the solution, but on subsequent work-up no fluorinated material was observed. In aqueous sodium carbonate solution at -5°C, using a 10% mixture of fluorine in nitrogen, no decomposition occured, as had been found using acetonitrile as solvent, [4.3]. It was found that a 20% mixture of fluorine in nitrogen could be bubbled through the solution at room temperature with no decomposition occuring, although no fluorinated material was observed. UV irradiation (which should greatly increase the fluorine atom concentration and hence promote reaction) of the mixture, contained in FEP tubing, also failed to yield fluorinated material.

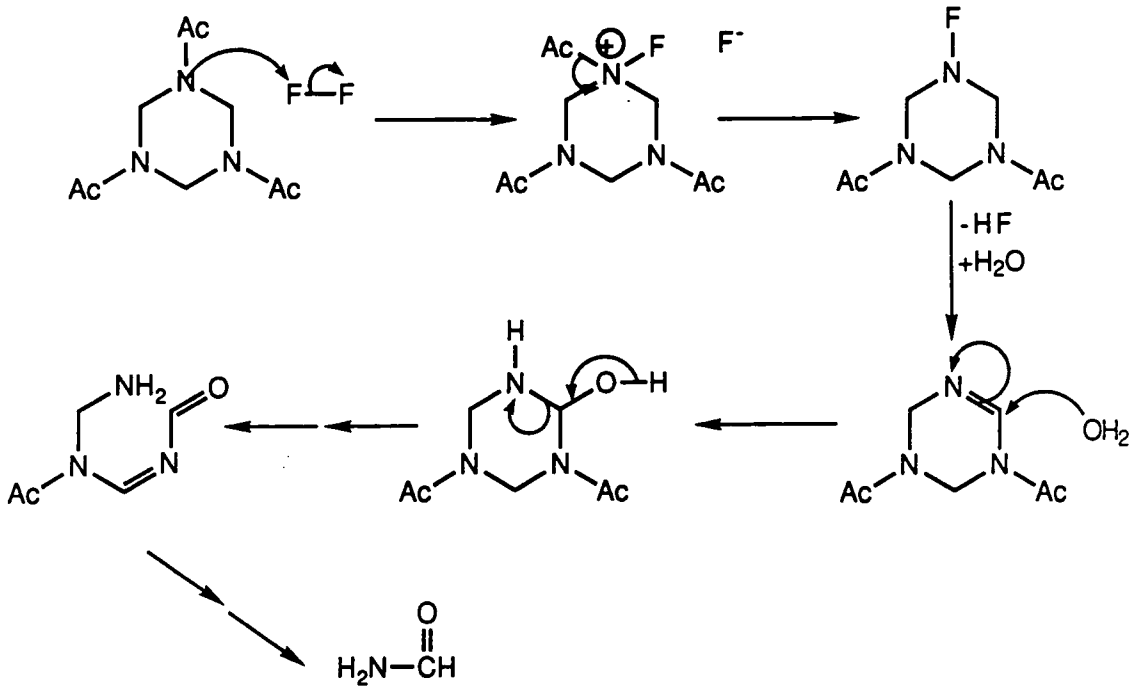
An attempt was made to fluorinate **TRAT** under more forcing conditions, in which the substrate, dissolved in aqueous sodium carbonate and contained in an autoclave, was charged to a pressure of 10 atmostpheres with a 30% mixture of fluorine in nitrogen, and heated to 100°C overnight. Removal of solvent under reduced pressure followed by extraction with ether and chloroform isolated an off-white solid, identified as hexamine. It would seem that the high pressure and temperature of the reaction decomposed the starting material to smaller fragments which subsequently recombined to give hexamine.

A simpler system *N*,*N'*-diacetylpiperazine (**71**) was also observed to remain unchanged in aqueous sodium carbonate solution during fluorination at room temperature, using a 20% mixture of fluorine in nitrogen High pressure fluorination under comparable conditions used for the high pressure fluorination of **TRAT** failed to

yield fluorinated material, although the substrate was not decomposed at the high temperature and pressure of the reaction.

IV.4.B.(1). Mechanism

It may be postulated that the mechanism of reaction of **TRAT** during fluorination is analogous to that of *N,N*-dimethylformamide[145](see Scheme 4.6), Scheme 4.11.



Scheme 4.11

Hydrolysis leads to decomposition of the intermediate cyclic imine initiated by the condensation of water into the reaction mixture during fluorination, and this would account for the loss of material during reaction together with the absence of any fluorinated product.

Direct fluorination of **TRAT** and **TAT** does not produce substitution of fluorine atoms in the 2,4 and 6 positions of the hexahydrotriazine ring. It seems reasonable that replacement of the acetyl substituent with a fluorine atom is occuring preferentially, followed by decomposition of the ring.

EXPERIMENTAL

INSTRUMENTATION

Gas Liquid Chromatographic Analysis

Gas liquid Chromatography (GLC) analysis was carried out on a Hewlett Packard 5890A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column. Preparative GLC was performed on a Varian Aerograph Model 920 (catharometer detector) gas chromatograph.

Distillation

Fractional distillation of product mixtures was carried out using a Fischer Spahltrohr MMS 255 small concentric tube apparatus. Boiling points were recorded during distillation.

Melting Points

Melting points were carried out at atmospheric pressure and are uncorrected.

Elemental Analysis

Carbon, hydrogen and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba 1106 Elemental Analyser. Analysis for halogens were performed as described in the literature[151].

Infrared Spectra

Infra Red spectra were recorded on either a Perkin-Elmer 457 or 577 Grating Spectrophotometer using conventional techniques.

NMR Spectra

Proton NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B (60MHz), a Bruker AC250 (250MHz) and a Varian VXR400S (400MHz) NMR spectrometer.

Fluorine NMR spectra were recorded on a Varian EM360l (56.45MHz), a Bruker AC250 (235MHz) and a Varian VXR400S (365MHz) NMR spectrometer.

Carbon NMR were recorded on a Bruker AC250 (63MHz) and a Varian VXR400S (100MHz) NMR spectrometer.

Mass Spectra

Mass spectra of solid samples were recorded on a VG 7070E spectrometer. G.C. mass spectra were recorded on the VG 7070E spectrometer linked to a Hewlett Packard 5790A gas chromatograph fitted with a 25m cross-linked methyl silicone capillary column.

Reagents and Solvents

In general chemicals were used as received from suppliers (Aldrich, Lancaster) and solvents were dried by standard procedures.

CHAPTER FIVE

EXPERIMENTAL TO CHAPTER TWO

CHAPTER FIVE

EXPERIMENTAL TO CHAPTER TWO

General Procedure

1. γ-ray Initiated Reactions

Solution and/or liquid reagents were introduced into a pyrex Carius tube (*c.a.*100ml) and degassed. Any gaseous reagents were transferred using normal vacuum line techniques. The tube was sealed with the reagents frozen (liquid air) and under vacuum. The tube was placed in a metal sleeve and, unless otherwise stated was then irradiated with γ-rays to a total dose of *c.a.* 10 Mrads at a temperature of 18°C. The tube was opened while the contents were frozen (liquid air) and any gaseous components were transferred under vacuum.

2. Peroxide Initiated Reactions

Solution and/or liquid reagents were introduced into a steel autoclave (125ml) and degassed. Any gaseous reagents were transferred using normal vacuum line techniques. The autoclave was then heated at the required temperature in a thermostatically controlled rocking furnace. The tube was opened while the contents were frozen (liquid air) and any gaseous components were transferred under vacuum.

V.1. Reactions of Amine Derivatives with Hexafluoropropene

V.1.A. Attempted Addition to Model Compounds for Explosives

V.1.A.(1). Attempted Addition to Hexamine

Peroxide Initiation at 80°C

A mixture of hexamine (1.29g, 9mmol), 2,2,2-trifluoroethanol (27.32g, 0.27mol), hexafluoropropene (15.32g, 0.1mol) and DBP (0.2g) was heated at 80°C in a rocking furnace overnight. Excess alkene (13.98g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (29.87g). Removal of solvent under reduced pressure gave an orange viscous residue (1.49g) which was shown to contain only starting material by NMR.

Peroxide Initiation at 140°C

A mixture of hexamine (1.68g, 12mmol), 2,2,2-trifluoroethanol (16.86g, 0.17mol), hexafluoropropene (11.45g, 76mmol) and DBP (0.25g) was heated at 140°C in a rocking furnace overnight. Excess alkene (10.3g) was removed by transfer under vacuum (~100mmHg) to leave a liguid. Removal of solvent under reduced pressure gave a brown viscous residue (2.1g) which was shown to contain only starting material by NMR.

γ-ray Initiation

A mixture of hexamine (1.06g, 8mmol), 2,2,2,-trifluoroethanol (11.18g, 0.11mol) and hexafluoropropene (6.96g, 46mmol) was irradiated with γ-rays. Excess alkene (4.63g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (14.33g). Removal of solvent under reduced pressure gave an orange viscous residue (1.71g) which was shown to contain only starting material by NMR.

UV Initiation

A mixture of hexamine (3.48g, 25mmol), 2,2,2,-trifluoroethanol (14.86g, 0.15mol) and hexafluoropropene (3.64g, 24mmol) was irradiated with medium pressure UV lamp (1000W) for ~24 hours. No alkene was recovered and a dark brown liquid remained (21.46g) which was shown to contain only starting material by NMR.

V.1.A.(2). **Attempted Addition to DAPT**

Peroxide Initiation at 80°C

A mixture of **DAPT** (1.07g, 7mmol), 2,2,2-trifluoroethanol (9.11g, 0.09mol), hexafluoropropene (12.15g, 80mmol) and DBP (0.1g) was heated at 80°C in a rocking furnace overnight. Excess alkene (11.24g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (10.73g). Removal of solvent under reduced pressure gave an orange viscous residue (1.8g) which was shown to contain only starting material by NMR.

Peroxide Initiation at 140°C

A mixture of **DAPT** (1.01g, 5mmol), 2,2,2-trifluoroethanol (4.62g, 46mmol), hexafluoropropene (12.16g, 81mmol) and DTBP (0.08g) was heated at 140°C in a rocking furnace overnight. Excess alkene (10.87g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (6.77g). Removal of solvent under reduced pressure gave a black viscous oil (1.4g) which was shown to contain only starting material by NMR.

γ-ray Initiation

In a 2,2,2-Trifluoroethanol Solvent

A mixture of **DAPT** (1.43g, 7mmol), 2,2,2-trifluoroethanol (19.54g, 0.2mol) and hexafluoropropene (8.99g, 60mmol) was irradiated with γ-rays. Excess alkene (7.41g) was removed by transfer under vacuum to give a liquid (21.79g). Solvent was removed under reduced pressure (~100mmHg) to leave an orange viscous residue (3.37g). Analysis of the residue by ^{19}F NMR indicated that only a trace of fluorinated material was present and the reaction was not investigated further.

In an Acetone Solvent

A mixture of **DAPT** (1.19g, 6mmol), acetone (30.27g, 0.52mol) and hexafluoropropene (9.95g, 67mmol) was irradiated with γ-rays. Excess alkene (7.53g) was removed by transfer under vacuum (~100mmHg) to give a liquid (33.17g). Removal of solvent under reduced pressure gave an orange viscous residue (1.61g). Analysis of the residue by ^{19}F NMR indicated that only a trace of fluorinated material was present and the reaction was not investigated further.

V.1.A.(3). **Attempted Addition to DAPT**

Peroxide Initiation at 80°C

A mixture of **TRAT** (1.42g, 7mmol), acetone (9.65g, 0.17mol), hexafluoropropene (5.47g, 37mmol) and DBP (0.15g) was heated at 80°C in a rocking furnace overnight. Excess alkene (7.97g) was removed by transfer under vacuum (~100mmHg) to leave a

liquid. Removal of solvent under reduced pressure gave a viscous brown oil (2.31g) which was shown to contain only starting material by NMR.

Peroxide Initiation at 140°C

A mixture of **TRAT** (1.15g, 5mmol), acetone (8.91g, 0.15mol), hexafluoropropene (7.06g, 47mmol) and DTBP (0.1g) was heated at 140°C in a rocking furnace overnight. Excess alkene (5.78g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (11.23g). Removal of solvent under reduced pressure gave a viscous brown oil (1.72g) which was shown to contain only starting material by NMR.

γ-ray Initiation

A mixture of **TRAT** (1.48g, 7mmol), acetone (9.72g, 0.17mol) and hexafluoropropene (9.4g, 63mmol) was irradiated with γ-rays. Excess alkene (7.81g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (12.63g). Removal of solvent under reduced pressure gave a pale orange viscous residue (1.67g) which was shown to contain only starting material by NMR.

UV Initiation in Quartz Rotaflo

TRAT (1.5g, 7mmol) dissolved in 2,2,2-trifluoroethanol (20.83g, 0.21mol) was charged to a quartz rotaflo fitted with a flexible gas reservoir charged with hexafluoropropene (3.92g, 26mmol). The rotaflo was subsequently irradiated with a medium pressure UV lamp (1000W) for ~45 hours after which the contents of the rotaflo were analysed. Removal of solvent under reduced pressure gave a viscous oil (1.73g) which was shown to contain only starting material by NMR.

UV Initiation

A mixture of **TRAT** (0.87g, 4mmol), acetone (20.8g, 0.48mol), and hexafluoropropene (14.23g, 95mmol) was irradiated with a medium pressure UV lamp (1000W). Excess alkene (12.87g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (12.63g). Removal of solvent under reduced pressure gave a moist

orange solid (1.67g).which was shown by ^{19}F NMR to contain a small quantity of fluorinated material. Washing the sample with distilled water dissolved the starting material, to leave a trace of a dark brown oil (<0.05g) which was decanted and analysed by mass spectrometry to be a mixture of mono-, *m/z* ($C1^+$) 380 (*M* + 17, 41%), and di-adducts, *m/z* ($C1^+$) 530 (*M* + 17, 4%).

V.1.A.(4). **Attempted Addition to TAT**

Peroxide Initiation at 140°C

A mixture of **TAT** (1.32g, 5mmol), 2,2,2-trifluoroethanol (12.63g, 0.13mol), hexafluoropropene (8.46g, 56mmol) and DTBP (0.1g) was heated at 140°C in a rocking furnace overnight. Excess alkene (6.47g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (15.53g). Solvent was removed under reduced pressure to leave a black viscous oil (1.61g) which was shown to contain only starting material by NMR.

γ-ray Initiation

A mixture of **TAT** (0.33g, 1mmol), acetone (26.88g, 0.46mol) and hexafluoropropene (5.74g, 38mmol) was irradiated with γ-rays. Excess alkene (4.2g) was removed by transfer under vacuum (100mmHg) to give a liquid (28.46g). Removal of solvent under reduced pressure gave a white solid (0.41g) which was shown to contain only starting material by NMR.

V.1.B. **Varying Substituents on Reactivity of Nitrogen Derivatives**

V.1.B.(1). **Acyl Derivatives of Amines**

V.1.B.(1).a. **Addition to *N,N*-Dimethylpropanamide**

γ-ray Initiation

A mixture of *N,N*-dimethylpropanamide (9.74g, 0.11mol), acetone (4.87g, 84mmol) and hexafluoropropene (13.33g, 89mmol) was irradiated with γ-rays. Excess alkene (2.46g) was removed under reduced pressure to leave a liquid (25.31g). Distillation of

this liquid gave *N*-(2,2,3,4,4,4-hexafluorobutyl)-*N*-methylpropanamide(**23**) (3.57g, 16%, 68% by GLC); b.p. 118-120°C /19mmHg; (Found: C, 38.15; H, 4.1; N, 5.35 F, 45.1. $C_8H_{11}NOF_6$ requires C, 38.25 H, 4.4 N, 5.6; F 45.4%); IR spectrum 1, NMR spectrum 1, mass spectrum 1. G.C. mass spectrometry also identified *N*,*N*-bis-(2,2,3,4,4,4-hexafluorobutyl)propanamide (**24**) (6% by GLC); mass spectrum 2.

V.1.B.(1).b. **Addition to *N*,*N*-Diethylacetamide (25)**

γ-ray Initiation

A mixture of *N*,*N*-diethylacetamide (**25**) (5.16g, 45mmol) and hexafluoropropene (4.82g, 32mmol) was irradiated with γ-rays. Excess alkene was transferred under vacuum to leave a liquid which was shown to contain only starting material by GLC.

Peroxide Initiation

A mixture of *N*,*N*-diethylacetamide (**25**) (6.28g, 55mmol), hexafluoropropene (4.87g, 32mmol) and DTBP (0.15g) was heated at 140°C in a rocking furnace overnight. Excess alkene (4.3g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (6.47g)., which was shown to contain only starting materials by GLC.

UV Initiation

A mixture of *N*,*N*-diethylacetamide (**25**) (10.14g, 88mmol), acetone (9.46g, 0.16mol) and hexafluoropropene (16.62g, 0.11mol) was irradiated for ~48 hours with a medium pressure UV lamp (1000W). Excess alkene (12.48g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (23.67g) which was found by G.C.mass spectrometry to be composed of starting material together with a mixture of mono- (3% by GLC), *m/z* (EI^+) 265 (M^+, 4%), 222 (3, $M^+ - CH_3CO$), and di-adducts (4% by GLC), *m/z* (EI^+) 415 (M^+, 6%)

V.1.B.(1).c. **Attempted Addition to *N,N*-Dibutylacetamide**

γ-ray Initiation

A mixture of *N,N*-dibutylacetamide (5.69g, 33mmol) and hexafluoropropene (2.35g, 16mmol) was irradiated with γ-rays. Excess alkene (2.27g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (5.57g) which was shown to contain only starting material by GLC.

Peroxide Initiation

A mixture of *N,N*-dibutylacetamide (7.12g, 42mmol), hexafluoropropene (6.48g, 43mmol) and DTBP (0.1g) was heated at 140°C in a rocking furnace overnight. Excess alkene (5.9g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (7.4g)., which was shown to contain only starting materials by GLC.

UV Initiation

A mixture of *N,N*-dibutylacetamide (4.16g, 24mmol), acetone (4.02g, 69mmol) and hexafluoropropene (1.94g, 13mmol) was irradiated for ~48 hours with a medium pressure UV lamp (1000W). Excess alkene (1.31g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (8.87g) which was shown to contain only starting material by GLC.

V.1.B.(1).d. **Addition to *N,N*-Diethylformamide (28)**

γ-ray Initiation

A mixture of *N,N*-diethylformamide (**28**) (12.64g, 0.125mol) and hexafluoropropene (29.33g, 0.196mol) was irradiated with γ-rays. Excess alkene (28.40g) was removed by transfer under vacuum (~100mmHg) to leave a liquid which was shown to contain only starting material by GLC.

Peroxide Initiation at 140°C

A mixture of *N,N*-diethylformamide (**28**) (4.91g, 49mmol), hexafluoropropene (12.46g, 83mmol) and DTBP (0.15g) was heated at 140°C in a rocking furnace

overnight. Excess alkene (11.71g) was removed by transfer under vacuum (~100mmHg) to leave a liquid which was shown to contain only starting materials by GLC.

UV Initiation

A mixture of *N*,*N*-diethylformamide (**28**) (8.46g, 84mmol) acetone (4.89g, 84mmol) and hexafluoropropene (13.33g, 89mmol) was irradiated for ~48 hours with a medium pressure UV lamp (1000W). Excess alkene (12.26g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (14.27g). The liquid was shown by GLC to contain starting material together with a mixture of di- (3% by GLC), *m/z* (EI^+) 386 (*M* - 15, 4%), and tri-adducts (1% by GLC), *m/z* (EI^+) 532 (*M* -19, 2%)

V.1.B.(1).e. **Attempted Addition to *N*-Methyldiacetamide (29)**

γ-ray Initiation

A mixture of *N*-methyldiacetamide (**29**) (3.78g, 33mmol) and hexafluoropropene (7.58g, 44mmol) was irradiated with γ-rays. Excess alkene (7.4g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (3.84g), which was found by GLC to contain only starting material.

Peroxide Initiation at 140°C

A mixture of *N*-methyldiacetamide (**29**) (1.68g, 15mmol), acetone (7.03g, 0.12mol), hexafluoropropene (8.48g, 57mmol) and DTBP (0.1g) was heated at 140°C in a rocking furnace overnight. Excess alkene (7.32g) was transferred under vacuum (~100mmHg) to leave a liquid (17.29g). The liquid was found to contain only starting material by GLC.

UV Initiation

A mixture of *N*-methyldiacetamide (**29**) (2.11g, 18mmol), acetone (4.19g, 72mmol) and hexafluoropropene (9.44g, 63mmol) was irradiated with a medium pressure UV lamp (1000W) for ~48 hours. Excess alkene (8.36g) was removed by

transfer under vacuum (~100mmHg) to leave a liquid (7.11g). The liquid was found to contain only starting material by GLC.

V.1.B.(1).f. **Addition to *N*-Methylpropanamide (32)**

γ-ray Initiation

A mixture of *N*-methylpropanamide (**32**) (11.31g, 0.13mol), and hexafluoropropene (23.42g, 0.16mol) was irradiated with γ-rays. Excess alkene (10.67g) was removed under reduced pressure to leave a liquid (23.84g). Distillation of this liquid gave *N*-(2,2,3,4,4,4-hexafluorobutyl)propanamide (**33**) (2.93g, 9.5%) b.p. 124-126°C/ 40mmHg; (Found: C, 35.55; H, 3.8; N, 6.2. $C_7H_9NOF_6$ requires C, 35.45; H, 3.8 N, 5.9%); IR spectrum 2, NMR spectrum 2, mass spectrum 3.

V.1.B.(1).g. **Addition to *N*-Ethylacetamide (34)**

γ-ray Initiation

A mixture of *N*-ethylacetamide (**34**) (8.81g, 0.1mol) and hexafluoropropene (14.75g, 0.1mol) was irradiated with γ-rays. No alkene was recovered and an off-white solid remained (23.23g). The solid was sublimed at 50°C/ <0.1mmHg to give *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)acetamide (**35**), (22.78g, 96%); m.p. 53-54°C; (Found: C, 35.55; H, 3.9; N, 5.8; F, 47.6. $C_7H_9NOF_6$ requires C, 35.45; H, 3.8; N, 5.9; F, 48.1%); IR spectrum 3, NMR spectrum 3, mass spectrum 4.

V.1.B.(1).h. **Addition to *N*-Propylacetamide (36)**

γ-ray Initiation

A mixture of *N*-propylacetamide (**36**) (9.69g, 96mmol) and hexafluoropropene (15.94g, 0.11mol) was irradiated with γ-rays. Excess alkene (1.82g) was removed by transfer under vacuum (~100mmHg) to leave a viscous oil (23.34g). Distillation of the oil (Spaltrohr) gave *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)acetamide (**37**), (17.59g, 73%); m.p. 38-40°C, b.p 73-74°C/ 2mmHg; (Found: C, 38.35; H, 4.3; N, 5.6; F, 44.9. $C_8H_{11}NOF_6$ requires C, 38.25; H, 4.4; N, 5.6; F, 45.4%); IR spectrum 4, NMR spectrum 4, mass spectrum 5.

V.1.B.(2). **Trimethylsilyl Derivatives of Amines**

V.1.B.(2).a. **Addition to *N*-Trimethylsilylpiperidine (38)**

γ-ray Initiation

A mixture of *N*-trimethylsilylpiperidine (**38**) (9.03g, 58mmol) and hexafluoropropene (3.39g, 23mmol) was irradiated with γ-rays. No alkene was recovered and a light brown liquid remained (12.12g). Distillation of the mixture gave 2-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylpiperidine (**39**) (0.35g, 5%) b.p. 106-108°C / 30mmHg); (Found: C, 43.3; H, 6.3; N, 4.95;. $C_{11}H_{19}NSiF_6$ requires C, 43.0 H, 6.2 N, 4.55%); IR spectrum 5, NMR spectrum 5, mass spectrum 6. A component identified as 2,6-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylpiperidine (**40**) (26% by GLC), mass spectrum 7, was also observed from G.C. mass spectrometry but could not be separated.

V.1.B.(2).b. **Addition to *N,N*-Dimethyltrimethylsilylamine (41)**

γ-ray Initiation

A mixture of *N,N*-dimethyltrimethylsilylamine (**41**) (9.24g, 79mmol) and hexafluoropropene (11.99g, 80mmol) was irradiated with γ-rays. Excess alkene (8.02g) was transferred under vacuum to leave a liquid (15.93g). Preparative scale GLC of the liquid (100°C, 10%SE30) gave *N,N*-bis-(2,2,3,4,4,4-hexafluorobutyl)trimethylsilyl-amine (**42**) (28% by GLC, 33% from recovered alkene); (Found: C, 31.05; H, 3.3; N, 3.65. $C_{11}H_{15}NSiF_{12}$ requires C, 31.65; H, 3.6 N, 3.35%); IR spectrum 6, NMR spectrum 6, mass spectrum 8.

V.1.B.(2).c. **Addition to *N,N*-Diethyltrimethylsilylamine (43)**

γ-ray Initiation

A mixture of *N,N*-diethyltrimethylsilylamine (**43**) (7.74g, 53mmol) and hexafluoropropene (4.93g, 33mmol) was irradiated with γ-rays. Excess alkene (3.49g) was transferred under vacuum to leave a liquid (9.07g). Distillation of the liquid gave *N,N*-bis-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)trimethylsilylamine (**44**) (1.72g, 23.5%, 95.4% pure by GLC) b.p. 109-110°C / 12mmHg). Preparative scale GLC (110°C /

10%SE30) gave a sample sufficiently pure for analysis (Found: C, 35.3; H, 4.45; N, 2.75. $C_{13}H_{19}NSiF_{12}$ requires C, 35.05; H, 4.25 N, 3.15%); IR spectrum 7, NMR spectrum 7, mass spectrum 9.

V.1.B.(3). Effect of Introducing an Oxygen Atom on the Reactivity of Nitrogen Derivatives

V.1.B.(3).a. Addition to Morpholine (47)

γ-ray Initiation

A mixture of morpholine (**47**) (8.83g, 0.1mol) and hexafluoropropene (14.12g, 94mmol) was irradiated with γ-rays. No alkene was recovered and a brown solid remained (22.65g). The solid was sublimed (25°C / 0.1mmHg) to give *N*-(2,3,3,3-tetrafluoropropanoyl)morpholine (**48**) (17.99g, 89%); m.p.70.5-71.5°C (lit.,[147] 71-71.8°C); (Found: C, 39.2; H, 4.2; N, 6.4, F, 35.4. Calc. for $C_7H_9NO_2F_4$: C, 39.05; H, 4.2; N, 6.5, F, 35.35%); IR spectrum 8, NMR spectrum 8, mass spectrum 10.

No Initiation

A mixture of morpholine (**47**) (4.22g, 49mmol) and hexafluoropropene (4.58g, 31mmol) was allowed to stand at room temperature for 24 hours. No alkene was recovered and a brown solid remained. The solid was sublimed (25°C / 0.1mmHg) to give *N*-(2,3,3,3-tetrafluoropropanoyl)morpholine (**48**) by comparison of m.p. and NMR.

V.1.B.(3).b. Addition to *N*-Acetylmorpholine (52)

Peroxide Initiation at 140°C

A mixture of *N*-acetylmorpholine (**52**) (5.07g, 39mmol), acetone (9.43g, 0.16mol), hexafluoropropene (23.55g, 0.16mol) and DTBP (0.1g) was heated to 140°C overnight in a rocking furnace. Excess alkene (21.7g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (16.2g). The liquid was analysed by G.C. mass spectrometry to be composed of mono-adduct (7% by GLC), *m/z* (EI^+) 279, (M^+, 6%).

UV Initiation

A mixture of *N*-acetylmorpholine (**52**) (10.03g, 78mmol), acetone (7.26g, 0.13mol) and hexafluoropropene (10.28g, 69mmol) was irradiated using a medium pressure UV lamp (1000W) for ~48 hours. Excess alkene (7.83g) was transferred under vacuum (~100mmHg) to leave a liquid (19.65g). The liquid was analysed by G.C. mass spectrometry to be composed of a mixture of mono- (11% by GLC), *m/z* (EI^+) 279, (M^+, 14%), and di-adducts (25% by GLC), *m/z* (EI^+) 429 (M^+, 0.4%) which could not be separated.

V.1.B.(3).c. **Competition Between *N*-Acetylmorpholine (52) and *p*-Dioxane (53)**

A mixture of *N*-acetylmorpholine (**52**) (3.34g, 26mmol), *p*-dioxane (**53**) (2.27g, 26mmol) and hexafluoropropene (0.87g, 6mmol) was irradiated with γ-rays. The product mixture was shown by comparison of GLC retention times to consist of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**54**) only.

V.1.B.(4). **Oxygen Containing Trimethylsilyl Derivatives**

V.1.B.(4).a. **Addition to *N*-Trimethylsilylmorpholine (55)**

γ-ray Initiation

A mixture of *N*-trimethylsilylmorpholine (**55**) (9.87g, 62mmol) and hexafluoropropene (5.06g, 34mmol) was irradiated with γ-rays. No alkene was recovered and a dark brown liquid remained (14.83g). Analysis of the liquid by G.C. mass spectrometry identified a minor component 3-(1,1,2,3,3,3-hexafluoro-propyl)-*N*-trimethylsilylmorpholine (**56**) (6% by GLC), mass spectrum 11, and a major component. Preparative scale GLC of the liquid (110°C /10%SE30) isolated the major component as 3,5-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylmorpholine (**57**) (32% by GLC); (Found: C, 33.8; H, 3.6; N, 2.7. $C_{13}H_{17}NOSiF_{12}$ requires C, 34.0 H, 3.7 N, 3.05; %); IR spectrum 9, NMR spectrum 9, mass spectrum 12.

V.1.B.(4).b. **Competition Between *N*-Trimethylsilylmorpholine (55) and *p*-Dioxane (53)**

A mixture of *N*-trimethylsilylmorpholine (**55**) (3.34g, 26mmol), p-dioxane (**53**) (2.27g, 26mmol) and hexafluoropropene (0.87g, 6mmol) was irradiated with γ-rays. The product mixture was shown by comparison of GLC retention times to consist of 3-(1,1,2,3,3,3-hexafluoro-propyl)-*N*-trimethylsilylmorpholine (**56**) (9% by GLC) and 3,5-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylmorpholine (**57**) (36% by GLC), together with a trace of 2-(1,1,2,3,3,3-hexafluoropropyl)oxolane (**54**) (2% by GLC).

V.1.B.(5). **Effect of Introducing a Second Nitrogen Atom-Diamine Derivatives**

V.1.B.(5).a. **Addition to 2-Imidazolidinone (58)**

γ-ray Initiation

A mixture of 2-imidazolidinone (**58**) (5.12g, 60mmol), 2,2,2-trifluoroethanol (17.89g, 0.18mol) and hexafluoropropene (10.34g, 69mmol) was irradiated with γ-rays. Excess alkene (1.49g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (31.64g). Removal of solvent under reduced pressure gave a solid (13.86g). The solid was washed with distilled water and dried to constant weight under vacuum over potassium hydroxide. The solid was sublimed at 100°C / < 0.1mmHg to give 4-(1,1,2,3,3,3-hexafluoropropyl)-2-imidazolidinone (**59**), (13.46g,92%); m.p. 156-157°C; (Found: C, 30.5; H, 2.4; N, 11.8; F, 48.9. $C_6H_6N_2OF_6$ requires C, 30.5; H, 2.55; N, 11.85; F, 48.3%); IR spectrum 10, NMR spectrum 10, mass spectrum 13.

V.1.B.(5).b. **Attempted Addition to 5,6-Dihydrouracil (60)**

γ-ray Initiation

A mixture of 5,6 dihydrouracil (**60**) (2.45g, 21mmol) and hexafluoropropene (15.89, 0.11mol) was irradiated with γ-rays. Excess alkene (15.75g) was removed by transfer under vacuum (~100mmHg) to give a solid. The solid was found to contain only starting material by mass spectrometry.

V.1.B.(5).c. **Attempted Addition to 2,4-Dioxohexahydrotriazine (61)**

γ-ray Initiation

A mixture of 2,4-dioxohexahydrotriazine (**61**) (5.2g, 45mmol) and hexafluoropropene (17.64g. 0.12mol) was irradiated with γ-rays. Excess alkene (17.57g) was removed by transfer under vacuum (~100mmHg) to give a solid. The solid was found to contain only starting material by mass spectrometry.

V.1.B.(5).d. **Addition to *N,N'*-Dimethylurea (65)**

γ-ray Initiation

A mixture of *N,N'*-dimethylurea (**65**) (2.95g, 34mmol) acetone (20.8g, 0.36mol) and hexafluoropropene (5.52g, 37mmol) was irradiated with γ-rays. No alkene was recovered and a liquid (28.1g) remained. Transfer under vacuum followed by G.C. mass spectrometry identified two components, *N*-(2,2,3,4,4,4-hexafluorobutyl)-*N'*-methylurea (**66**), mass spectrum 14, and a di-adduct (**67**). Separation of (**66**) and (**67**) was not possible either by distillation or column chromatography. The mixture was reacted with excess hexafluoropropene and removal of solvent under reduced pressure gave a solid (8.85g)., which was sublimed at 50°C/ <0.1mmHg to give *N,N'*-bis-(2,2,3,4,4,4-hexafluorobutyl)urea (**67**), m.p. 84-86°C, (Found: C, 28.25; H, 2.2; N, 7.0; F, 58.8. $C_9H_8N_2OF_{12}$ requires C, 27.85; H, 2.05; N, 7.2; F, 58.2%); IR spectrum 11, NMR spectrum 11, mass spectrum 15.

V.1.B.(5).e. **Attempted Addition to *N,N'*-diacetyl-1,2-ethanediamine (68)**

γ-ray Initiation

A mixture of *N,N'*-diacetyl-1,2-ethanediamine (**68**) (0.79g, 5.5mmol), acetone (28.17g, 0.49mol) and hexafluoropropene (2.3g, 15mmol) was irradiated with γ-rays. Excess alkene (1.02g) was removed by transfer under vacuum (~100mmHg) to leave a liquid. Removal of solvent under reduced pressure gave a viscous oil (0.98g) which was found to contain only starting material by NMR.

Peroxide Initiation at 140°C

A mixture of *N,N'*-diacetyl-1,2-ethanediamine (**68**) (0.83g, 6mmol), acetone (32.16g, 0.55mol), hexafluoropropene (4.82g, 32mmol) and DTBP (0.05g) was heated at 140°C in a rocking furnace overnight. Excess alkene (4.49g) was transferred under vacuum (~100mmHg) to leave a liquid (31.84g). Removal of solvent under reduced pressure gave a viscous oil (1.03g) which was found to contain only starting material by NMR.

UV Initiation

A mixture of *N,N'*-diacetyl-1,2-ethanediamine (**68**) (0.96g, 7mmol), 2,2,2-trifluoroethanol (29.4g, 0.29mol), acetone (5.62g, 97mmol) and hexafluoropropene (6.24g, 42mmol) was irradiated for ~72 hours with a medium pressure UV lamp (1000W). Excess alkene (4.73g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (37.16g). Removal of the solvent under reduced pressure gave a moist solid. Addition of distilled water dissolved the starting material to leave a trace of a viscous oil (<0.05g) which was found by mass spectrometry to be composed of a mixture of mono-, *m/z* (EI^+) 294 (M^+, 3%), di-, *m/z* (EI^+) 444 (M^+, 6%), and tri-adducts, *m/z* (EI^+) 594 (M^+, 2%), which were not investigated further.

V.1.B.(5).f. **Attempted Addition to *N,N'*-diacetyl-1,6-hexanediamine (69)**

γ-ray Initiation

A mixture of *N,N'*-diacetyl-1,6-hexanediamine (**69**) (0.86g, 4mmol), acetone (24.87g, 0.43mol) and hexafluoropropene (4.82g, 32mmol) was irradiated with γ-rays. Excess alkene (2.9g) was transferred under vacuum (~100mmHg) to leave a liquid (19.91g). Removal of solvent under reduced pressure gave an oily residue (1.34g), which was found to contain only starting material by NMR.

Peroxide Initiation at 140°C

A mixture of *N,N'*-diacetyl-1,6-hexanediamine (**69**) (2.38g, 12mmol), 2,2,2-trifluoroethanol (19.32g, 0.19mol), hexafluoropropene (6.39g, 43mmol) and DTBP (0.15g) was heated at 140°C in a rocking furnace overnight. Excess alkene (5.41g) was transferred under vacuum (~100mmHg) to leave a liquid (22.63g). Removal of solvent under reduced pressure gave an oily residue (2.73g), which was found to contain only starting material by NMR.

UV Initiation

A mixture of *N,N'*-diacetyl-1,6-hexanediamine (**69**) (2.29g, 11.5mmol), 2,2,2-trifluoroethanol (18.85g, 0.19mol), acetone (8.47g, 0.15mol) and hexafluoropropene (7.37g, 49.1mmol) was irradiated for ~72 hours with a medium pressure UV lamp (1000W). Excess alkene (6.11g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (30.57g). Removal of solvent under reduced pressure gave an off white solid (2.6g). Addition of distilled water dissolved the starting material to leave a trace of a viscous oil (<0.05g) which was found by mass spectrometry to be composed of a mixture of mono-, *m/z* (EI^+) 350 (M^+, 5%), di-, *m/z* (EI^+) 500 (M^+, 17%), and tri-adducts, *m/z* (EI^+) 650 (M^+, 2%), which were not investigated further.

V.1.B.(5).g. **Inhibition Between TRAT and *N*-Ethylacetamide (34)**

A mixture of *N*-ethylacetamide (**34**) (1.45g, 17mmol), **TRAT** (0.54g, 3mmol), acetone (22.39g, 0.39mol) and hexafluoropropene (2.7g, 18mmol) was irradiated with γ-rays. No alkene was recovered, and following the removal of solvent under reduced pressure *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)acetamide (**35**) was isolated.

V.1.B.(6) **Acyl Derivatives**

V.1.B.(6).a. **Attempted Addition to *N*-acetyl-*N'*-methylpiperazine (70)**

γ-ray Initiation

N-acetyl-*N'*-methylpiperazine (**70**) (2.04g, 15mmol) and hexafluoropropene (1.58g, 10.5mmol) was irradiated with γ-rays. Following irradiation two layers were observed.

Volatile material (1.4g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (2.14g) which was shown to contain only starting material by GLC.

V.1.B.(6).b. **Addition to *N,N'*-Diacetylpiperazine (71)**

γ-ray Initiation

A mixture of *N,N'*-diacetylpiperazine (**71**) (1.12g, 7mmol), acetone (18.86g, 0.33mol), and hexafluoropropene (8.23g,55mmol) was irradiated with γ-rays. Excess alkene (5.68g) was transferred under vacuum (~100mmHg) to leave a liquid (22.14g). Solvent was removed under reduced pressure to leave a viscous oil.(1.33g) which was shown to contain only starting material by NMR.

Peroxide Initiation at 140°C

A mixture of *N,N'*-diacetylpiperazine (**71**) (1.43g, 8mmol), acetone (12.13g, 0.21mol), hexafluoropropene (5.17g, 35mmol) and DTBP (0.1g) was heated to 140°C overnight in a rocking furnace. The product (14.68g) was shown to contain only starting material by NMR.

UV Initiation

A mixture of *N,N'*-diacetylpiperazine (**71**) (2.27g, 13mmol), acetone (12.79g, 0.22mol) and hexafluoropropene (11.38g, 76mmol) was irradiated using a medium pressure UV lamp (1000W) for ~72 hours. Excess alkene (10.87g) was transferred under vacuum (~100mmHg) to leave a liquid (15.43g). Removal of solvent under reduced pressure gave a moist orange solid (2.83g).which was shown by ^{19}F NMR to contain a small quantity of fluorinated material. Washing the sample with distilled water dissolved the starting material, to leave a trace of a dark brown oil (<0.05g) which was decanted and analysed by mass spectrometry to be a mixture of mono-, *m/z* (EI^+) 319 (M^+, 53%), 277 (100, M -CH_3CO), di-, *m/z* (EI^+) 470 (M^+, 3%), 427 (19, M -CH_3CO), and tri-adducts, *m/z* (EI^+) 620 (M^+, 0.4%), 577 (0.6, M -CH_3CO) which were not investigated further.

V.1.B.(6).c. **Synthesis and Attempted Addition to *N,N'*-Diacetyl-hexahydropyrimidine (72)**

A solution of 1,3-Diaminopropane (34.0ml, 0.4mol) and distilled water (100ml) at 0°C was slowly titrated with concentrated hydrochloric acid (75.8ml) to a methyl orange end-point. 1,3-Diaminopropane (34.0ml) was added, the temperature brought to and maintained at 20-25°C, and the solution titrated with formalin (64.8ml, 0.8mol) over 30 minutes. The resulting solution was allowed to stand at room temperature for 2 hours, and made alkaline by the addition of sodium hydroxide (86.3g). The mixture was filtered throgh a sintered glass funnel, and the upper layer (54.07g) separated. This was refluxed with toluene (100ml) in a Dean-Stark water separator for 2 hours. The toluene solution was fractionally distilled and the fraction boiling at 140-145°C was collected (8.26g, 96mmol). Acetic anhydride (39.1g, 0.38mol) was added dropwise and the solution refluxed for 2 hours. The solution was distilled to remove excess acetic anhydride and the remaining oil distilled (Spaltrohr) to give *N,N'*-diacetylhexahydropyrimidine (72), (2.58g,4%); b.p. 148-150°C at 0.5 mmHg; (Found: C, 56.75; H, 8.65; N, 16.6. Calc. for $C_8H_{14}N_2O_2$: C, 56.5; H, 8.25; N, 16.5%); ν_{max}/cm^{-1} 1730 (C=O), no N-H; *m/z* (EI^+) 170 (M^+, 0.8%), 127 (0.3, M -CH_3CO), 84 (0.4, M-2×CH_3CO).

γ-ray Initiation

A mixture of *N,N'*-diacetylhexahydropyrimidine (72) (0.50g, 3mmol), acetone (1.88g, 33mmol), and hexafluoropropene (2.42g, 16mmol) was irradiated with γ-rays. Excess alkene (1.8g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (2.7g) which was shown to contain only starting material by GLC.

Peroxide Initiation at 80°C

A mixture of *N,N'*-diacetylhexahydropyrimidine (72) (0.75g, 4mmol), acetone (2.3g, 40mmol), hexafluoropropene (3.6g, 24mmol) and DBP (0.1g) was heated at 80°C in a Carius furnace for ~24 hours. Excess alkene (2.2g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (4.2g) which was shown to contain only starting material by GLC.

Peroxide Initiation at 140°C

A mixture of *N,N'*-diacetylhexahydropyrimidine (**72**) (0.8g, 5mmol), acetone (1.5g, 26mmol), hexafluoropropene (1.8g, 12mmol) and DTBP (0.15g) was heated at 140°C in a Carius furnace for ~24 hours. Excess alkene (0.6g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (3.4g) which was shown to contain only starting material by GLC.

V.1.B.(6).d. **Attempted Addition to *N,N'*-Diformylpiperazine (73)**

γ-ray Initiation

A mixture of *N,N'*-diformylpiperazine (**73**) (1.98g, 14mmol), 2,2,2-trifluoroethanol (14.51g, 0.145mol), and hexafluoropropene (19.11g, 0.13mol) was irradiated with γ-rays. Excess alkene (17.19g) was transferred under vacuum (~100mmHg) to leave a liquid (16.36g). Solvent was removed under reduced pressure to leave a pale yellow solid.(1.33g) which was shown to contain only starting material by NMR.

Peroxide Initiation at 140°C

A mixture of *N,N'*-diformylpiperazine (**73**) (2.18g, 15mmol), 2,2,2-trifluoroethanol (15.91g, 0.16mmol), hexafluoropropene (11.42g, 76mmol) and DTBP (0.1g) was heated to 140°C overnight in a rocking furnace. Excess alkene (10.7g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (18.7g). Removal of solvent under reduced pressure gave a pale yellow solid (2.35g) which was shown to contain only starting material by NMR.

UV Initiation

A mixture of *N,N'*-diformylpiperazine (**73**) (1.45g, 10mmol), 2,2,2-trifluoroethanol (13.26g, 0.13mol) and hexafluoropropene (8.43g, 56mmol) was irradiated using a medium pressure UV lamp (1000W) for ~48 hours. Excess alkene (7.91g) was transferred under vacuum (~100mmHg) to leave a liquid (15.05g). Removal of solvent under reduced pressure gave a pale yellow solid (1.72g).which was shown to contain only starting material by NMR.

V.1.B.(7). **Trimethylsilyl Derivatives**

V.1.B.(7).a. **Synthesis and Attempted Addition to *N,N'*-Di(trimethylsilyl)piperazine (74)**

N,N'-Di(trimethylsilyl)piperazine (**74**) was prepared from piperazine using chlorotrimethylsilane[148], b.p.210-216°C, δ_H (250MHz,$CDCl_3$,Me_4Si) 0.14(18H,s, Me_3Si), 2.4 (8H, br s,CH_2).

γ-ray Initiation

A mixture of *N,N'*-di(trimethylsilyl)piperazine (**74**) (4.34g, 19mmol) and hexafluoro-propene (1.5g, 1mmol) was irradiated with γ-rays. No alkene was recovered and a brown liquid remained (5.75g). The liquid was analysed by ^{19}F NMR and G.C.mass spectrometry to be composed of a mixture of mono- (4.1% by GLC), *m/z* (EI^+) 380 (M^+, 43%), di- (11% by GLC), *m/z* (EI^+) 530 (M^+, 5%) and tri-adducts (1.9% by GLC), *m/z* (EI^+) 680 (M^+, 22%). Owing to the complexity of products and the low yield the reaction was not investigated further.

V.2. **Reactions of Amine Derivatives with Chlorotrifluoroethene**

V.2.A. **Effect of Varying Substituents on Reactivity of Nitrogen Derivatives**

V.2.A.(1) **Tertiary Amines**

V.2.A.(1).a. **Addition to *N*-Methylpiperidine (11)**

γ-ray Initiation

A mixture of *N*-methylpiperidine (**11**) (8.26g, 83mmol) and chlorotrifluoroethene (6.57g, 56mmol) was irradiated with γ-rays. No alkene was recovered and a liquid (14.39g) remained. Preparative scale GLC of the liquid (120°C, 10%SE30) gave *N*-(3-chloro-2,3,3-trifluoropropyl)piperidine (**75**) (13% by GLC) (Found: C, 44.85; H, 6.25; N, 6.65; $C_8H_{13}NF_3Cl$ requires C, 44.55; H, 6.05; N, 6.50%); IR spectrum 12, NMR spectrum 12, mass spectrum 16, and 2-(2-chloro-1,1,2-trifluoroethyl)-*N*-(3-chloro-2,2,3-trifluoropropyl)piperidine (**76**); (43% by GLC) (Found: C, 35.75; H, 3.8; N,

3.75; $C_{10}H_{13}NF_6Cl_2$ requires C, 36.15; H, 3.9; N, 4.2%); IR spectrum 13, NMR spectrum 13, mass spectrum 17.

V.2.A.(2). **Cyclic Amides**

V.2.A.(2).a. **Addition to *N*-Acetylpiperidine (19)**

γ-ray Initiation

A mixture of *N*-acetylpiperidine (**19**) (9.14g, 72mmol), acetone (7.11g, 0.12mol), and chlorotrifluoroethene (6.89g, 59mmol) was irradiated with γ-rays. Excess alkene (2.19g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (20.72g). The liquid was analysed by ^{19}F NMR and G.C. mass spectrometry to be composed of a mixture of mono-adduct (27% by GLC), *m/z* (EI^+) 243 (M^+, 2%), and telomeric di- (7.3% by GLC), *m/z* (EI^+) 359 (M^+, 0.3%) and tri-adducts (3.4% by GLC), *m/z* (EI^+) 475 (M^+, 1%). It was possible to separate the starting material from the adduct mixture, but it was not possible to separate the adducts from each other either by distillation or column chromatography.

V.2.A.(2).b. **Attempted Addition to *N*-Methylacetamide (30)**

γ-ray Initiation

A mixture of *N*-methylacetamide (**30**) (4.18g, 57mmol) acetone (7.03g, 0.12mol) and chlorotrifluoroethene (7.3g, 63mmol) was irradiated with γ-rays. Excess alkene (5.0g) was removed by transfer under vacuum to leave a liquid (13.4g). This liquid was transferred under vacuum and found by GLC to contain starting material. A brown solid resin remained (1.4g) which would not transfer under vacuum and was insoluble in laboratory solvents (polymerised chlorotrifluoroethene).

UV Initiation

A mixture of *N*-methylacetamide (**30**) (3.95g, 54mmol) acetone (8.4g, 0.14mol) and chlorotrifluoroethene (6.23g, 53mmol) was irradiated for ~48 hours with a medium pressure UV lamp (1000W). Excess alkene (4.2g) was removed by transfer under vacuum to leave a liquid (14.11g). This liquid was transferred under vacuum and found

by GLC to contain starting material. A brown solid resin remained (1.4g) which would not transfer under vacuum and was insoluble in laboratory solvents (polymerised chlorotrifluoroethene).

V.2.A.(2).c. **Attempted Addition to *N*-Ethylacetamide (34)**

γ-ray Initiation

A mixture of *N*-ethylacetamide (**34**) (7.24g, 83mmol), acetone (7.77g, 0.13mol) and chlorotrifluoroethene (11.51g, 0.1mol) was irradiated with γ-rays. Excess alkene (8.17g) was removed by transfer under vacuum to leave a liquid (17.1g). This liquid was transferred under vacuum and found by GLC to contain starting material. A brown solid resin remained (2.2g) which would not transfer under vacuum and was insoluble in laboratory solvents (polymerised chlorotrifluoroethene).

UV Initiation

A mixture of *N*-ethylacetamide (**34**) (6.14g, 71mmol) acetone (5.92g, 0.1mol) and chlorotrifluoroethene (8.37g, 72mmol) was irradiated for ~120 hours with a medium pressure UV lamp (1000W). Excess alkene (6.58g) was removed by transfer under vacuum to leave a liquid (13.60g). This liquid was transferred under vacuum and found by GLC to contain starting material. A brown solid resin remained (1.4g) which would not transfer under vacuum and was insoluble in laboratory solvents (polymerised chlorotrifluoroethene).

V.2.A.(2).d. **Attempted Addition to *N*-Propylacetamide (36)**

γ-ray Initiation

A mixture of *N*-propylacetamide (**36**) (10.88g, 0.1mol), acetone (5.87g, 0.1mol) and chlorotrifluoroethene (16.1g, 0.14mol) was irradiated with γ-rays. Excess alkene (14.42g) was removed by transfer under vacuum to leave a liquid (12.31g). This liquid was transferred under vacuum and found by GLC to contain starting material. A brown solid resin remained (1.3g) which would not transfer under vacuum and was insoluble in laboratory solvents (polymerised chlorotrifluoroethene).

UV Initiation

A mixture of *N*-propylacetamide (**36**) (9.88g, 98mmol) acetone (7.14g, 0.3mol) and chlorotrifluoroethene (13.6g, 0.12mol) was irradiated for ~120 hours with a medium pressure UV lamp (1000W). Excess alkene (6.58g) was removed by transfer under vacuum to leave a liquid (13.60g). This liquid was transferred under vacuum and found by GLC to contain starting material. A brown solid resin remained (1.4g) which would not transfer under vacuum and was insoluble in laboratory solvents (polymerised chlorotrifluoroethene).

V.2.A.(3). **Trimethylsilyl Derivatives of Amines**

V.2.A.(3).a. **Addition to *N*-Trimethylsilylpiperidine (38)**

γ-ray Initiation

A mixture of *N*-trimethylsilylpiperidine (**38**) (10.6g, 68mmol) and chlorotrifluoroethene (5.02g, 43mmol) was irradiated with γ-rays. Excess alkene (0.53g) was removed by transfer under vacuum to leave a liquid (14.86g). Preparative scale GLC (120°C/ 10%SE30) of the liquid gave 2-(2-chloro-1,1,2-trifluoroethyl)-*N*-trimethylsilylpiperidine (**78**) (47% by GLC); (Found: C, 43.95; H, 7.05; N, 5.45. $C_{10}H_{19}NSiClF_3$ requires C, 43.9 H, 6.95 N, 5.1%); IR spectrum 14, NMR spectrum 14, mass spectrum 18.

V.2.A.(3).b. **Addition to *N,N*-Dimethyltrimethylsilylamine (41)**

γ-ray Initiation

A mixture of *N,N*-dimethyltrimethylsilylamine (**41**) (10.6g, 91mmol) and chlorotrifluoroethene (5.02g, 43mmol) was irradiated with γ-rays. Excess alkene (0.53g) was transferred under vacuum to leave a liquid (14.86g). Preparative scale GLC of the liquid (105°C, 10%SE30) gave *N*-(3-chloro-2,3,3-trifluoropropyl)-*N*-methyl(trimethylsilyl)-amine (**79**) (45% by GLC, 43% from recovered alkene); (Found: C, 36.05; H, 6.95; N, 6.55; F, 24.3. $C_7H_{15}NSiF_3Cl$ requires C, 36.0; H, 6.4 N, 6.0; F, 24.4%); IR spectrum 15, NMR spectrum 15, mass spectrum 19.

V.2.A.(3).c. **Addition to *N,N*-Diethyltrimethylsilylamine (43)**

γ-ray Initiation

A mixture of *N,N*-diethyltrimethylsilylamine (**43**) (7.35g, 51mmol) and chlorotrifluoroethene (5.49g, 47mmol) was irradiated with γ-rays. Excess alkene (4.68g) was transferred under vacuum to leave a liquid (8.11g). Preparative scale GLC of the liquid (120°C/ 10%SE30) gave *N*-(3-chloro-2,2,3-trifluoro-1-methylpropyl)-*N*-ethyl(trimethylsilyl)amine (**80**) (15% by GLC, 14% from recovered alkene); (Found: C, 41.45; H, 7.5; N, 5.55. $C_9H_{19}NSiF_3Cl$ requires C, 41.3; H, 7.25 N, 5.35%); IR spectrum 16, NMR spectrum 16, mass spectrum 20.

V.2.B. **Effect of Introducing an Oxygen Atom on the Reactivity of Nitrogen Derivatives**

V.2.B.(1) **Oxygen Containing Acyl Derivatives**

V.2.B.(1).a. **Attempted Addition to *N*-Acetylmorpholine (52)**

γ-ray Initiation

A mixture of *N*-acetylmorpholine (**52**) (5.38g, 42mmol), acetone (6.57g, 0.11mol), and chlorotrifluoroethene (2.9g, 25mmol) was irradiated with γ-rays. Excess alkene (0.66g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (14.03g). The liquid was analysed by ^{19}F NMR and G.C. mass spectrometry to be composed of a mixture of mono-adduct (11% by GLC), *m/z* (EI^+) 245 (M^+, 2%), and telomeric di- (13.4% by GLC), *m/z* (EI^+) 361 (M^+, 0.4%) and tri-adducts (5.5% by GLC), *m/z* (EI^+) 477 (M^+, 2%). It was possible to separate the starting material from the adducts, but it was not possible to separate the adducts from each other either by distillation or column chromatography.

Peroxide Initiation at 140°C

A mixture of *N*-acetylmorpholine (**52**) (6.75g, 52mmol), acetone (5.43g, 94mmol), and chlorotrifluoroethene (3.85g, 33mmol) and DTBP (0.1g) was heated to 140°C overnight in a rocking furnace. Excess alkene (1.2g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (14.7g). The liquid was analysed by ^{19}F NMR

and G.C. mass spectrometry to be composed of a mixture of mono-adduct (4% by GLC), *m/z* (EI^+) 245 (M^+, 1.3%), and telomeric di- (5.1% by GLC), *m/z* (EI^+) 361 (M^+, 0.7%) and tri-adducts (1.7% by GLC), *m/z* (EI^+) 477 (M^+, 1%).

V.2.B.(2). Oxygen Containing Trimethylsilyl Derivatives

V.2.B.(2).a. Addition to *N*-Trimethylsilylmorpholine (55) γ-ray Initiation

A mixture of *N*-trimethylsilylmorpholine (**55**) (10.76g, 68mmol) and chlorotrifluoroethene (5.72g, 49mmol) was irradiated with γ-rays. No alkene was recovered and a dark brown liquid remained (16.3g). Preparative scale GLC of the liquid (110°C /10%SE30) gave 3-(2-chloro-1,1,2-trifluoroethyl)-*N*-trimethylsilylmorpholine (**81**) (48% by GLC); (Found: C, 39.95; H, 6.35; N, 5.75. $C_9H_{17}NOSiClF_3$ requires C, 39.2 H, 6.15 N, 5.1; %); IR spectrum 17, NMR spectrum 17, mass spectrum 21.

V.3. Reactions of Amine Derivatives with Perfluorocyclobutene and Perfluorocyclopentene

V.3.A. Effect of Varying Substituents on Reactivity of Nitrogen

V.3.A.(1). Tertiary Amines

V.3.A.(1).a. Addition of *N*-methylpiperidine (11) to Perfluorocyclobutene

γ-ray Initiation

A mixture of *N*-methylpiperidine (**11**) (2.98g, 30mmol) and perfluorocyclobutene (5.26g, 32mmol) was irradiated with γ-rays. Excess alkene (1.88g) was removed under reduced pressure (~100mmHg) to leave a brown/black tar which was not investigated further.

No Initiation

A mixture of *N*-methylpiperidine (**11**) (5.6g, 57mmol) and perfluorocyclobutene (10.19g, 63mmol) was allowed to stand at room temperature for 24 hours. Excess alkene was removed under reduced pressure to leave a brown/black tar which was not investigated further.

V.3.A.(2). Acyl Derivatives

V.3.A.(2).a. Attempted Addition of *N*-Acetylpiperidine (19) to Perfluorocyclobutene

γ-ray Initiation

A mixture of *N*-acetylpiperidine (**19**) (7.56g, 60mmol), and perfluorocyclobutene (8.37g, 52mmol) was irradiated with γ–rays. Excess alkene (7.73g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (8.13g), which was shown to contain only starting material by GLC.

Peroxide Initiation at 140°C

A mixture of *N*-acetylpiperidine (**19**) (6.38g, 50mmol), and perfluorocyclobutene (5.16g, 32mmol) and DTBP (0.15g) was heated to 140°C overnight in a rocking furnace.

Excess alkene (4.3g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (6.9g), which was shown to contain only starting material by GLC.

V.3.A.(2).b. **Attempted Addition of *N*-Acetylpiperidine (19) to Perfluorocyclopentene**

γ-ray Initiation

A mixture of *N*-acetylpiperidine (**19**) (4.19g, 33mmol), acetone (5.23g, 0.11mol) and perfluorocyclopentene (9.47g, 45mmol) was irradiated with γ-rays. Excess alkene (9.37g) was removed by transfer under vacuum (~100mmHg) to leave a liquid which was shown to contain starting material by GLC.

Peroxide Initiation at 140°C

A mixture of *N*-acetylpiperidine (**19**) (4.75g, 37mmol), acetone (7.2g, 0.12mol), perfluorocyclopentene (7.31g, 34mmol) and DTBP (0.2g) was heated to 140°C overnight in a rocking furnace. Excess alkene (9.37g) was removed by transfer under vacuum (~100mmHg) to leave a liquid which was shown to contain starting material by GLC.

V.3.A.(2).c. **Addition of *N*-Methylacetamide (30) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N*-methylacetamide (**30**) (4.55g, 62mmol) and perfluorocyclobutene (6.89g, 43mmol) was irradiated with γ-rays. Excess alkene (6.33g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (4.85g). The liquid was found by G.C.mass spectrometry to be composed of starting material together with a small amount of *N*-[(1,2,2,3,3,4-hexafluorocyclobutyl)-methyl]acetamide (**82**) (12% by GLC) which was not separated.

UV Initiation

A mixture of *N*-methylacetamide (**30**) (3.78g, 52mmol) acetone (7.23g, 0.15mol) and perfluorocyclobutene (9.96g, 62mmol) was irradiated for ~120 hours with a medium

pressure UV lamp (1000W). Excess alkene (1.97g) was removed by transfer under vacuum to leave a liquid (18.76g). Removal of solvent under reduced pressure followed by distillation gave *N*-[(1,2,2,3,3,4-hexafluorocyclobutyl)-methyl]acetamide (**82**) (4.76g, 39%); b.p 115-117°C/ 2mmHg; (Found: C, 36.0; H, 3.25; N, 6.25; F, 48.7. $C_7H_7NOF_6$ requires C, 35.75; H, 3.0; N, 5.95; F, 48.5%); IR spectrum 18, NMR spectrum 18, mass spectrum 22.

V.3.A.(2).d. **Addition of *N*-Methylacetamide (30) to Perfluorocyclopentene**

γ-ray Initiation

A mixture of *N*-methylacetamide (**30**) (7.43g, 0.1mol) and perfluorocyclopentene (24.73g, 0.12mol) was irradiated with γ-rays. Excess alkene (22.8g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (9.01g). The liquid was found by G.C.mass spectrometry to be composed of starting material together with a small amount of *N*-[(1,2,2,3,3,4,4,5-octafluorocyclopentyl)-methyl]acetamide (**83**) (4% by GLC) which was not separated.

UV Initiation

A mixture of *N*-methylacetamide (**30**) (3.78g, 52mmol) acetone (7.23g, 0.15mol) and perfluorocyclopentene (9.96g, 47mmol) was irradiated for ~120 hours with a medium pressure UV lamp (1000W). Excess alkene (1.97g) was removed by transfer under vacuum to leave a liquid (18.76g). Removal of solvent under reduced pressure followed by distillation gave *N*-[(1,2,2,3,3,4,4,5-octafluorocyclopentyl)-methyl]acetamide (**83**) (2.22g, 15%); b.p 115-117°C/ 2mmHg; (Found: C, 33.5; H, 2.1; N, 4.85; F, 53.0. $C_8H_7NOF_8$ requires C, 33.7; H, 2.45; N, 4.9; F, 53.3%); IR spectrum 19, NMR spectrum 19, mass spectrum 23.

V.3.A.(2).e. **Addition of *N*-Ethylacetamide (34) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N*-ethylacetamide (**34**) (4.91g, 56mmol) and perfluorocyclobutene (11.48g, 0.1mol) was irradiated with γ-rays. Alkene (2.28g) was removed by transfer under vacuum (~100mmHg) to leave and an pale yellow solid (13.87g). The solid was sublimed at 50°C/ <0.1mmHg to give *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)ethyl]-acetamide (**84**), (10.87g, 78%); m.p. 60-62°C; (Found: C, 38.25; H, 3.5; N, 5.65; F, 46.0. $C_8H_9NOF_6$ requires C, 38.55; H, 3.6; N, 5.6; F, 45.8%); IR spectrum 20, NMR spectrum 20, mass spectrum 24.

V.3.A.(2).f. **Addition of *N*-Ethylacetamide (34) to Perfluorocyclopentene**

γ-ray Initiation

A mixture of *N*-ethylacetamide (**34**) (6.78g, 78mmol), acetone (4.74g, 82mmol) and perfluorocyclopentene (16.62g, 78mol) was irradiated with γ-rays. Alkene (2.81g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (25.26g). Removal of solvent under reduced pressure followed by Spaltrohr distillation gave *N*-[1-(1,2,2,3,3,4,4,5-octafluorocyclopentyl)ethyl]acetamide (**85**), (2.79g, 12%); b.p. 100-102°C/ 2mmHg; (Found: C, 35.85; H, 3.1; N, 4.6; F, 50.4. $C_9H_9NOF_8$ requires C, 36.1; H, 3.0; N, 4.7; F, 50.85%); IR spectrum 21, NMR spectrum 21, mass spectrum 25.

V.3.A.(2).g. **Addition of *N*-Propylacetamide (36) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N*-propylacetamide (**36**) (9.77g, 0.1mol) acetone (11.19g, 0.19mol) and perfluorocyclobutene (15.32g, 95mmol) was irradiated with γ-rays. Excess alkene (15.32g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (21.59g). The liquid was found by G.C. mass spectrometry to be composed of starting

material together with a small amount of *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)-propyl]acetamide (**86**) (7% by GLC) which was not separated.

UV Initiation

A mixture of *N*-propylacetamide (**36**) (6.14g, 61mmol) acetone (5.96g, 0.12mol) and perfluorocyclobutene (11.36g, 70mmol) was irradiated for ~72 hours with a medium pressure UV lamp (1000W). Excess alkene (9.41g) was removed by transfer under vacuum to leave a liquid (13.87g). Removal of solvent under reduced pressure followed by distillation gave *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)-propyl]acetamide (**86**) (3.85g, 24%); b.p 115-117°C/ 2mmHg; (Found: C, 40.95; H, 4.25; N, 5.2; F, 42.6. $C_9H_{11}NOF_6$ requires C, 41.05; H, 4.2; N, 5.3; F, 43.35%); IR spectrum 22, NMR spectrum 22, mass spectrum 26.

V.3.A.(3). **Trimethylsilyl Derivatives of Amines**

V.3.A.(3).a. **Addition of *N*-Trimethylsilylpiperidine (38) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N*-trimethylsilylpiperidine (**38**) (10.48g, 67mmol) and perfluorocyclobutene (11.87g, 73mmol) was irradiated with γ-rays. Volatile material (7.46g) was removed by transfer under vacuum (~100mmHg) to leave a black liquid (14.59g) which rapidly decomposed to a solid which was identified as *N*-(trifluorocyclobut-1-en-4-onyl)piperidine (**88**) (10.57g,77%); m.p.49-51°C (Found: C, 52.4; H, 4.8; N, 6.65 $C_9H_{10}NOF_3$ requires C, 52.7 H, 4.9 N, 6.8%); IR spectrum 23, NMR spectrum 23, mass spectrum 27.

No Initiation

A mixture of *N*-trimethylsilylpiperidine (**38**) (7.68g, 49mmol) and perfluorocyclobutene (14.08g, 87mmol) was allowed to stand at room temperature for 24 hours. Excess alkene was removed under reduced pressure to leave a liquid which was identified as *N*-(trifluorocyclobut-1-en-4-onyl)piperidine (**88**) from IR and NMR spectra.

V.3.A.(3).b. **Addition of *N*-Trimethylsilylpiperidine (38) to Perfluorocyclopentene**

γ-ray Initiation

A mixture of *N*-trimethylsilylpiperidine (**38**) (10.35g, 66mmol) and perfluorocyclopentene (13.2g, 63mmol) was irradiated with γ-rays. A volatile component (3.4g) was removed under reduced pressure to leave a liquid (19.68g). The liquid was found to be *N*-(heptafluorocyclopent-1-enyl)piperidine (**89**) (15.35g, 88%); (Found: C, 43.35; H, 3.55; N, 4.8 F, 47.8. $C_{10}H_{10}NF_7$ requires C, 43.3 H, 3.6 N, 5.05; F 48.0%); IR spectrum 24, NMR spectrum 24, mass spectrum 28.

No Initiation

A mixture of *N*-trimethylsilylpiperidine (**38**) (9.46g, 60mmol) and perfluorocyclopentene (12.67g, 60mmol) was allowed to stand at room temperature for 24 hours. Excess alkene was removed under reduced pressure to leave a liquid which was identified as *N*-(heptafluorocyclopent-1-enyl)piperidine (**89**) from IR and NMR spectra.

V.3.A.(3).c. **Addition of *N,N*-Dimethyltrimethylsilylamine (41) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N,N*-dimethyltrimethylsilylamine (**41**) (8.78g, 75mmol) and perfluorocyclobutene (17.37g, 0.107mol) was irradiated with γ-rays. Volatile material (5.47g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (20.47g). Distillation of the liquid gave 1-(*N,N*-dimethylamino)pentafluorocyclobut-1-ene (**90**) (12.62g,90%); b.p. 86-88°C / 117mmHg (lit.,[80] 88°C / 117mmHg); NMR 25.

No Initiation

A mixture of *N,N*-dimethyltrimethylsilylamine (**41**) (5.42g, 46mmol) and perfluorocyclobutene (7.61g, 47mmol) was allowed to stand for 24 hours. Volatile material (1.23g) was removed by transfer under vacuum (~100mmHg) to leave a liquid

(11.64g) which was identified as 1-(*N*,*N*-dimethylamino)pentafluorocyclobut-1-ene (**90**), by b.p. and NMR.

V.3.A.(3).d. **Addition of *N*,*N*-Dimethyltrimethylsilylamine (41) to Perfluorocyclopentene**

γ-ray Initiation

A mixture of *N*,*N*-dimethyltrimethylsilylamine (**41**) (4.53g, 39mmol) and perfluorocyclopentene (9.23g, 44mmol) was irradiated with γ-rays. A volatile fraction (5.54g) was transferred under vacuum (~100mmHg) to leave a liquid (8.05g) which rapidly decomposed to give 1-(*N*,*N*-dimethylamino)-pentafluorocyclopent-1-en-5-one (**91**) (6.62g, 79%); m.p.64-66°C (Found: C, 38.5; H, 2.55; N, 5.95 $C_7H_6NOF_5$ requires C, 39.05; H, 2.8 N, 6.5%); IR spectrum 25, NMR spectrum 26, mass spectrum 29.

No Initiation

A mixture of *N*,*N*-dimethyltrimethylsilylamine (**41**) (8.3g, 71mmol) and perfluorocyclopentene (18.2g, 86mmol) was allowed to stand for 24 hours. Volatile material was removed by transfer under vacuum to leave a liquid which rapidly decomposed to 1-(*N*,*N*-dimethylamino)-pentafluorocyclopent-1-en-5-one (**91**) from m.p. and NMR.

V.3.A.(3).e. **Addition of *N*,*N*-Diethyltrimethylsilylamine (43) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N*,*N*-diethyltrimethylsilylamine (**43**) (6.63g, 46mmol) and perfluorocyclobutene (8.3g, 51mmol) was allowed to stand for 24 hours. Volatile material (3.1g)was transferred under vacuum to leave a dark brown liquid (11.9g). Distillation of the liquid gave 1-(*N*,*N*-diethylamino)-pentafluorocyclobut-1-ene (**92**).b.p. 75-77°C / 54mmHg (lit.,[149] 76-77°C / 52-54mmHg); (87% by GLC); IR spectrum 26, NMR

spectrum 27, mass spectrum 30, which decomposed rapidly so that an elemental analysis could not be obtained.

V.3.A.(3).f. **Addition of *N,N*-Diethyltrimethylsilylamine (43) to Perfluorocyclopentene**

γ-ray Initiation

A mixture of *N,N*-diethyltrimethylsilylamine (**43**) (7.02g, 48mmol) and perfluorocyclopentene (5.77g, 27mmol) was irradiated with γ-rays. No alkene was recovered and a dark brown liquid remained (12.72g). The liquid was found to contain only one component by GLC identified as 1-(*N,N*-diethylamino)-heptafluorocyclopent-1-ene (**93**) (6.73g, 94%); (Found: C, 40.45; H, 3.65; N, 5.5; F, 49.8. $C_9H_{10}NF_7$ requires C, 40.75 H, 3.75 N, 5.3 F, 50.2%); IR spectrum 27, NMR spectrum 28, mass spectrum 31.

No Initiation

A mixture of *N,N*-diethyltrimethylsilylamine (**43**) (5.65g, 39mmol) and perfluorocyclopentene (9.48g, 45mmol) was allowed to stand for 24 hours at room temperature. A volatile component (2.47g) was removed by transfer under vacuum (~100mmHg) and a dark brown liquid remained (12.53g). The liquid was identified as 1-(*N,N*-diethylamino)-heptafluorocyclopent-1-ene (**93**) by comparison of GLC retention times and NMR.

V.3.B. **Effect of Introducing an Oxygen Atom on the Reactivity of Nitrogen Derivatives**

V.3.B.(1). **Oxygen Containing Tertiary Amines**

V.3.B.(1).a. **Addition of *N*-Methylmorpholine (49) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N*-methylmorpholine (**49**) (5.73g, 57mmol) and perfluorocyclobutene (10.59g, 65mmol) was irradiated with γ-rays. Excess alkene (1.35g) was removed

under reduced pressure (~10mmHg) to leave a brown solid (9.47g). Recrystallisation of the solid from water gave (3,3-difluorocyclobutan-2,4-onyl)morpholinium betaine (**94**) (9.11g,73%); m.p. 212-214°C (lit.,[91] 215°C); (Found: C, 49.65; H, 5.35; N, 6.2. Calc. for $C_9H_{11}NO_3F_2$ C, 49.3 H, 5.0 N, 6.4; %); IR spectrum 28, NMR spectrum 29, mass spectrum 32.

No Initiation

A mixture of *N*-methylmorpholine (**49**) (5.6g, 55mmol) and perfluorocyclobutene (10.19g, 63mmol) was allowed to stand at room temperature for 24 hours. Excess alkene was removed under reduced pressure to leave a brown solid (14.2g). Following recrystallisation from water the solid was identified as (3,3-difluorocyclobutan-2,4-onyl)morpholinium betaine (**94**) from IR and NMR spectra.

V.3.B.(2). Oxygen Containing Acyl Derivatives

V.3.B.(2).a. Attempted Addition of *N*-Acetylmorpholine (52) to Perfluorocyclobutene

γ-ray Initiation

A mixture of *N*-acetylmorpholine (**52**) (5.05g, 39mmol), acetone (4.42g, 76mmol) and perfluorocyclobutene (5.17g, 32mmol) was irradiated with γ-rays. Excess alkene (4.29g) was transferred under vacuum (~100mmHg) to leave a liquid (9.44g), which was found to contain starting material by GLC.

Peroxide Initiation at 140°C

A mixture of *N*-acetylmorpholine (**52**) (4.63g, 36mmol), acetone (10.97g, 0.19mol), perfluorocyclobutene (15.89g, 98mmol) and DTBP (0.15g) was heated to 140°C overnight in a rocking furnace. Excess alkene (12.78g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (18.5g) which was shown to contain only starting material by GLC.

V.3.B.(2).b. **Attempted Addition of *N*-Acetylmorpholine (52) to Perfluorocyclopentene**

γ-ray Initiation

A mixture of *N*-acetylmorpholine (**52**) (6.13g, 47mmol), acetone (8.63g, 0.18mol) and perfluorocyclopentene (8.94g, 42mmol) was irradiated with γ-rays. Excess alkene (8.68g) was transferred under vacuum (~100mmHg) to leave a liquid (14.8g), which was found to contain starting material by GLC.

Peroxide Initiation at 140°C

A mixture of *N*-acetylmorpholine (**52**) (6.8g, 53mmol), acetone (7.43g, 0.13mol), perfluorocyclopentene (12.44g, 59mmol) and DTBP (0.15g) was heated to 140°C overnight in a rocking furnace. Excess alkene (9.65g) was removed by transfer under vacuum (~100mmHg) to leave a liquid (16.72g) which was shown to contain only starting material by GLC.

V.3.B.(3). **Oxygen Containing Trimethylsilyl Derivatives**

V.3.B.(3).a. **Addition of *N*-Trimethylsilylmorpholine (55) to Perfluorocyclobutene**

γ-ray Initiation

A mixture of *N*-trimethylsilylmorpholine (**55**) (6.19g,39mmol) and perfluorocyclobutene (4.38g, 27mmol) was irradiated with γ-rays. Volatile material (4.34g) was removed by transfer under vacuum (~100mmHg) to leave an orange/brown solid. Sublimation of the solid (50°C / <1mmHg) gave white crystals of *N*-(pentafluorcyclobut-1-enyl)morpholine (**95**) (2.35g, 38%); m.p.75-77°C (Found: C, 41.65; H, 3.5; N, 6.0 F, 40.8 $C_8H_8NOF_5$ requires C, 41.9 H, 3.5 N, 6.1; F 41.5%); IR spectrum 29, NMR spectrum 30, mass spectrum 33. Compound (**95**) decomposed rapidly to a brown solid which was recrystallised from chloroform to give *N*-(trifluorocyclobut-1-en-4-onyl)morpholine (**96**) (1.23g, 22%); m.p. 86-87°C (85.7-86.4°C[149]); IR spectrum 30, NMR spectrum 31, mass spectrum 34.

No Irradiation

A mixture of *N*-trimethylsilylmorpholine (**55**) (9.87g, 62mmol) and perfluorocyclobutene (5.14g, 32mmol) was allowed to stand at room temperature for 24 hours. Volatile material (1.58g) was removed by transfer under vacuum (~100mmHg) to leave an orange/brown solid which was sublimed (50°C / <1mmHg) and identified as *N*-(pentafluorcyclopent-1-enyl)morpholine (**95**) by m.p. and NMR.

V.4. Reactions of Acetamide Derivatives

V.4.A. Reduction-Synthesis of Secondary Amine Derivatives

V.4.A.(1). Reduction of (35)

A solution of adduct (**35**), (31.05g, 0.13mol) in diethylether (150ml) was added dropwise and with stirring to a mixture of lithium aluminium hydride (25g, 0.65mol) in diethylether (200ml) over 30 minutes. The solution was stirred for a further 1.5 hours after which water was added dropwise (vigorous stirring), the mixture filtered, and the ether layer separated. A 20% solution of potassium hydroxide (400ml) was added to the filtered solid, which was extracted with ether 3x 100ml. The ether layer was dried over magnesium sulphate and distilled to give of *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethylamine (**97**), (8.12g, 28%), b.p. 84-86°C/ 98mmHg (Found: C, 37.65; H, 5.0; N, 6.45; F, 50.1. $C_7H_{11}NF_6$ requires C, 37.65; H, 4.95; N, 6.3; F, 51.1%); IR spectrum 31, NMR spectrum 32, mass spectrum 35.

V.4.A.(2). Reduction of (37)

A solution of adduct (**37**), (7.3g, 29mmol) in diethylether (100ml) was added dropwise and with stirring to a mixture of lithium aluminium hydride (4g, 0.1mol) in diethylether (100ml) over 30 minutes. The solution was stirred for a further 1.5 hours, then water was added dropwise (vigorous stirring), the mixture filtered, and the ether layer separated. A 20% solution of potassium hydroxide (200ml) was added to the filtered solid, which was extracted with ether x3 (100ml) portions. The ether layer was dried over magnesium sulphate and distilled to give *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)-*N*-ethylamine (**98**), (2.18g, 32%), b.p.128-130°C (Found: C, 40.9; H,

5.65; N, 6.4. $C_8H_{13}NF_6$ requires C, 40.5; H, 5.5; N, 5.9%); IR spectrum 32, NMR spectrum 33, mass spectrum 36.

V.4.A.(3). **Reduction of (84)**

A solution of adduct (**84**), (10.68g, 43mmol) in diethylether (150ml) was added dropwise and with stirring to a mixture of lithium aluminium hydride (2.5g, 66mmol) in diethylether (50ml) over 30 minutes. The solution was stirred for a further 30 minutes, then water was added dropwise (vigorous stirring), the mixture filtered, and the ether layer separated. A 20% solution of potassium hydroxide (150ml) was added to the filtered solid, which was extracted with ether x2 (100ml) portions. The ether layer was dried over magnesium sulphate and distilled (64-66°C / 25mmHg) to give a mixture which was assigned by ^{19}F NMR, IR and G.C. mass spectrometry to be a mixture of *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)ethyl]-acetamide (**84**), *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)ethyl]amine (**99**) and *N*-[1-(2,2,3,3,4-pentafluorocyclobut-1-enyl)ethyl]amine (**100**), which could not be separated.

V.4.B. **Reactions of Secondary Amine Derivatives**

V.4.B.(1). **Reaction of (97)**

V.4.B.(1).a. **With Phenylisothiocyanate**

A mixture of (**97**), (1.26g, 6mmol), ethanol (3ml) and phenylisothiocyanate (0.8g, 6mmol) was refluxed for 30 minutes. On cooling the solution no crystalline material separated and G.C. packed column revealed starting materials.

V.4.B.(1).b. **With Hexafluoropropene**

A mixture of (**97**), (1.17g, 5mmol) and hexafluoropropene (3.47g, 23mmol) was allowed to stand at room temperature for 5 days. Excess alkene (3.2g) was transferred under reduced pressure (~100mmHg) to leave a liquid which was found to contain starting material by GLC.

V.4.B.(1).c. **With Methyl Iodide**

A mixture of (**97**), (1.35g, 6mmol) and methyl iodide (4.56g, 32mmol) was heated at 100°C in a Carius furnace. Removal of solvent under reduced pressure gave a liquid. The liquid was found to contain *N*-[2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethylmethylamine (15%) by G.C. mass spectrometry. Owing to the small amount of product no separation was attempted.

V.4.B.(1).d. **With Acetyl Chloride**

Acetyl chloride (2g, 25mmol) was added dropwise to a stirred solution of (**97**), (1.37g, 6mmol), triethylamine (0.7g, 7mmol) and diethylether (5ml). The solution was allowed to reflux gently for 3 hours, then filtered and micro-distilled to give a viscous brown oil (1.1g). The oil was distilled (Kugelrohr) to give *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethylacetamide (**101**) (0.48g, 30%); b.p.124-125°C / 0.01mmHg (Found: C, 41.0; H, 5.05; N, 5.95. $C_9H_{13}NOF_6$ requires C, 40.75; H, 4.9; N, 5.3%); IR spectrum 33, NMR spectrum 34, mass spectrum 37.

V.4.C. **Attempted Synthesis of an Halogenated Imine from (35)**

V.4.C.(1). **Reaction with Sulphuryl Chloride**

A mixture of adduct (**35**), (5.16g, 22mmol) in sulphuryl chloride (25g, 0.185mol) was heated at 125°C in a rocking furnace for 8 hours. Distillation of the excess sulphuryl chloride gave a very viscous green resin. Sublimation of the resin (50°C / <0.1mmHg) gave a white crystalline solid *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-1,2,2-trichloroethenylamine (**103**), (4.35g, 61%), m.p. 37-38°C (Found: C, 24.3; H, 1.75; N, 4.0; F, 35.6; Cl, 31.2. $C_7H_6NF_6Cl_3$ requires C, 25.9; H, 1.85; N, 4.3; F, 35.15; Cl, 32.8%); IR spectrum 34, NMR spectrum 35, mass spectrum 38.

V.4.C.(2). **Reaction with Thionyl Chloride**

A mixture of adduct (**35**), (4.16g, 18mmol) and thionyl chloride (10g, 84mmol) was heated at 125°C in a rocking furnace for 8 hours. Distillation of excess phosphorous oxychloride gave a viscous brown oil. Sublimation of this oil (50°C / <0.1mmHg) gave

N-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-1,2,2-trichloroethenylamine (**103**) (1.46g, 25%) from m.p. and NMR.

V.4.C.(3). **Reaction with Phosphorous Pentachloride**

A mixture of adduct (**35**), (3.68g, 16mmol) and phosphorous pentachloride (8g, 39mmol) was heated at 125°C in a rocking furnace for 8 hours. The product was poured into ice water and extracted with dichloromethane. The solvent was dried over magnesium sulphate, then removed under reduced pressure to give a small amount of a viscous black oil (1.3g). The oil was found to contain only a trace of fluorinated material by NMR. Distillation under reduced pressure (Kugelrohr), sublimation and recrystallisation failed to separate any solid.

V.4.C.(4). **Reaction with Phosphorous Oxychloride**

A mixture of adduct (**35**), (3.68g, 16mmol) and phosphorous oxychloride (8g, 39mmol) was heated at 125°C in a rocking furnace for 8 hours. Distillation of excess phosphorous oxychloride gave a viscous brown oil. Sublimation of this oil (50°C / <0.1mmHg) gave *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-1,2,2-trichloroethenyl-amine (**103**) (0.98g, 19%) from m.p. and NMR.

V.4.D. **Attempted Synthesis of an Halogenated Imine from (37)**

V.4.D.(1). **Reaction with Sulphuryl Chloride**

V.4.D.(1).a. **At 125°C**

A mixture of adduct (**37**), (0.63g, 8mmol) in sulphuryl chloride (6g, 44mmol) was heated at 125°C in a Carius furnace for 8 hours. Micro-distillation of excess sulphuryl chloride gave a viscous brown resin. Sublimation of the resin failed to separate a solid. Molecular distillation gave a small amount of liquid (0.24g) which was found to be composed of a complex mixture of adducts by G.C. mass spectrometry which could not be assigned.

V.4.D.(1).b. **At 100°C**

A mixture of adduct (**37**), (0.77g, 3mmol) in sulphuryl chloride (5g, 37mmol) was heated at 100°C in a Carius furnace for 8 hours. Distillation of the excess sulphuryl chloride gave a viscous brown resin. Molecular distillation gave a small amount of liquid (0.36g) which was found to be composed of starting material together with a complex mixture of adducts by G.C.mass spectrometry which could not be assigned.

V.5. Acetone / *tert*-Butanol Ratio

A mixture of the substrate and DTBP, ca. 0.1g, 10%(mol), was placed in a Carius tube (ca. 5ml) and thoroughly degassed. The tube was sealed with the contents frozen (liquid air) and under vacuum, then heated at 140°C for 8 hours. The tube was opened while the contents were frozen (liquid air) and after warming to room temperature and following transfer under vacuum, the contents were analysed by capillary GLC A mixture of acetone/*tert*-butanol of known composition was used as a GLC response factor calibration.

V.5.(1). *N,N*-Dimethylacetamide (21)

A mixture of *N,N*-dimethylacetamide (**21**) (1.16g, 13mmol) and DTBP (0.14g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 0.14.

V.5.(2). *N,N*-Diethylacetamide (25)

A mixture of *N,N*-diethylacetamide (**25**) (1.34g, 12mmol) and DTBP (0.14g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 0.26.

V.5.(3). *N*-Acetylpiperidine (19)

A mixture of *N*-acetylpiperidine (**19**) (1.40g, 11mmol) and DTBP (0.20g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 0.41.

V.5.(4). ***N*-Acetylmorpholine (52)**

A mixture of *N*-acetylmorpholine (**52**) (1.65g, 13mmol) and DTBP (0.17g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 0.23.

V.5.(5). **TRAT**

A mixture of **TRAT** (1.00g, 5mmol), 2,2,2-trifluoroethanol (4.31g, 43mmol) and DTBP (0.12g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 2.19.

V.5.(6). **DAPT**

A mixture of **DAPT** (1.00g, 5mmol), 2,2,2-trifluoroethanol (4.10g, 41mmol) and DTBP (0.13g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 1.97.

V.5.(7). ***N*-Methylpiperidine (11)**

A mixture of *N*-methylmorpholine (**11**) (1.74g, 18mmol) and DTBP (0.14g) was heated at 140°C. No acetone was detected..

V.5.(8). ***N*-Methylmorpholine (49)**

A mixture of *N*-methylmorpholine (**49**) (1.14g, 11mmol) and DTBP (0.1g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 0.02.

V.5.(9). ***N,N'*-Diacetyl-1,2-ethanediamine (68)**

A mixture of *N,N'*-diacetyl-1,2-ethanediamine (**68**) (0.97g, 7mmol) and DTBP (0.17g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 0.35.

V.5.(10). ***N,N'*-Diacetyl-1,6-hexanediamine (69)**

A mixture of *N,N'*-diacetyl-1,6-hexanediamine (**69**) (1.19g, 6mmol) and DTBP (0.15g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 0.25.

V.5.(11). **Hexamine**

A mixture of hexamine (1.40g, 14mmol) and DTBP (0.11g) was heated at 140°C. The product mixture was transferred under vacuum and the acetone/*tert*-butanol ratio shown to be 2.48.

CHAPTER SIX

EXPERIMENTAL TO CHAPTER THREE

CHAPTER SIX

EXPERIMENTAL TO CHAPTER THREE

VI.1.A. Preparation of Trifluoroacetaldehyde[124]

A slurry of lithium aluminium hydride (12.6g, 0.33mol.) in dry diethylether (375ml.) was added cautiously over a period of 3 hours to a rapidly stirred solution of trifluoroacetic acid (60.36g, 0.53mol.) in dry diethylether (500ml.) at -5°C -10°C (ice/salt bath) under an atmostphere of nitrogen. Stirring was continued for a further 3 hours after which the reaction mixture was hydrolysed cautiously with distilled water (30ml.), followed by 98% sulphuric acid (40ml.) in distilled water (100ml.). The solution was filtered and the ether layer separated. The solvent was removed by distillation to leave the crude aldehyde hydrate, identified by comparison of IR spectrum[150]. The crude aldehyde hydrate was added dropwise to a stirred solution of phosphorous pentoxide (23.12g, 0.16mol.) in 98% sulphuric acid (83ml.) at 85-90°C. The free aldehyde (11.51g, 22%); b.p. -20°C, identified by comparison of IR spectrum[121,126], was collected in a series of traps and transferred under vacuum to a rotaflo which was stored at -15°C prior to use.

VI.2. Attempted Preparation of 2,4,6-tris(trifluoromethyl)-hexahydro-s-triazine (112).

VI.2.A. Following Literature Method[33]

Trifluoroacetaldehyde (13.07g, 0.13mol.) was added as a gas below the surface of a stirred solution of ammonia (3.23g, 0.19mol.)in dry diethylether (100ml.) at -50°C. Following a short reflux (Dry Ice condenser) the mixture was warmed and excess ammonia and diethylether removed by distillation, heating to a pot temperature of 70°C. Toluene (50ml.) was added and the water of reaction removed azeotropically using a Dean-Stark apparatus. The solvent was removed under reduced pressure to give a semi-crystalline residue (0.68g). Sublimation of the residue at 50°C / <0.1mmHg gave a white crystalline solid (0.21g, 1.7%); m.p.79-81°C (lit.,[33] 83-84°C); (Found: C, 25.0; H, 1.9; N, 14.0. $C_6H_6N_3F_9$ requires C, 24.8; H, 2.1; N, 14.4%); ν_{max} ($CDCl_3$)/cm^{-1} 3390 (NH), 1700 (C=N, C=O); δ_F (235MHz; $CDCl_3$; $CFCl_3$) 60 (3F, m, CF_3), 70 (1F, m,

CF_3); δ_C (62.9MHz; $CDCl_3$; Me_4Si) 122 (2xq, J 280 Hz, 2xCF_3), 62 (q, J 33.5 Hz, C-CF_3), 65 (q, J 33.5 Hz, C-CF_3), 70 (q, J 36.9 Hz, C-CF_3).

VI.2.B. Autoclave Conditions

A mixture of trifluoroacetaldehyde (11.51g, 0.12mol.), dry diethylether (25ml.) and ammonia (2.57g, 0.15mol.) was rocked in a rocking furnace at room temperature overnight. Excess ammonia was vented (bubbled through HCl) and diethylether removed under reduced pressure to leave a viscous brown oil (6.79g). Toluene (50ml.) was added and the water of reaction removed azeotropically using a Dean-Stark apparatus. The toluene was removed under reduced pressure to leave a semi-crystalline residue (3.57g) Sublimation of the residue at 60°C / <0.1mmHg gave a white crystalline solid (2.95g); m.p.78-80°C (lit.,[33] 83-84°C); (Found: C, 24.45; H, 2.1; N, 14.3. $C_6H_6N_3F_9$ requires C, 24.8; H, 2.1; N, 14.4%); ν_{max} ($CDCl_3$)/cm^{-1} 3340, 3315 (NH); δ_F (235MHz; $CDCl_3$; $CFCl_3$) 64 (1F, s, CF_3), 69 (14F, s, CF_3); δ_C (62.9MHz; $CDCl_3$; Me_4Si) 122 (2xq, J 226 Hz, 2xCF_3), 64 (q, J 33 Hz, C-CF_3), 69 (q, J 33 Hz, C-CF_3).

VI.3. Dehydration of Heptafluorobutyraldehyde Hydrate

Heptafluorobutyraldehyde hydrate (50g) was added dropwise to a stirred solution of phosphorus pentoxide (21.47g, 0.15mol.) in 98% sulphuric acid (100ml.) at 100-110°C. The free aldehyde (33.0g, 72%); b.p. 29°C; identified by comparison of IR spectrum[121], was collected in a series of traps and transferred under vacuum to a rotaflo which was stored at -15°C prior to use.

VI.3.A. Attempted Preparation of 2,4,6-tris(heptafluorobutyl)-hexahydro-s-triazine (116)

A mixture of heptafluorobutyraldehyde (13.0g, 66mmol.), dry diethylether (20ml.) and ammonia (2.61g, 0.15mol.) was heated at 50°C for 15 hours in a rocking furnace. Excess ammonia was vented (bubbled through HCl) and diethylether removed under reduced pressure. Toluene (50ml.) was added and the water of reaction removed azeotropically using a Dean-Stark apparatus. The toluene was removed under reduced

pressure to leave a viscous oil. (1.68g). The oil was analysed by GLC/ packed column to be composed of 3 components in the ratio 10:1:1. Preparative scale GLC (130°C/ 10%SE30) separated the major component as an easily subliming white crystalline solid, 2,4,5-tris(heptafluoropropyl)-4,5-dihydroimidazole (**116**); (Found: C, 24.85; H, 5.0; N, 4.55. $C_{12}H_3N_2F_{21}$ requires C, 25.1; H, 5.25; N, 4.9%); IR spectrum 35, NMR spectrum 36, mass spectrum 39.

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER FOUR

CHAPTER SEVEN

EXPERIMENTAL TO CHAPTER FOUR

VII.1. Direct Fluorination of TRAT

VII.1.A. In Acetonitrile

VII.1.A.(1). At -20°C

A solution of **TRAT** (1.63g, 8mmol) in acetonitrile (14.47g, 0.35mol) was cooled to -20°C under a flow of nitrogen, then elemental fluorine, as a 10% mixture in nitrogen (0.56g, 15mmol) was bubbled through the solution at *c.a.* 1.5cm^3 per minute. Once the addition was complete the solution was warmed to room temperature with nitrogen bubbling through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR.

A 20% mixture of elemental fluorine in nitrogen (1.12g, 0.03mol) was bubbled through the above solution at -20°C. Once the addition was complete the solution was warmed to room temperature with nitrogen bubbling through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR. Removal of solvent under reduced pressure gave starting material by ^{1}H NMR.

VII.1.A.(2). At -5°C

A solution of **TRAT** (1.63g, 8mmol) in acetonitrile (15g, 0.37mol) was cooled to -5°C under a flow of nitrogen, then elemental fluorine, as a 10% mixture in nitrogen (0.56g, 15mmol) was bubbled through the solution at *c.a.* 1.5cm^3 per minute. Once the addition was complete the solution was warmed to room temperature with nitrogen bubbling through the reaction mixture. The solution was found to contain HF (δ_F -150ppm) by ^{19}F NMR. Removal of solvent under reduced pressure gave a pale green oil (1.2g) which could not be identified.

VII.2. Direct Fluorination of TAT

VII.2.A. In Acetonitrile

VII.2.A.(1). At -5°C

A solution of **TAT** (2.25g, 8mmol) in acetonitrile (17.3g, 0.42mol) was cooled to -5°C under a flow of nitrogen, then elemental fluorine, as a 10% mixture in nitrogen (0.56g, 15mmol) was bubbled through the solution at *c.a.* 1.5cm^3 per minute. Once the addition was complete the solution was warmed to room temperature with nitrogen bubbling through the reaction mixture. The solution was found to contain HF (δ_F -150ppm) by ^{19}F NMR. Removal of solvent under reduced pressure gave a pale green oil (1.2g) which could not be identified.

VII.3. Direct Fluorination of TRAT

VII.3.A. In Pyridine

A solution of **TRAT** (0.53g, 3mmol) in pyridine (13.24g, 0.17mol) was cooled to -30°C under a flow of nitrogen, then elemental fluorine, as a 10% mixture in nitrogen (0.56g, 15mmol) was bubbled through the solution at *c.a.* 1.5cm^3 per minute. Once the addition was complete the solution was warmed to room temperature with nitrogen bubbling through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR.

A 20% mixture of elemental fluorine in nitrogen (1.12g, 0.03mol) was bubbled through the above solution at -30°C. Once the addition was complete the solution was warmed to room temperature with nitrogen bubbling through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR.

A 30% mixture of elemental fluorine in nitrogen (1.68g, 0.045mol) was bubbled through the above solution. Once the addition was complete the solution was warmed to room temperature with nitrogen bubbling through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR Removal of pyridine under reduced pressure followed by recrystallisation gave starting material by ^{1}H NMR.

VII.4. Direct Fluorination of TRAT

VII.4.A. In a Sodium Carbonate Solution

A solution of **TRAT** (0.53g, 3mmol), distilled water (14ml) and sodium carbonate (4.15g) was maintained at room temperature and elemental fluorine, as a 10% mixture in nitrogen (0.56g, 0.015mol) was bubbled through the solution at *c.a.* 1.5cm^3 per minute. Once the addition was complete nitrogen was bubbled through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR.

A 20% mixture of elemental fluorine in nitrogen (1.12g, 0.03mol) was bubbled through the above solution. Once the addition was complete nitrogen was bubbled through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR.

VII.5. Direct Fluorination of TRAT

VII.5.A. In a Sodium Carbonate Solution (UV Initiated)

A solution of **TRAT** (0.15g, 1mmol), distilled water (5ml) and sodium carbonate (0.31g) was irradiated at room temperature in FEP tubing with a UV lamp (1000W), whilst elemental fluorine, as a 10% mixture in nitrogen (0.56g, 0.015mol) was bubbled through the solution at *c.a.* 1.5cm^3 per minute. Once the addition was complete nitrogen was bubbled through the reaction mixture. The solution was shown to contain no fluorinated material by ^{19}F NMR.

VII.5.B. High Pressure Fluorination of TRAT

A mixture of **TRAT** (2.22g, 10mmol), distilled water (58.6ml), sodium carbonate (2.37g) and elemental fluorine (0.64g, 0.017mol) was heated at 100°C in a rocking furnace for 8 hours. Once the addition was complete nitrogen was bubbled through the reaction mixture. The solution was shown to contain no fluorinated material by ^{19}F NMR Removal of solvent under reduced pressure followed by extraction with chloroform gave a brown solid (1.35g). Sublimation of the solid (50°C/0.1mmHg) gave

a white crystalline solid (0.88g) which was shown to be hexamine by ^{1}H NMR and mass spectrometry .

VII.6. Direct Fluorination of *N,N'*-Diacetylpiperazine (71)

VII.6.A. In a Sodium Carbonate Solution

A solution of *N,N'*-diacetylpiperazine (**71**) (2.06g, 12mmol), distilled water (30ml) and sodium carbonate (1.22g) was maintained at room temperature and elemental fluorine, as a 10% mixture in nitrogen (0.56g, 15mmol) was bubbled through the solution at *c.a.* 1.5cm^3 per minute. Once the addition was complete nitrogen was bubbled through the reaction mixture. The solution was found to contain no fluorinated material by ^{19}F NMR.

VII.6.B. High Pressure Fluorination of *N,N'*-Diacetylpiperazine (71)

A mixture of *N,N'*-diacetylpiperazine (**71**) (1.65g, 10mmol), distilled water (50ml), sodium carbonate (1.84g) and elemental fluorine (0.64g, 0.017mol) was heated at 100°C in a rocking furnace for 8 hours. Once the addition was complete nitrogen was bubbled through the reaction mixture. The solution was shown to contain no fluorinated material by ^{19}F NMR Removal of solvent under reduced pressure followed by extraction with acetone gave starting material by ^{1}H NMR and mass spectrometry.

VII.7. High Pressure Fluorination of Hexamine

A mixture of hexamine (2.1g, 15mmol), distilled water (60ml), sodium carbonate (2g) and elemental fluorine (0.64g, 0.017mol) was heated at 100°C in a rocking furnace for 8 hours. Once the addition was complete nitrogen was bubbled through the reaction mixture. The solution was shown to contain no fluorinated material. Removal of solvent under reduced pressure followed by extraction with acetone gave starting material by NMR and mass spectrometry.

APPENDICES

APPENDIX ONE

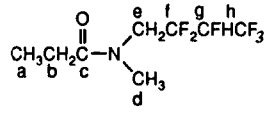
NMR Spectra

1. *N*-(2,2,3,4,4,4-hexafluorobutyl)-*N*-methylpropanamide (**23**)
2. *N*-(2,2,3,4,4,4-hexafluorobutyl)propanamide (**33**)
3. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)acetamide (**35**)
4. *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)acetamide (**37**)
5. 2-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylpiperidine (**39**)
6. *N,N*-bis-(2,2,3,4,4,4-hexafluorobutyl)trimethylsilylamine (**42**)
7. *N,N*-bis-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)trimethylsilylamine (**44**)
8. *N*-(2,3,3,3-tetrafluoropropanoyl)morpholine (**48**)
9. 3,5-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylmorpholine (**57**)
10. 4-(1,1,2,3,3,3-hexafluoropropyl)-2-imidazolidinone (**59**)
11. *N,N'*-bis-(2,2,3,4,4,4-hexafluorobutyl)urea (**67**)
12. *N*-(3-chloro-2,3,3-trifluoropropyl)piperidine (**75**)
13. 2-(2-chloro-1,2,2-trifluoroethyl)-*N*-(3-chloro-2,2,3-trifluoropropyl)piperidine (**76**)
14. 2-(2-chloro-1,2,2-trifluoroethyl)-*N*-trimethylsilylpiperidine (**78**)
15. *N*-(3-chloro-2,3,3,-trifluoropropyl)-*N*-methyl(trimethylsilyl)amine (**79**)
16. *N*-(3-chloro-2,3,3-trifluoro-1-methylpropyl)-*N*-ethyl(trimethylsilyl)amine (**80**)
17. 3-(2-chloro-1,2,2-trifluoroethyl)-*N*-trimethylsilylmorpholine (**81**)
18. *N*-[(1,2,2,3,3,4-hexafluorocyclobutyl)-methyl]acetamide (**82**)
19. *N*-[(1,2,2,3,3,4,4,5-octafluorocyclopentyl)-methyl]acetamide (**83**)
20. *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)ethyl]acetamide (**84**)
21. *N*-[1-(1,2,2,3,3,4,4,5-octafluorocyclopentyl)ethyl]acetamide (**85**)
22. *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)propyl]acetamide (**86**)
23. *N*-(trifluorocyclobut-1-en-4-onyl)piperidine (**88**)
24. *N*-(heptafluorocyclopent-1-enyl)piperidine (**89**)
25. 1-(*N,N*-dimethylamino)-pentafluorocyclobut-1-ene (**90**)
26. 1-(*N,N*-dimethylamino)-pentafluorocyclopent-1-en-5-one (**91**)

27. 1-(*N*,*N*-diethylamino)-pentafluorocyclobut-1-ene (**92**)
28. 1-(*N*,*N*-diethylamino)-heptafluorocyclopent-1-ene (**93**)
29. (3,3-difluorocyclobutan-2,4-onyl)morpholinium betaine (**94**)
30. *N*-(pentafluorocyclobut-1-enyl)morpholine (**95**)
31. *N*-(trifluorocyclobut-1-en-4-onyl)morpholine (**96**)
32. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethylamine (**97**)
33. *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)-*N*-ethylamine (**98**)
34. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl-*N*-ethylacetamide (**101**)
35. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-1,2,2-trichloroethenylamine (**103**)
36. 2,4,5-tris-(heptafluoropropyl)-4,5-dihydroimidazole (**116**)

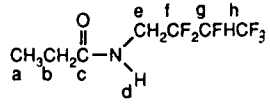
All NMR spectra were recorded in *d*-chloroform except for spectra 10 and 11 which were recorded in d_6-acetone. All spectra were internally referenced using $CFCl_3$ and Me_4Si.

No.1 *N*-(2,2,3,4,4,4-hexafluorobutyl)-*N*-methyl-propanamide (23)



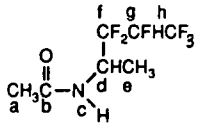
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.16	t J_{ab}=7.3	3H	a
2.41	q J_{ab}=7.3	2H	b
3.14	s	3H	d
3.90	ddd $^3J_{HF}$=14.5, $^4J_{HF}$=0.8	2H	e
4.10	ddd $^3J_{HF}$=13.8, $^4J_{HF}$=1.7		
4.95	dofm J_{HF}=42	1H	g
^{19}F			
-74.0	s	3F	h
-113.1, -114.2	AB J_{AB}=258.9	2F	f
-211.3	d J_{HF}=42.7	1F	g
^{13}C			
9.0	s		a
26.6	s		b
37.3	s		d
49.3	dofd $^2J_{CF}$=25.7		e
84.9	dofm $^1J_{CF}$=200.1		g
Series of lines between 114.7-125.0	Unassigned		f,h

No.2 *N*-(2,2,3,4,4,4-hexafluorobutyl)propanamide (33)



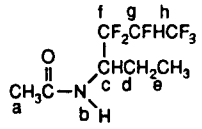
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.18	t J_{ab}=7.6	3H	a
2.31	q J_{ab}=7.6	2H	b
3.81, 3.98	m	2H	e
4.91	dofm J_{HF}=44	1H	g
6.45	s(broad)	1H	d
^{19}F			
-74.2	s	3F	h
-113.6, -117.0	AB J_{AB}=271	2F	f
-211.5	d J_{HF}=38.4	1F	g
^{13}C			
9.4	s		a
29.2	s		b
40.5	dofd J=26.4		e
84.5	dofm J=201		g
Series of lines between 113.9-124.8	Unassigned		f,h
174.8	s		c

No.3 *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)acetamide
(35)



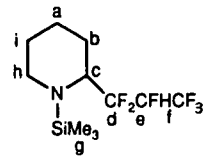
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.30	s		3H	e
1.33	s			
2.04	s		3H	a
2.05	s			
4.7	m		1H	d
5.0	d of m	J_{HF}=44.8	1H	g
7.40	d of d	$^3J_{NH-CH}$=9	1H	c
^{19}F				
-74.4	s		3F	h
-74.7	s			
-118.9	AB	J_{AB}=270.2	2F	f
-123.6				
-121.7	AB	J_{AB}=271.3		
-126.8				
-211.4	d	J_{HF}=41.2	1F	g
-128.5	d	J_{HF}=42.1		
^{13}C				
12.7	s			e
13.7	s			
22.7	s			a
22.8	s			
45.8	d of d	$^2J_{CF}$=30.3, 22.7		d
47.2	d of d	$^2J_{CF}$=25.2		
84.2	m			g
Series of lines between 112.0-124.0				f,h
171.1	s			b
171.2	s			

No.4 *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)acetamide (37)



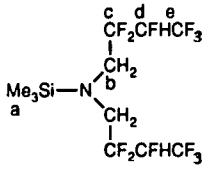
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.0	t	J_{ed}=7.4	3H	e
1.6	m		2H	d
2.06	s		3H	a
2.08	s			
3.65-5.47	m		2H	c,g
6.29	m		1H	b
^{19}F				
-74.4	s		3F	h
-74.6	s			
-117.6	AB	J_{AB}=271.9	2F	f
-123.1				
-121.8	AB	J_{AB}=271.9		
-124.8				
-211.0	d	J_{HF}=44.0	1F	g
-211.4	d	J_{HF}=42.8		

No.5 2-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilyl-piperidine (39)



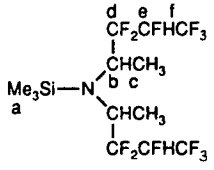
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
0.18	s	9H	g
1.14-1.82	m	6H	a,b,i
2.82	m	2H	h
3.32	m	1H	c
4.80 (major isomer)	d of m J_{HF}=43.8	1H	e
5.06 (minor isomer)	d of m J_{HF}=42.8		
^{19}F			
-72.9 (minor isomer)	m	3F	f
-73.2 (major isomer)	m		
-109.4	AB J_{AB}=272.1 (major isomer)	2F	d
-111.2			
-112.6	AB J_{AB}=270.0 (minor isomer)		
-116.1			
-209.4	d J_{HF}=42.9 (minor isomer)	1F	e
-210.0	d J_{HF}=43.6 (major isomer)		

No.6 *N,N*-bis-(2,2,3,4,4,4-hexafluorobutyl)trimethylsilyl-amine (42)



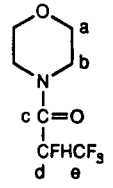
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
0.22	s	9H	a
3.60	d of d $^3J_{HF}$=19.9	2H	b
4.96	d of m J_{HF}=41.9	1H	d
^{19}F			
-75.0	s	6F	e
-110.6	AB J_{AB}=264.4	4F	c
-115.5			
-211.3	d J_{HF}=43.3	2F	d

No.7 *N,N*-bis-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-trimethylsilylamine (44)



Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
0.18	s	9H	a
1.30	m	6H	c
3.80	m	2H	b
4.76	d of m J_{HF}=44	2H	e
^{19}F			
-73.5	s	6F	f
Series of lines between -112.6- -113.2	Unassigned	4F	d
-209.8	broad s	2F	e

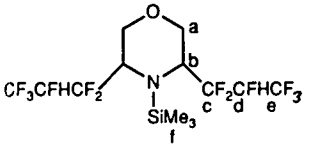
No.8 *N*-(2,3,3,3-tetrafluoropropanoyl)morpholine (48)



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
3.60-3.74	m		8H	a and b
5.4	d of q	J_{HF}=46.5 $^3J_{HF}$=6.4	1H	d
^{19}F				
-75.8	s		3F	e
-198.8	d	J_{HF}=45.2	1F	d
^{13}C				
43.4	s			b
46.2	s			
66.6	s			a
85.5	d of q	$^1J_{CF}$=201.9 $^2J_{CF}$=34.5		d
121.1	q of d	$^1J_{CF}$=281.8 $^2J_{CF}$=26.1		e
159.4	s			c

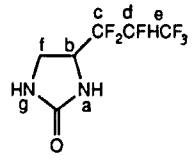
^{13}C DEPT spectrum was also recorded, confirming the presence of CH_2 groups at 43.4, 46.2 and 66.6ppm.

No.9 3,5-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylmorpholine (57)



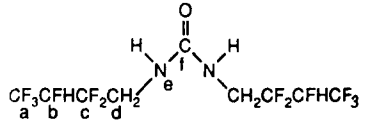
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.17	s		9H	f
3.43	m		4H	a
4.95	m		2H	d
3.98	m		2H	b
^{19}F				
-74.2	s		6F	e
-74.6	s			
Series of lines between -110.5--125.1	AB's (overlapping)		4F	c
-209.8	d	J_{HF}=36.7	2F	d
-210.7	d	J_{HF}=38.6		

No.10 4-(1,1,2,3,3,3-hexafluoropropyl)-2-imidazolidinone (59)



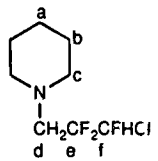
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
(spectrum recorded in d_6-acetone)			
^{1}H			
3.64	m	2H	f
3.78	t J_{fb}=9.8		
4.45	m	1H	b
6.18	s(broad)	1H	g
6.64	s(broad)	1H	a
6.75	s(broad)		
5.72	m	1H	
^{19}F			
-79.0	m	3F	e
-79.1	m		
-122.2	AB J_{AB}=269.7	2F	c
-123.7			
-126.9	s(unassigned)		
-218.6	d of m J_{HF}=37.6	1F	d
-220.0	d of m J_{HF}=42.5		

No.11 N,N'-bis-(2,2,3,4,4,4-hexafluorobutyl)urea (67)



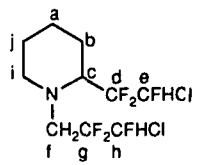
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
(spectrum recorded in d_6-acetone)			
^{1}H			
3.90	m	4H	d
5.55	d of m J_{HF}=44.8	2H	b
6.48	s(broad)	2H	e
^{19}F			
-73.7	s	6F	a
-115.7	AB J_{AB}=265.8	4F	c
-118.2			
-212.8	d J_{HF}=40	2F	b
^{13}C			
42.3	t $^2J_{CF}$=26.5		d
85.1	d of m $^1J_{CF}$=191.1		b
Series of lines between 115.7-126.5	Unassigned		a,c
158.5	s		f

No.12 *N*-(3-chloro-2,3,3-trifluoropropyl)piperidine (**75**)



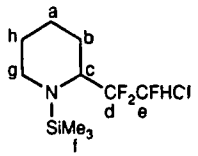
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.35-1.77	m	6H	a,b
2.54	m	4H	c
2.86	m	2H	d
6.45	d of m J_{HF}=47.5	1H	f
^{19}F			
-115.2	AB J_{AB}=169.2	2F	e
-116.2			
-156.5	d J_{HF}=47.3	1F	f

No.13 2-(2-chloro-1,1,2-trifluoroethyl)-*N*-(3-chloro-2,2,3-trifluoropropyl)piperidine (**76**)



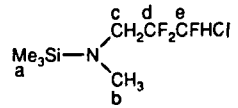
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.26-1.57	m	6H	a,b,j
1.77	m	2H	i
2.53	m	1H	c
2.91	m	2H	f
6.49	d of m J_{HF}=47.8	2H	e,h
^{19}F			
Series of lines between -112.2- -119.8	AB's(overlapping)	4F	d,g
-152.3	d J_{HF}=46.4	2F	e,h
-156.9	d J_{HF}=45.4		

No.14 2-(2-chloro-1,1,2-trifluoroethyl)-*N*-trimethylsilyl-piperidine (78)



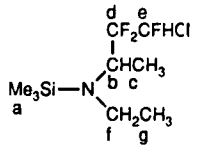
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
0.13	s	9H	f
1.25-1.96	m	6H	a,b,h
2.60	t $J_{g,h}$=11.7	2H	g
3.14	m	1H	c
6.43	d of m J_{HF}=47.8	1H	e
^{19}F			
-123.8- -127.5	AB's(overlapping)	2F	d
-152.5	d J_{HF}=53.4	1F	e
-158.8	d J_{HF}=34.6		

No.15 *N*-(3-chloro-2,3,3-trifluoropropyl)-*N*-methyl-(trimethylsilyl)amine (79)



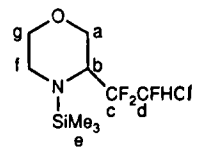
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
0.11	s	9H	a
2.54	s	3H	b
3.24	ddd $^3J_{HF}$=10.4 $^4J_{HF}$=1.8	2H	c
6.12	ddd $^2J_{HF}$=47.8 $^3J_{HF}$=9.1,4.3	1H	e
^{19}F			
-113.4 -118.0	AB J_{AB}=260.6	2F	d
-153.7	d J_{HF}=50.6	1F	e

No.16 *N*-(3-chloro-2,2,3-trifluoro-1-methylpropyl)-*N*-ethyl(trimethylsilyl)amine (80)



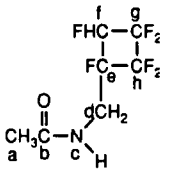
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.19	s		9H	a
1.13	t	J_{fg}=6.8	3H	g
1.36	d	J_{cb}=6.8	3H	c
2.95	q	J_{fg}=6.8	2H	f
3.70	m		1H	b
6.48	m		1H	e
^{19}F				
Series of lines between -120.0--121.1	AB's(overlapping)		2F	d
-151.2	d	J_{HF}=46.4	1F	e
-158.1	d	J_{HF}=57.9		

No.17 3-(2-chloro-1,1,2-trifluoroethyl)-*N*-trimethylsilyl-morpholine (81)



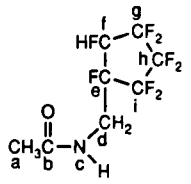
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.15	s		9H	e
2.45-3.89	m		6H	a,f,g
4.24	m		1H	b
6.39	m		1H	d
^{19}F				
Series of lines between -110.4--124.5	AB's(overlapping)		2F	c
-151.2	d	J_{HF}=45.4	1F	d
-156.1	d	J_{HF}=52.0		

No.18 *N*-[(1,2,2,3,3,4-hexafluorocyclobutyl)-methyl]-acetamide (82)



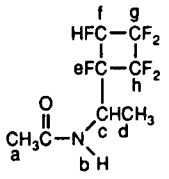
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
2.05	s(major isomer)	3H	a
2.07	s(minor isomer)		
3.65	m(major isomer)	2H	d
4.14	m(minor isomer)		
5.57	d of m J_{HF}=53.8	1H	f
7.05	s(broad)(major isomer)	1H	c
7.76	s(broad)(minor isomer)		
^{19}F			
Series of lines between -126.4- -134.3	AB's(overlapping)	4F	g,h
-177.5	m(major isomer)	1F	e
-194.6	m(minor isomer)		
-216.3	d J_{HF}=49.7	1F	f
-218.3	d J_{HF}=51.6		
^{13}C			
22.7	s(minor isomer)		a
23.0	s(major isomer)		
35.3	d J=19.5 (major isomer)		d
37.6	d J=21.4 (minor isomer)		
Series of lines between 85.0-95.8	Unassigned		e,f
Series of lines between109.1-117.0	Unassigned		g,h
170.7	s(major isomer)		b
171.5	s(minor isomer)		

No.19 *N*-[(1,2,2,3,3,4,4,5-octafluorocyclopentyl)-methyl]-acetamide (83)



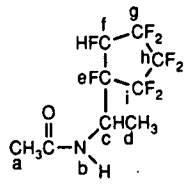
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
2.05	s		3H	a
2.06	s			
3.61-4.12	m		2H	d
5.13	m		1H	f
6.87	m		1H	c
7.11	m			
^{19}F				
Series of lines between -111.1--136.6	AB's(overlapping)		6F	g,h,i
-177.5	s		1F	e
-189.6	s			
-210.2	d	J_{HF}=47.4	1F	f
-223.3	d	J_{HF}=45.9		
^{13}C				
22.5	s			a
22.7	s			
35.4	d	$^{2}J_{CF}$=19.7		d
37.5	d	$^{2}J_{CF}$=22.1		
Series of lines between 84.7-96.3	Unassigned			e,f
Series of lines between 103.0-120.0	Unassigned			g,h,i
171.1	s			b
171.6	s			

No.20 *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)ethyl]-acetamide (79)



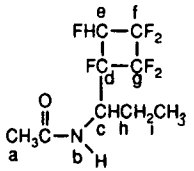
Chemical Shift (ppm)	Multiplicity / Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.31	s	3H	d
1.34	s		
2.00	s	3H	a
4.90	m	1H	c
5.18	d of m J_{HF}=47.8	1H	f
6.20	s(broad)	1H	b
^{19}F			
Series of lines between -116.8- -135.8	AB's(overlapping)	4F	g,h
-185.0	s	1F	e
-186.1	s		
-214.5	d J_{HF}=46.6	1F	f
-216.2	d J_{HF}=46.4		
-220.4	d J_{HF}=47.5		

No.21 *N*-[1-(1,2,2,3,3,4,4,5-octafluorocyclopentyl)ethyl]-acetamide (85)



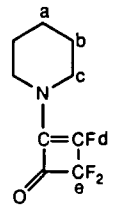
Chemical Shift (ppm)	Multiplicity / Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.37	m	3H	d
2.04	s	3H	a
4.57-5.24	m	2H	c,f
6.05	m	1H	b
^{19}F			
Series of lines between -114.9- -134.5	AB's(overlapping)	6F	g,h,i
-189.8	s	1F	e
-191.2	s		
-197.1	s		
-201.8	s		
-207.7	d J_{HF}=47.0	1F	f
-209.2	d J_{HF}=47.8		
-221.8	d J_{HF}=45.2		
-222.6	d J_{HF}=45.9		

No.22 *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)-propyl]-acetamide (86)



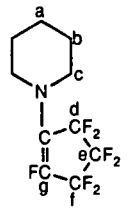
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
0.97	m	3H	i
1.6	m	2H	h
1.77	m		
2.045	s	3H	a
2.05	s		
2.07	s		
4.48	m	1H	c
4.67	m		
5.13	m	1H	e
6.18	d(broad) J_{bc}=9.2	1H	b
6.32	d(broad) J_{bc}=9.6		
^{19}F			
Series of lines between -115.8- -134.4	AB(overlapping)	4F	f,g
-182.6	s	1F	d
-83.7	s		
-200.6	s		
-212.6	dofd J_{HF}=48.2	1F	e
-214.6	dofd J_{HF}=48.9		

No.23 *N*-(trifluorocyclobut-1-en-4-onyl)piperidine (88)



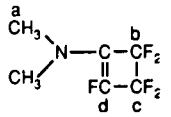
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.78	s(broad)	6H	a,b
3.57	m	4H	c
^{19}F			
-113.1	d J_{ef}=25.6	2F	e
-131.5	t J_{ef}=25.6	1F	d

No.24 *N*-(heptafluorocyclopent-1-enyl)piperidine (89)



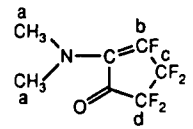
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.71	s(broad)	6H	a,b
3.44	s(broad)	4H	c
^{19}F			
-109.2	s	2F	d or f
-111.4	s	2F	d or f
-128.5	s	2F	e
-166.7	s	1F	g

No.25 1-(*N,N*-dimethylamino)-pentafluorocyclobut-1-ene (90)



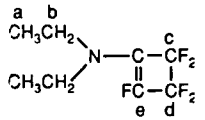
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
2.85	s		a
^{19}F			
-109.8	s	2F	b or c
-114.9	s	2F	b or c
-156.8	s	1F	d

No.26 1-(*N,N*-dimethylamino)-pentafluorocyclopent-1-en-5-one **(91)**



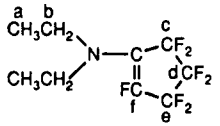
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
3.01	s		a
^{19}F			
-114.0	s	2F	d
-125.2	s	2F	c
-158.1	s	1F	b

No.27 1-(*N,N*-diethylamino)-pentafluorocyclobut-1-ene **(92)**



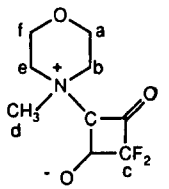
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
0.92	t	J_{ab}=8	3H	a
2.93	q	J_{ab}=8	2H	b
^{19}F				
-111.6	s		2F	c or d
-115.6	s		2F	c or d
-155.3	s		1F	e

No.28 1-(*N,N*-diethylamino)-heptafluorocyclopent-1-ene (93)



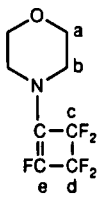
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
1.20	t	J_{AB}=7.1	3H	a
3.70	q	J_{AB}=7.1	2H	b
^{19}F				
-108.8	s		2F	c or e
-110.7	s		2F	c or e
-128.1	s		2F	d
-170.9	s		1F	f

No.29 (3,3-difluorocyclobutan-2,4-onyl)morpholinium betaine (94)



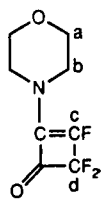
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
3.12	m		4H	a,f
3.67	s(broad)		3H	d
4.29	m		4H	b,e
^{19}F				
-108.2	s			c

No.30 *N*-(pentafluorocyclobut-1-enyl)morpholine (**95**)



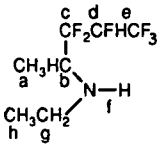
Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
3.42	m	4H	a
3.70	m	4H	b
^{19}F			
-109.6	s	2F	c or d
-113.3	s	2F	c or d
-148.3	s	1F	e

No.31 *N*-(trifluorocyclobut-1-en-4-onyl)morpholine (**96**)



Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
3.57	m		4H	a
3.86	m		4H	b
^{19}F				
-110.6	d	J_{cd}=25.4	2F	d
-128.5	t	J_{cd}=25.4	1F	c

No.32 *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethylamine (97)

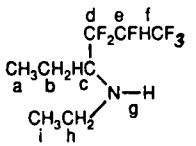


Chemical Shift (ppm)	Multiplicity / Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
0.7	s(broad)	1H	f
1.075	t J_{gh}=7.2	3H	h
1.08	t J_{gh}=7.0		
1.24	s	3H	a
1.26	s		
2.49-3.18	m	3H	b,g
5.43	m	1H	d
^{19}F			
-74.4	s	3F	e
-74.9	s		
-118.5	AB J_{AB}=267.5	2F	c
-123.4			
-123.5	AB J_{AB}=268.3		
-130.9			
-212.9	d J_{HF}=41.7	1F	d
-217.5	d J_{HF}=41.7		

^{13}C			
11.6	s		a
13.2	s		
15.4	s		h
42.0	s		g
42.1	s		
53.1	dofd	$^{2}J_{CF}$=28.1,21.9	b
53.4	dofd	$^{2}J_{CF}$=24.4	
83.6	m		d
Series of lines between 116.6-123.2	Unassigned		c,e

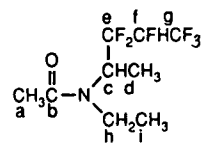
No.33 *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)-*N*-ethylamine

(98)



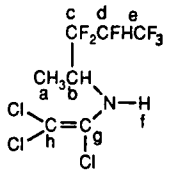
Chemical Shift (ppm)	Multiplicity / Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.05-1.86	m	9H	a,b,i,g
2.70-2.94	m	3H	c,h
5.35	m	1H	e
^{19}F			
-73.6	m	3F	f
Series of lines between -114.6--127.3	Unassigned	2F	d
-211.4	m	1F	e
-214.5	m		
^{13}C			
10.5	s		a
10.9	s		
15.6	s		i
20.3	s		b
21.6	s		
42.9	s		h
43.2	s		
58.7	m		c
61.8	m		
84.4	m		e
Series of lines between 113.1-125.6	Unassigned		d,f

No.34 *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethyl-acetamide (101)



Chemical Shift (ppm)	Multiplicity / Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.25	m	3H	i
1.39	m	3H	d
2.17	s	3H	a
2.20	s		
3.40	m	2H	h
4.92	m	1H	f
5.34	m	1H	c
^{19}F			
-73.7	m	3F	g
Series of lines between -112.3--127.6	Unassigned	2F	e
-209.3	dofd J_{HF}=42.5	1F	f
-209.6	dofd J_{HF}=43.3		
^{13}C			
11.5	s		i
15.95	s		d
21.5	s		a
21.7	s		
39.5	s		h
49.2	m		c
50.6	m		
Series of lines between 82.0-86.8	Unassigned		f
Series of lines between 114.6-125.6	Unassigned		e,g
172.4	s		b
172.7	s		

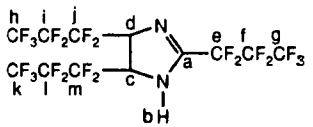
No.35 *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-1,2,2-trichloroethenylamine (103)



Chemical Shift (ppm)	Multiplicity Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H			
1.43	s	3H	a
1.45	s		
4.67	m	1H	b
4.95	m	1H	d
6.70	s(broad)	1H	f
6.78	s(broad)		
^{19}F			
-73.8	s	3F	e
-73.9	s		
-118.2	AB J_{AB}=281.3	2F	c
-122.2			
-119.8	AB J_{AB}=277.7		
-122.6			
-210.2	d J_{HF}=42.9	1F	d
-210.9	d J_{HF}=38.4		

^{13}C			
12.0	s		a
13.8	s		
48.3	dofd $^{2}J_{CF}$=23.2		b
49.4	dofd $^{2}J_{CF}$=30.5, 24.8		
84.4	m		d
Series of lines between 114.4-125.0	Unassigned		c,e
91.8	s		g
161.8	s		h
162.0	s		

No.36 2.4.5-tris-(heptafluoropropyl)-4.5-dihydroimidazole



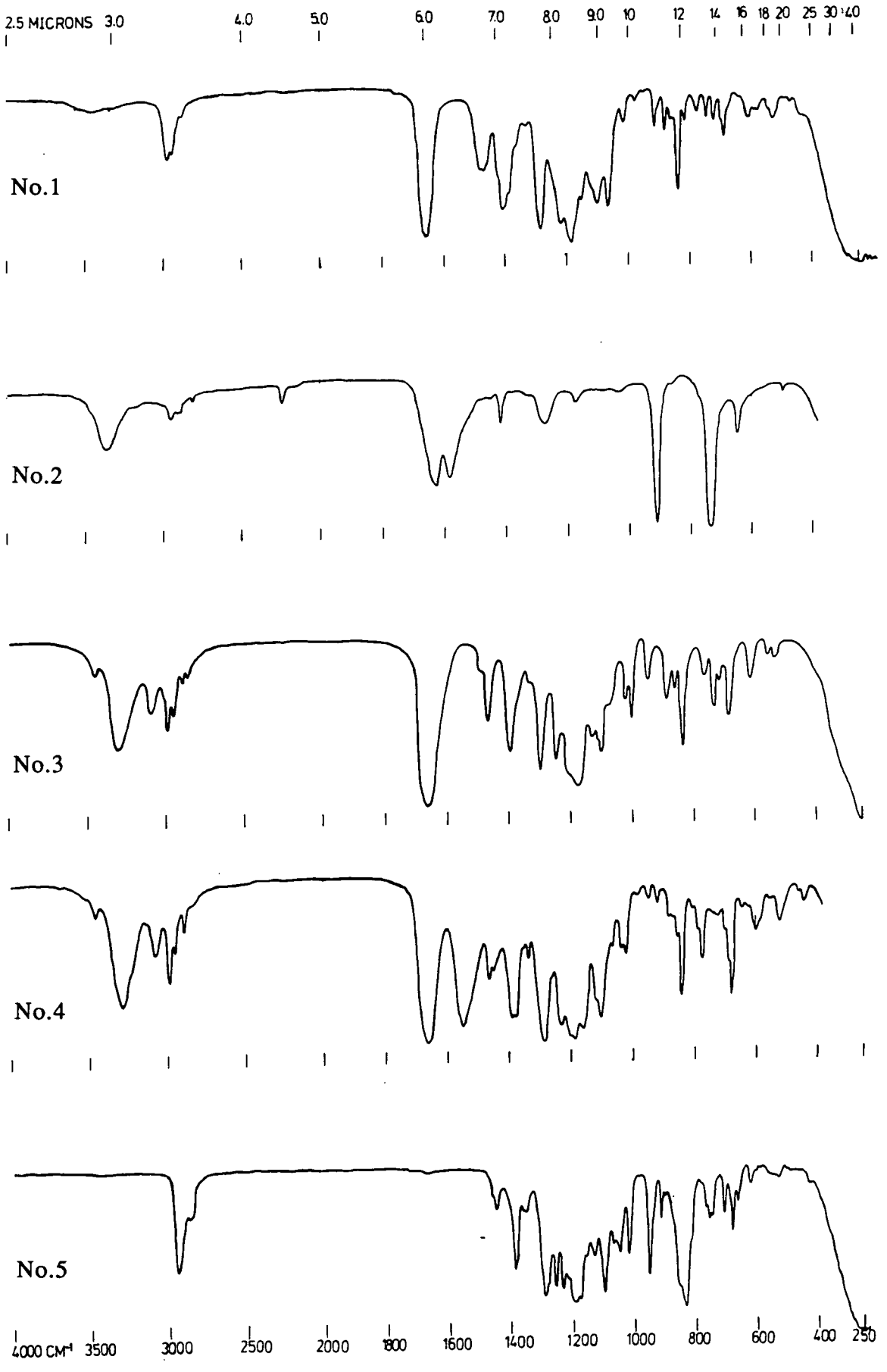
Chemical Shift (ppm)	Multiplicity	Coupling Constant (Hz)	Relative Intensity	Assignment
^{1}H				
4.78	dofd	$^{3}J_{HF}$=21.2, $^{3}J_{HF'}$=10.4	1H	c or d
5.15	dofd	$^{3}J_{HF}$=26.6, $^{3}J_{HF'}$=10.2	1H	c or d
5.61	s		1H	b
^{19}F				
-80.2	m		9F	g,h,k
-80.5	m			
Series of lines between -113.0- -126.8	Unassigned		12F	e,f,i,j,l,m
^{13}C				
58.8	dofd	$^{2}J_{CF}$=32, $^{2}J_{CF'}$=23.3		c or d
69.1	dofd	$^{2}J_{CF}$=28.5, $^{2}J_{CF'}$=23.4		c or d
Series of lines between 105-123				e,f,g,h,i,j,k,l,m
156.8	dofd	$^{2}J_{CF}$=28.4		a

APPENDIX TWO

Infra Red Spectra

1. *N*-(2,2,3,4,4,4-hexafluorobutyl)-*N*-methylpropanamide (**23**)
2. *N*-(2,2,3,4,4,4-hexafluorobutyl)propanamide (**33**)
3. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)acetamide (**35**)
4. *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)acetamide (**37**)
5. 2-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylpiperidine (**39**)
6. *N*,*N*-bis-(2,2,3,4,4,4-hexafluorobutyl)trimethylsilylamine (**42**)
7. *N*,*N*-bis-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)trimethylsilylamine (**44**)
8. *N*-(2,3,3,3-tetrafluoropropanoyl)morpholine (**48**)
9. 3,5-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylmorpholine (**57**)
10. 4-(1,1,2,3,3,3-hexafluoropropyl)-2-imidazolidinone (**59**)
11. *N*,*N'*-bis-(2,2,3,4,4,4-hexafluorobutyl)urea (**67**)
12. *N*-(3-chloro-2,3,3-trifluoropropyl)piperidine (**75**)
13. 2-(2-chloro-1,2,2-trifluoroethyl)-*N*-(3-chloro-2,2,3-trifluoropropyl)piperidine (**76**)
14. 2-(2-chloro-1,2,2-trifluoroethyl)-*N*-trimethylsilylpiperidine (**78**)
15. *N*-(3-chloro-2,3,3,-trifluoropropyl)-*N*-methyl(trimethylsilyl)amine (**79**)
16. *N*-(3-chloro-2,3,3-trifluoro-1-methylpropyl)-*N*-ethyl(trimethylsilyl)amine (**80**)
17. 3-(2-chloro-1,2,2-trifluoroethyl)-*N*-trimethylsilylmorpholine (**81**)
18. *N*-[(1,2,2,3,3,4-hexafluorocyclobutyl)-methyl]acetamide (**82**)
19. *N*-[(1,2,2,3,3,4,4,5-octafluorocyclopentyl)-methyl]acetamide (**83**)
20. *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)ethyl]acetamide (**84**)
21. *N*-[1-(1,2,2,3,3,4,4,5-octafluorocyclopentyl)ethyl]acetamide (**85**)
22. *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)propyl]acetamide (**86**)
23. *N*-(trifluorocyclobut-1-en-4-onyl)piperidine (**88**)
24. *N*-(heptafluorocyclopent-1-enyl)piperidine (**89**)
25. 1-(*N*,*N*-dimethylamino)-pentafluorocyclopent-1-en-5-one (**91**)
26. 1-(*N*,*N*-diethylamino)-pentafluorocyclobut-1-ene (**92**)

27. 1-(*N*,*N*-diethylamino)-heptafluorocyclopent-1-ene (**93**)
28. (3,3-difluorocyclobutan-2,4-onyl)morpholinium betaine (**94**)
29. *N*-(pentafluorocyclobut-1-enyl)morpholine (**95**)
30. *N*-(trifluorocyclobut-1-en-4-onyl)morpholine (**96**)
31. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethylamine (**97**)
32. *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)-*N*-ethylamine (**98**)
33. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl-*N*-ethylacetamide (**101**)
34. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-1,2,2-trichloroethenylamine (**103**)
35. 2,4,5-tris-(heptafluoropropyl)-4,5-dihydroimidazole (**116**)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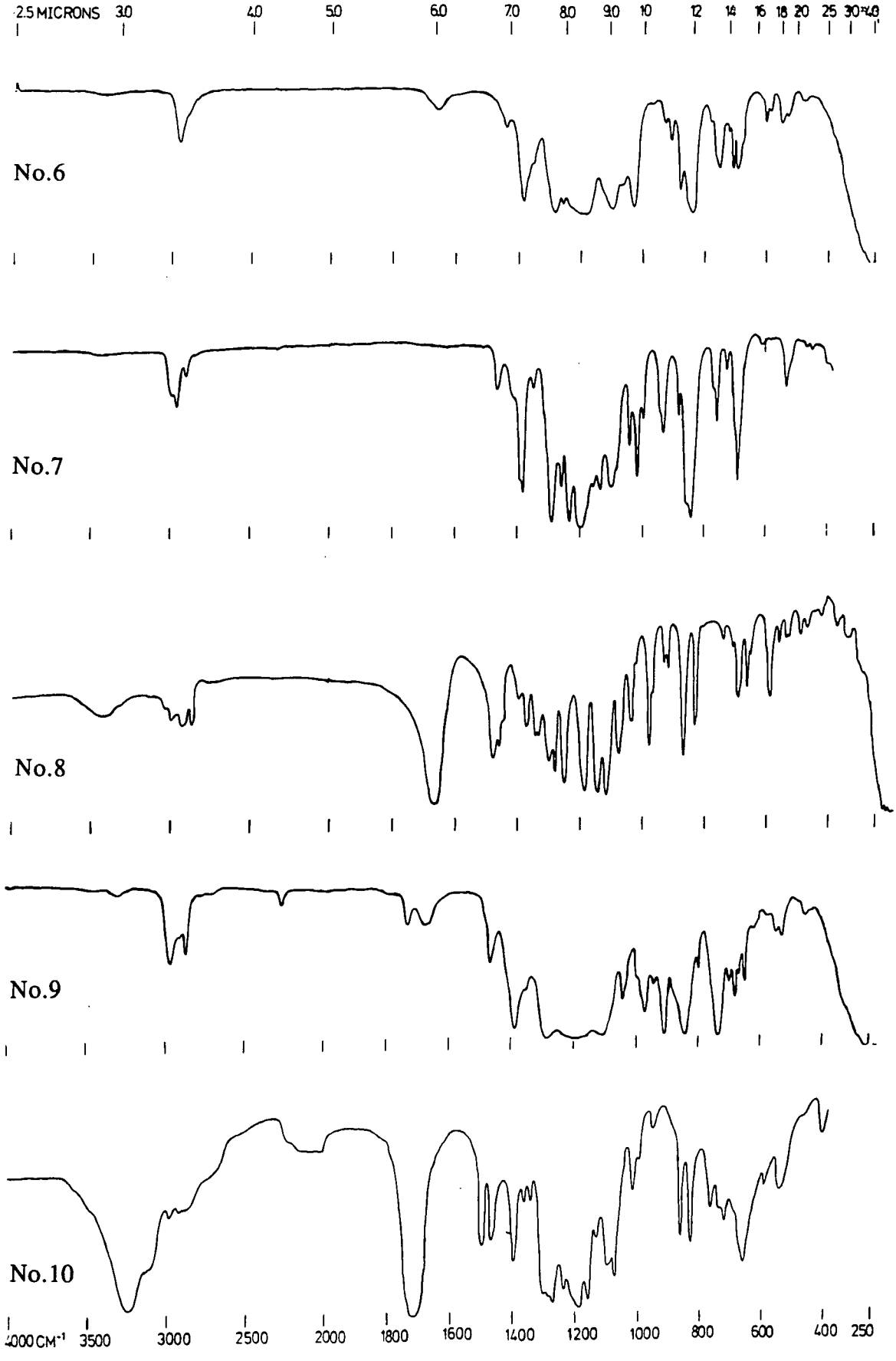
No.1
No.2
No.3
No.4
No.5
4000 CM⁻¹ 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250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No.6
No.7
No.8
No.9
No.10
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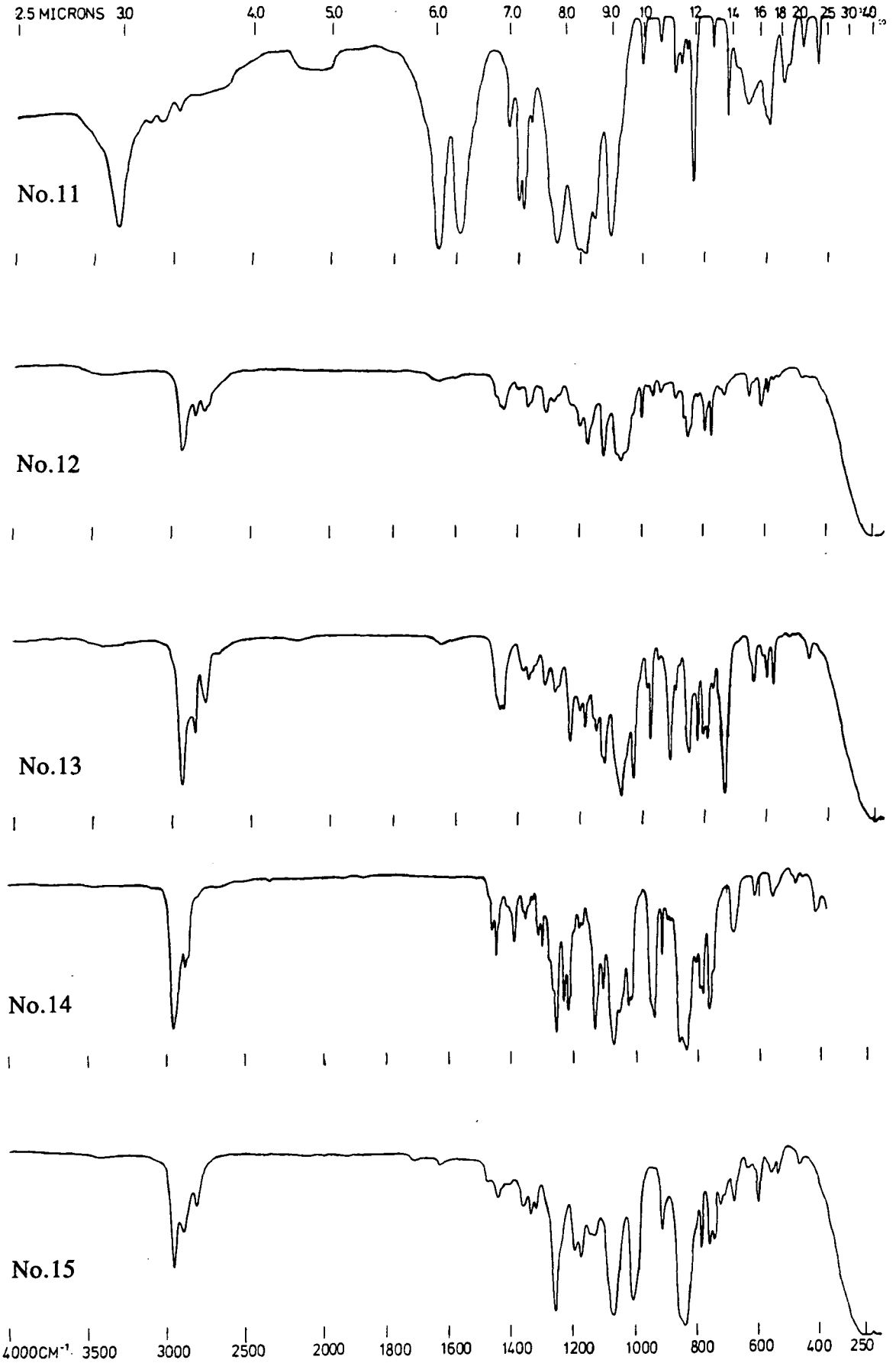
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No.12
No.13
No.14
No.15
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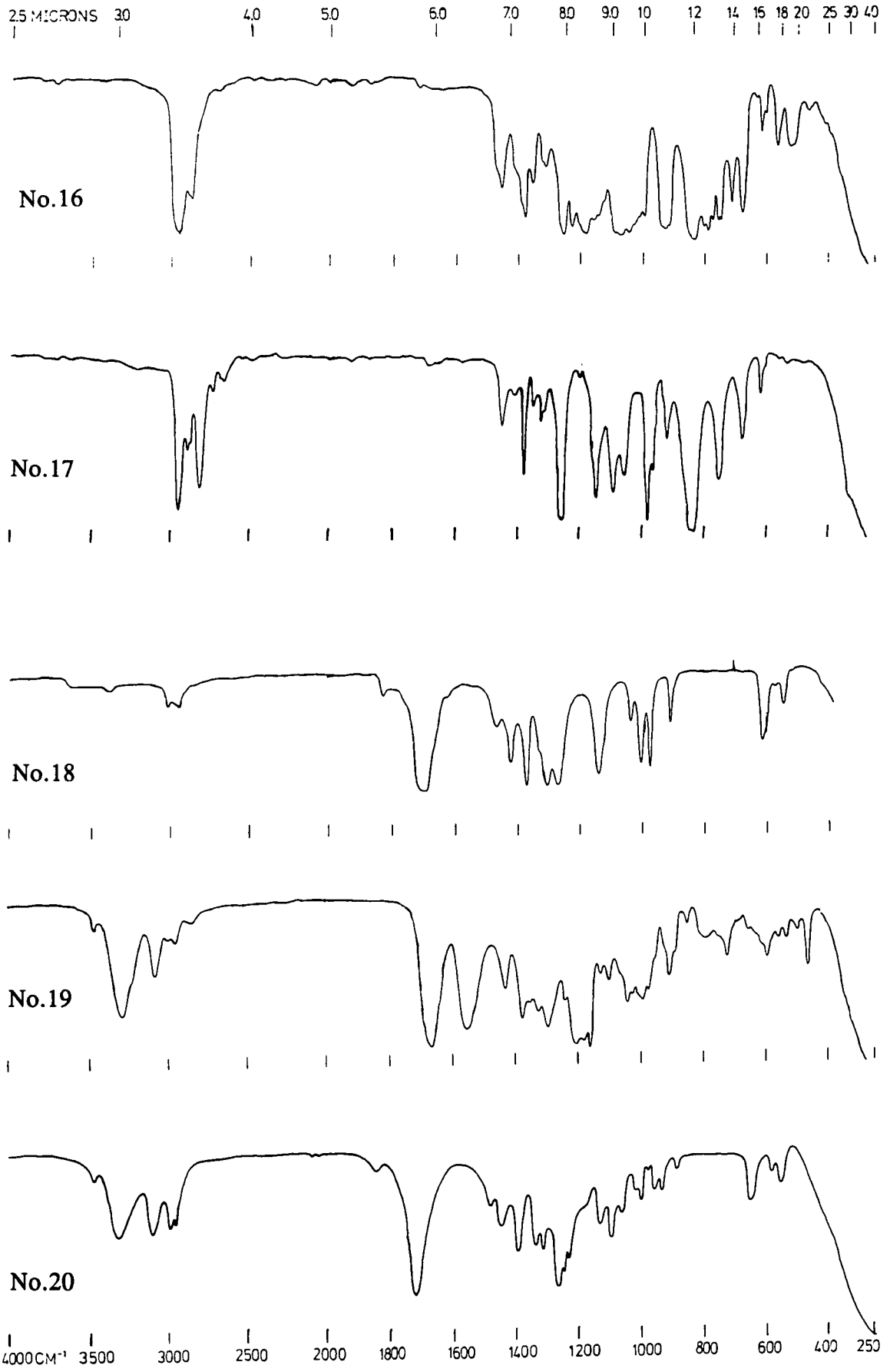
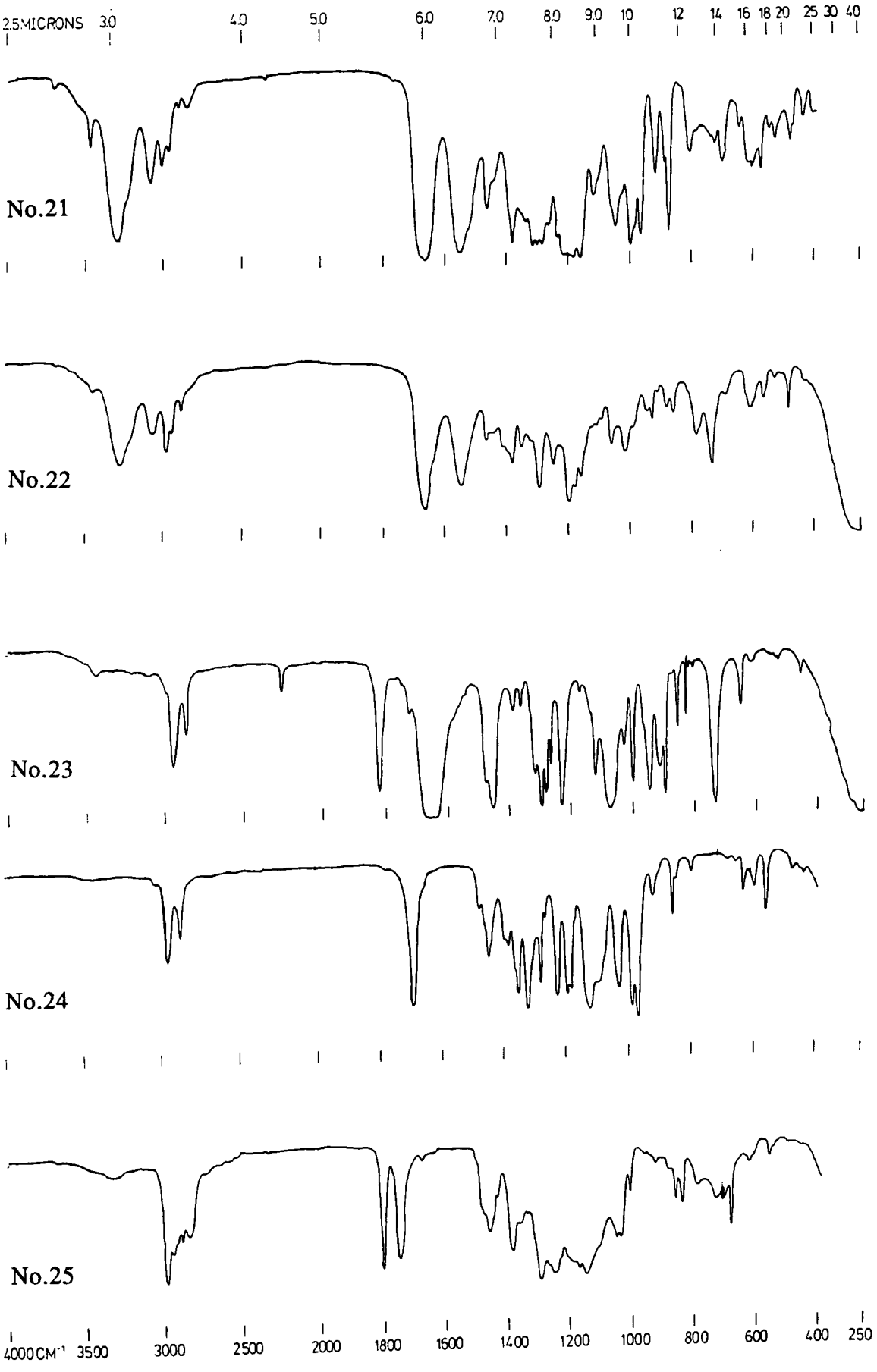

2.5 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 18 20 25 30 40
No.16
No.17
No.18
No.19
No.20
4000 CM⁻¹ 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250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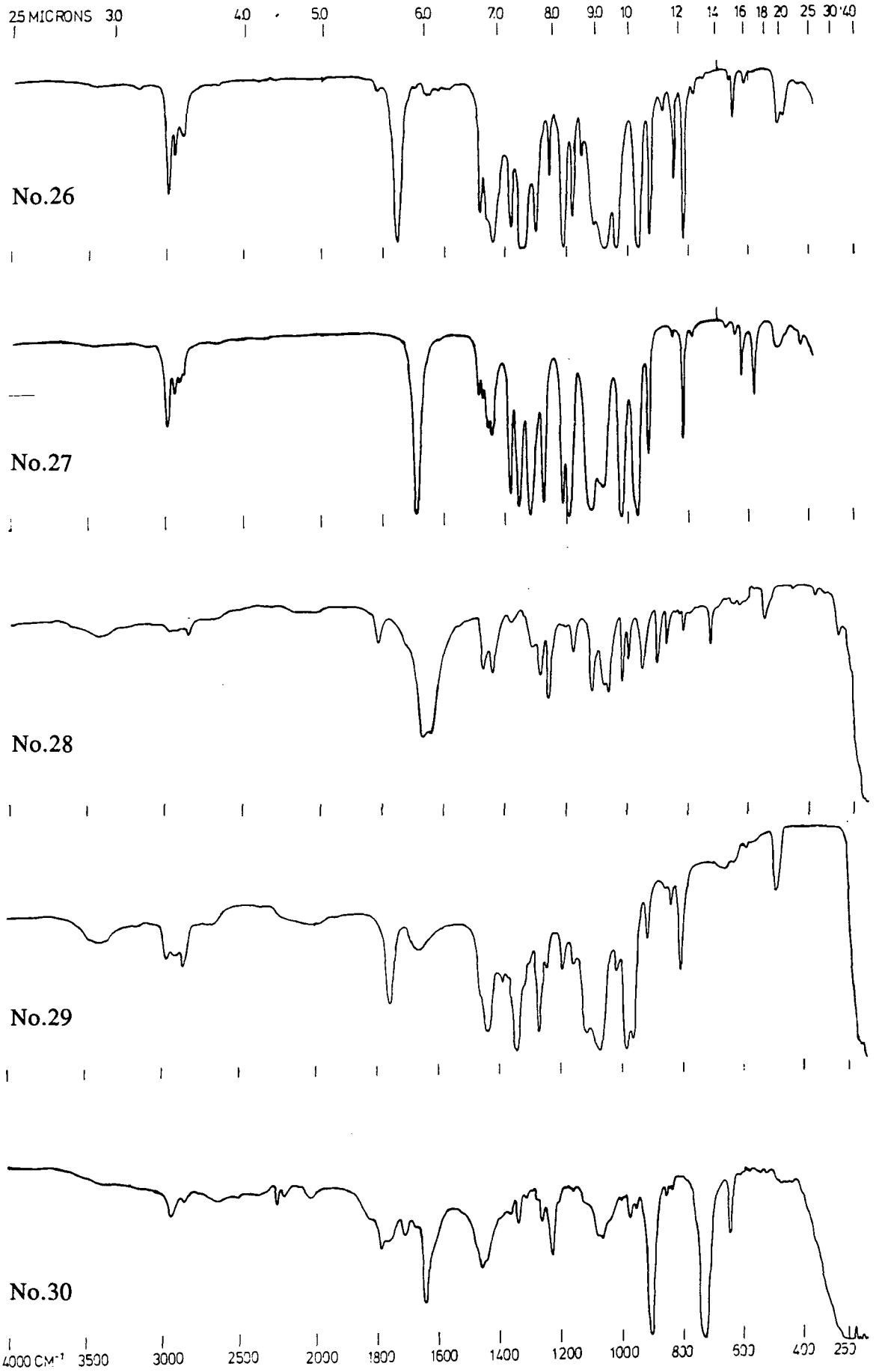
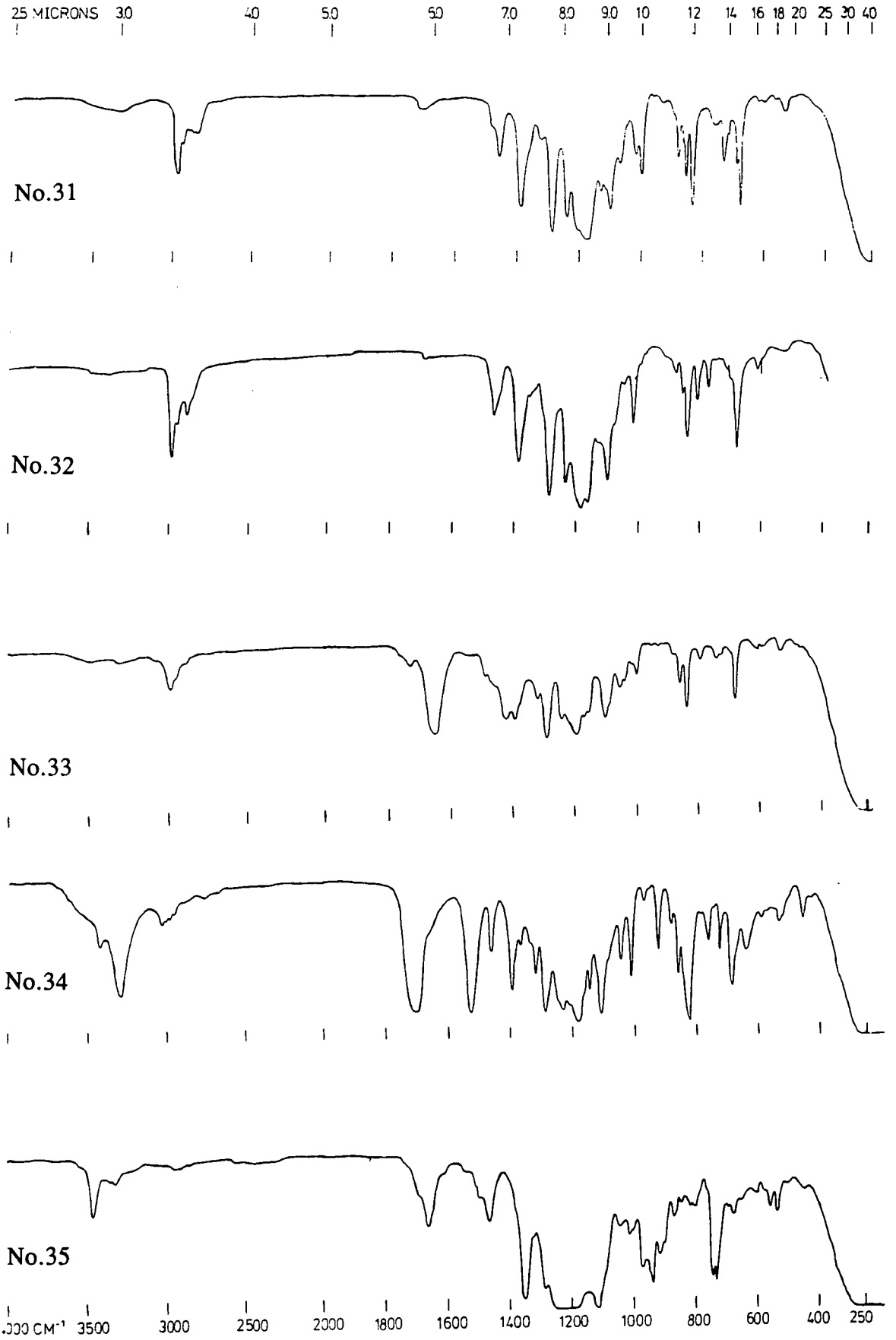
No.21
No.22
No.23
No.24
No.25
4000 CM⁻¹ 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250


25 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 18 20 25 30 40
No.26
No.27
No.28
No.29
No.30
4000 CM⁻¹ 3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250


25 MICRONS 3.0 4.0 5.0 6.0 7.0 8.0 9.0 10 12 14 16 18 20 25 30 40
No.31
No.32
No.33
No.34
No.35
3500 3000 2500 2000 1800 1600 1400 1200 1000 800 600 400 250

APPENDIX THREE

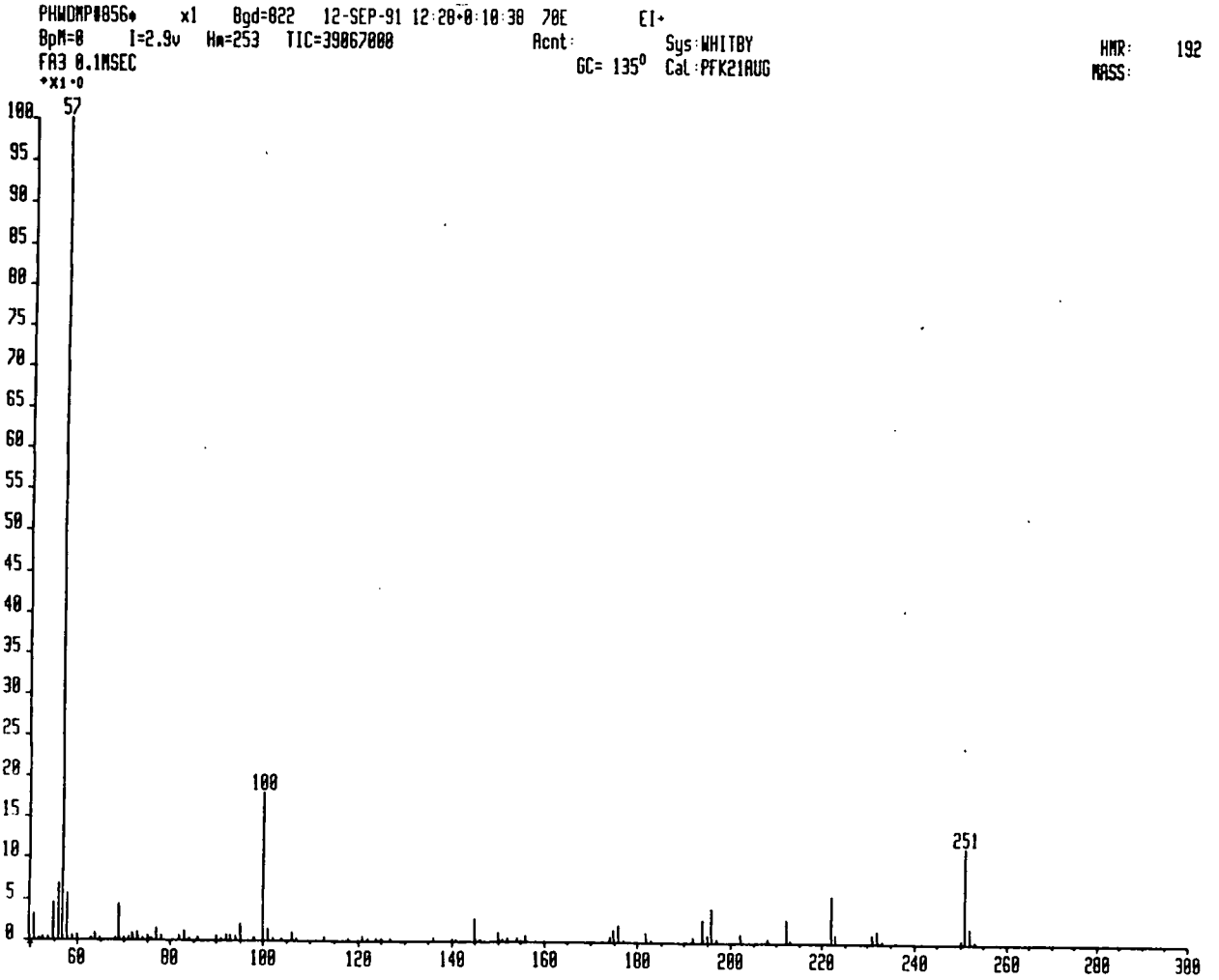
Mass Spectra

1. *N*-(2,2,3,4,4,4-hexafluorobutyl)-*N*-methylpropanamide (**23**)
2. *N*,*N*-bis-(2,2,3,4,4,4-hexafluorobutyl)propanamide (**24**)
3. *N*-(2,2,3,4,4,4-hexafluorobutyl)propanamide (**33**)
4. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)acetamide (**35**)
5. *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)acetamide (**37**)
6. 2-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylpiperidine (**39**)
7. 2,5-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylpiperidine (**40**)
8. *N*,*N*-bis-(2,2,3,4,4,4-hexafluorobutyl)trimethylsilylamine (**42**)
9. *N*,*N*-bis-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)trimethylsilylamine (**44**)
10. *N*-(2,3,3,3-tetrafluoropropanoyl)morpholine (**48**)
11. 3-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylmorpholine (**56**)
12. 3,5-bis-(1,1,2,3,3,3-hexafluoropropyl)-*N*-trimethylsilylmorpholine (**57**)
13. 4-(1,1,2,3,3,3-hexafluoropropyl)-2-imidazolidinone (**59**)
14. *N*-(2,2,3,4,4,4-hexafluorobutyl)-*N'*-methylurea (**66**)
15. *N*,*N'*-bis-(2,2,3,4,4,4-hexafluorobutyl)urea (**67**)
16. *N*-(3-chloro-2,3,3-trifluoropropyl)piperidine (**75**)
17. 2-(2-chloro-1,2,2-trifluoroethyl)-*N*-(3-chloro-2,2,3-trifluoropropyl)piperidine (**76**)
18. 2-(2-chloro-1,2,2-trifluoroethyl)-*N*-trimethylsilylpiperidine (**78**)
19. *N*-(3-chloro-2,3,3,-trifluoropropyl)-*N*-methyl(trimethylsilyl)amine (**79**)
20. *N*-(3-chloro-2,3,3-trifluoro-1-methylpropyl)-*N*-ethyl(trimethylsilyl)amine (**80**)
21. 3-(2-chloro-1,2,2-trifluoroethyl)-*N*-trimethylsilylmorpholine (**81**)
22. *N*-[(1,2,2,3,3,4-hexafluorocyclobutyl)-methyl]acetamide (**82**)
23. *N*-[(1,2,2,3,3,4,4,5-octafluorocyclopentyl)-methyl]acetamide (**83**)
24. *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)ethyl]acetamide (**84**)
25. *N*-[1-(1,2,2,3,3,4,4,5-octafluorocyclopentyl)ethyl]acetamide (**85**)
26. *N*-[1-(1,2,2,3,3,4-hexafluorocyclobutyl)propyl]acetamide (**86**)

27. *N*-(trifluorocyclobut-1-en-4-onyl)piperidine (**88**)
28. *N*-(heptafluorocyclopent-1-enyl)piperidine (**89**)
29. 1-(*N*,*N*-dimethylamino)-pentafluorocyclopent-1-en-5-one (**91**)
30. 1-(*N*,*N*-diethylamino)-pentafluorocyclobut-1-ene (**92**)
31. 1-(*N*,*N*-diethylamino)-heptafluorocyclopent-1-ene (**93**)
32. (3,3-difluorocyclobutan-2,4-onyl)morpholinium betaine (**94**)
33. *N*-(pentafluorocyclobut-1-enyl)morpholine (**95**)
34. *N*-(trifluorocyclobut-1-en-4-onyl)morpholine (**96**)
35. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-ethylamine (**97**)
36. *N*-(1-ethyl-2,2,3,4,4,4-hexafluorobutyl)-*N*-ethylamine (**98**)
37. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl-*N*-ethylacetamide (**101**)
38. *N*-(2,2,3,4,4,4-hexafluoro-1-methylbutyl)-*N*-1,2,2-trichloroethenylamine (**103**)
39. 2,4,5-tris-(heptafluoropropyl)-4,5-dihydroimidazole (**116**)

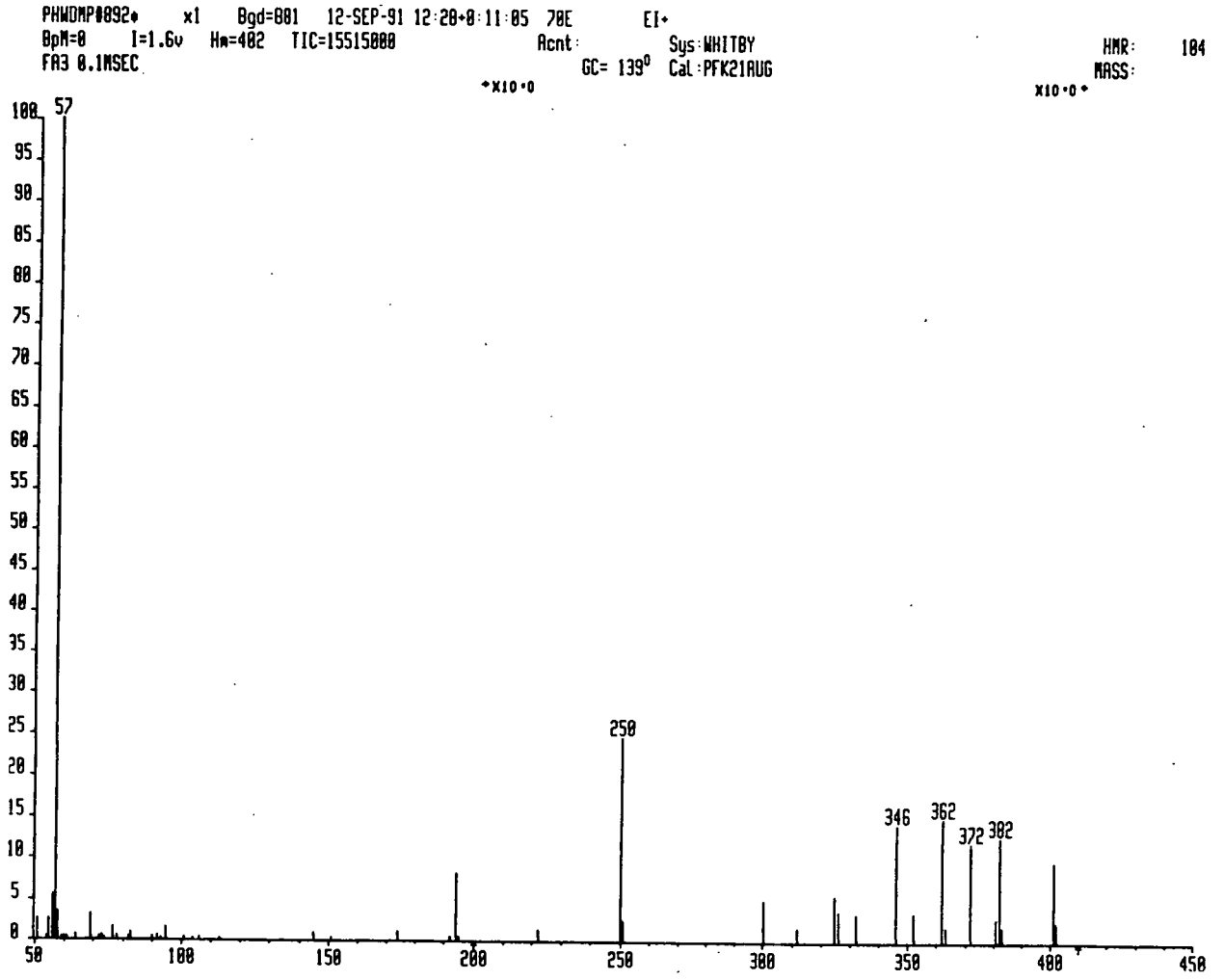
All mass spectra were recorded in the electron ionisation mode (EI^+) except for spectra 10 and 32 which were recorded in the chemical ionisation mode (CI^+).

Mass Spectrum No.1 M.W. 251



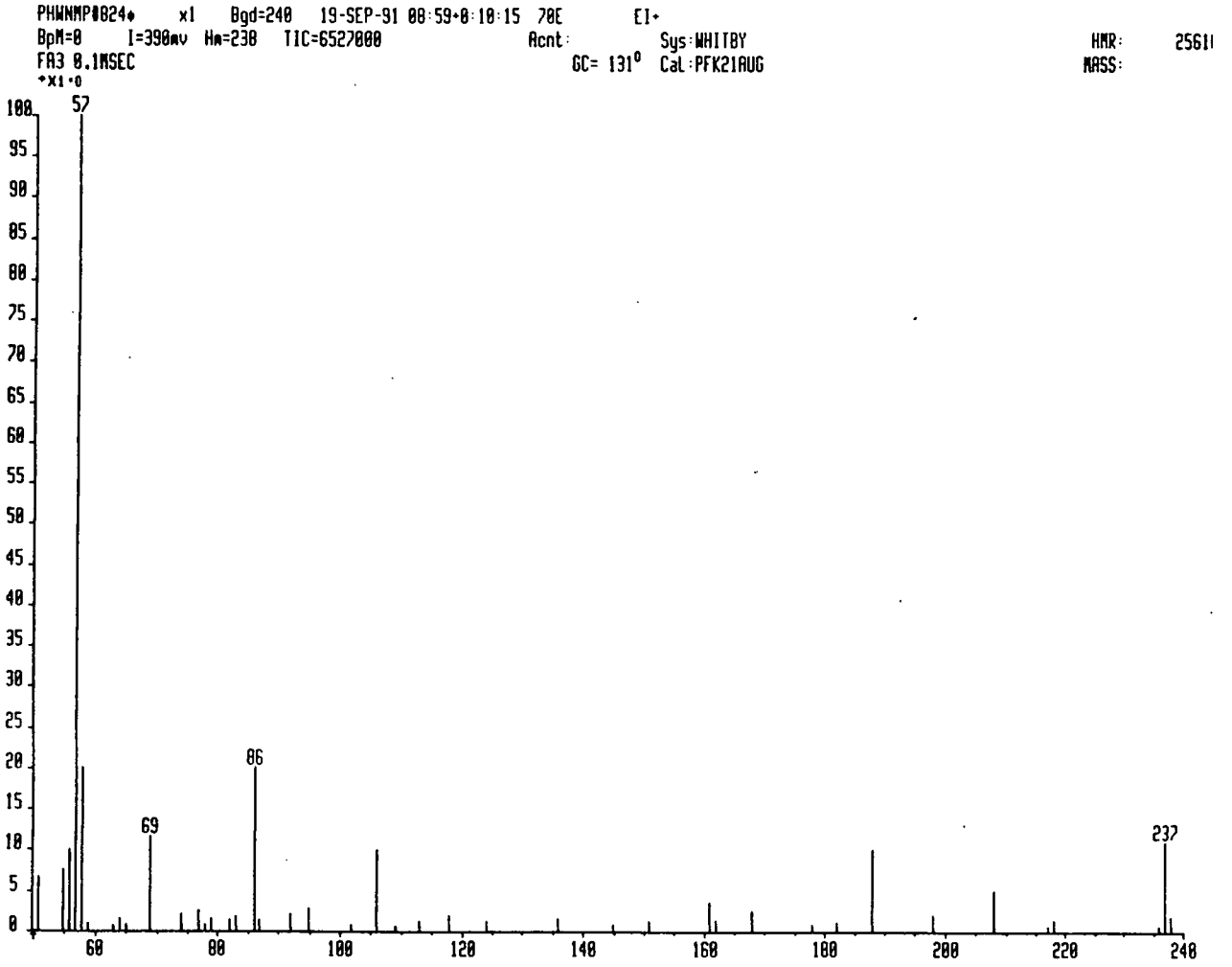
Mass	% Base
55.83	6.67
56.85	100.00
57.86	5.54
100.02	17.85
221.97	5.57
250.02	0.24
251.02	11.33
252.03	1.69
253.05	0.11

Mass Spectrum No.2 M.W. 401



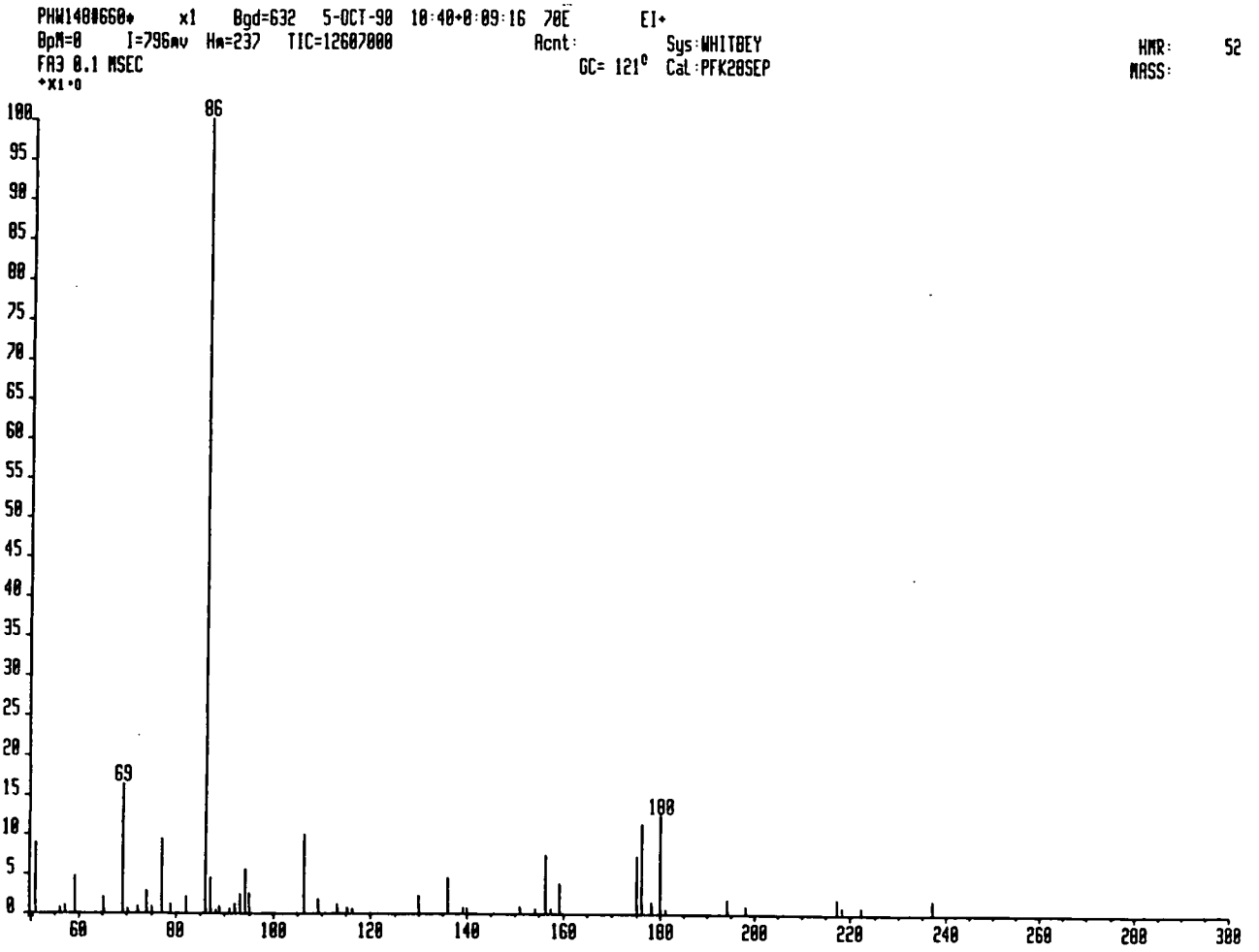
Mass	% Base
55.84	5.47
56.85	100.00
194.00	8.12
250.04	2.45
251.04	0.25
300.07	0.50
312.02	0.16
325.07	0.56
326.07	0.36
332.05	0.34
346.07	1.41
352.04	0.35
362.08	1.50
363.07	0.17
372.06	1.20
381.12	0.28
382.11	1.28
383.16	0.18
401.11	0.97
402.14	0.23

Mass Spectrum No.3 M.W. 237



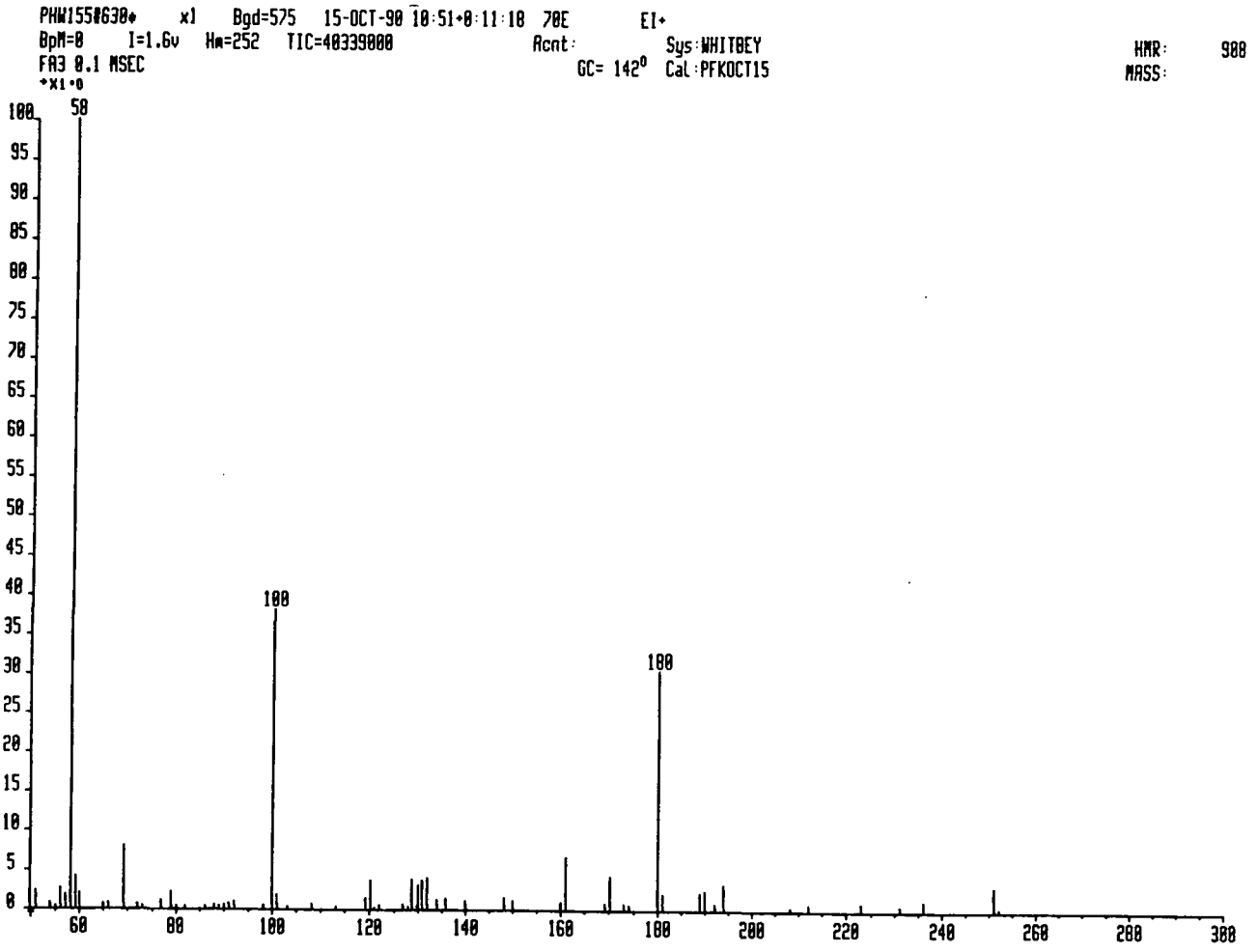
Mass	% Base		
50.77	6.64	216.97	0.62
54.81	7.38	217.98	1.29
55.82	10.00	235.96	0.62
56.83	100.00	236.97	10.89
57.84	19.99	238.00	1.72
58.85	0.86		
62.85	0.59		
63.87	1.48		
64.89	0.70		
68.89	11.48		
73.92	2.11		
76.94	2.50		
77.94	0.74		
78.95	1.52		
81.95	1.25		
82.93	1.68		
85.99	19.99		
86.97	1.25		
91.94	2.03		
94.93	2.81		
101.95	0.66		
105.93	10.00		
108.96	0.62		
112.92	1.13		
117.94	1.87		
123.92	1.21		
135.97	1.52		
144.92	0.74		
150.93	1.17		
160.94	3.44		
161.94	1.25		
167.93	2.50		
177.96	0.74		
181.98	0.98		
187.92	10.00		
197.97	1.87		
207.94	5.00		

Mass Spectrum No.4 M.W. 237



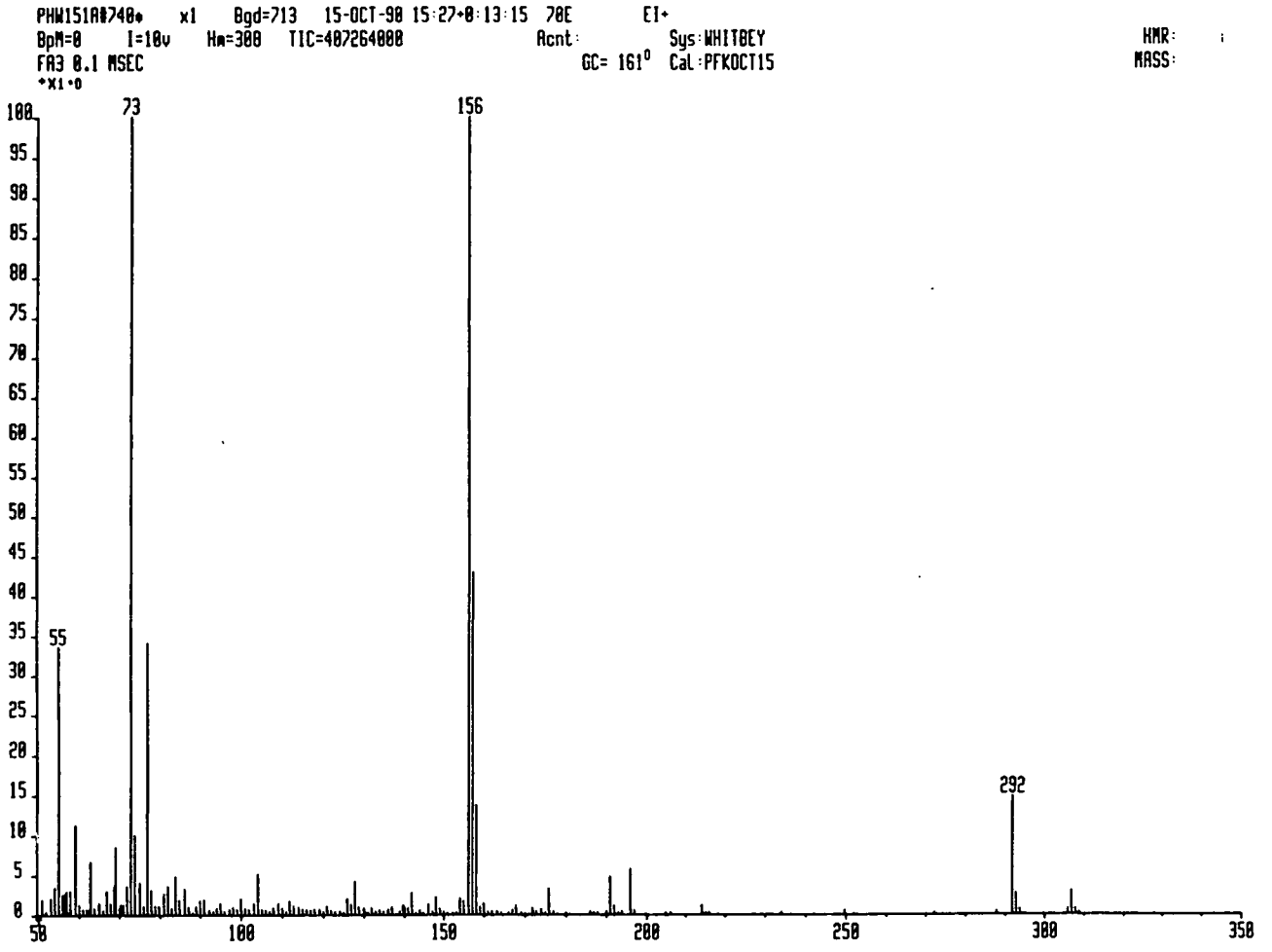
Mass	% Base		
51.06	8.81	178.23	1.38
56.07	0.54	180.20	12.34
57.13	0.94	181.21	0.50
59.10	4.56	194.23	1.61
65.10	1.95	198.26	0.98
69.07	16.28	217.26	1.88
70.11	0.38	218.27	0.79
72.12	0.73	222.25	0.69
74.12	2.72	237.28	1.69
75.09	0.38		
75.13	0.79		
77.10	9.27		
79.11	1.00		
82.08	1.92		
86.15	100.00		
87.15	4.46		
88.16	0.34		
89.11	0.73		
91.14	0.48		
92.12	1.07		
93.14	2.22		
94.14	5.46		
95.11	2.47		
106.15	9.87		
109.14	1.65		
113.12	1.11		
115.15	0.54		
116.15	0.44		
130.17	2.13		
136.19	4.41		
139.17	0.56		
140.15	0.61		
151.15	0.82		
154.17	0.46		
156.19	7.26		
157.20	0.46		
159.18	3.62		
175.22	7.09		
176.22	11.15		

Mass Spectrum No.5 M.W. 251



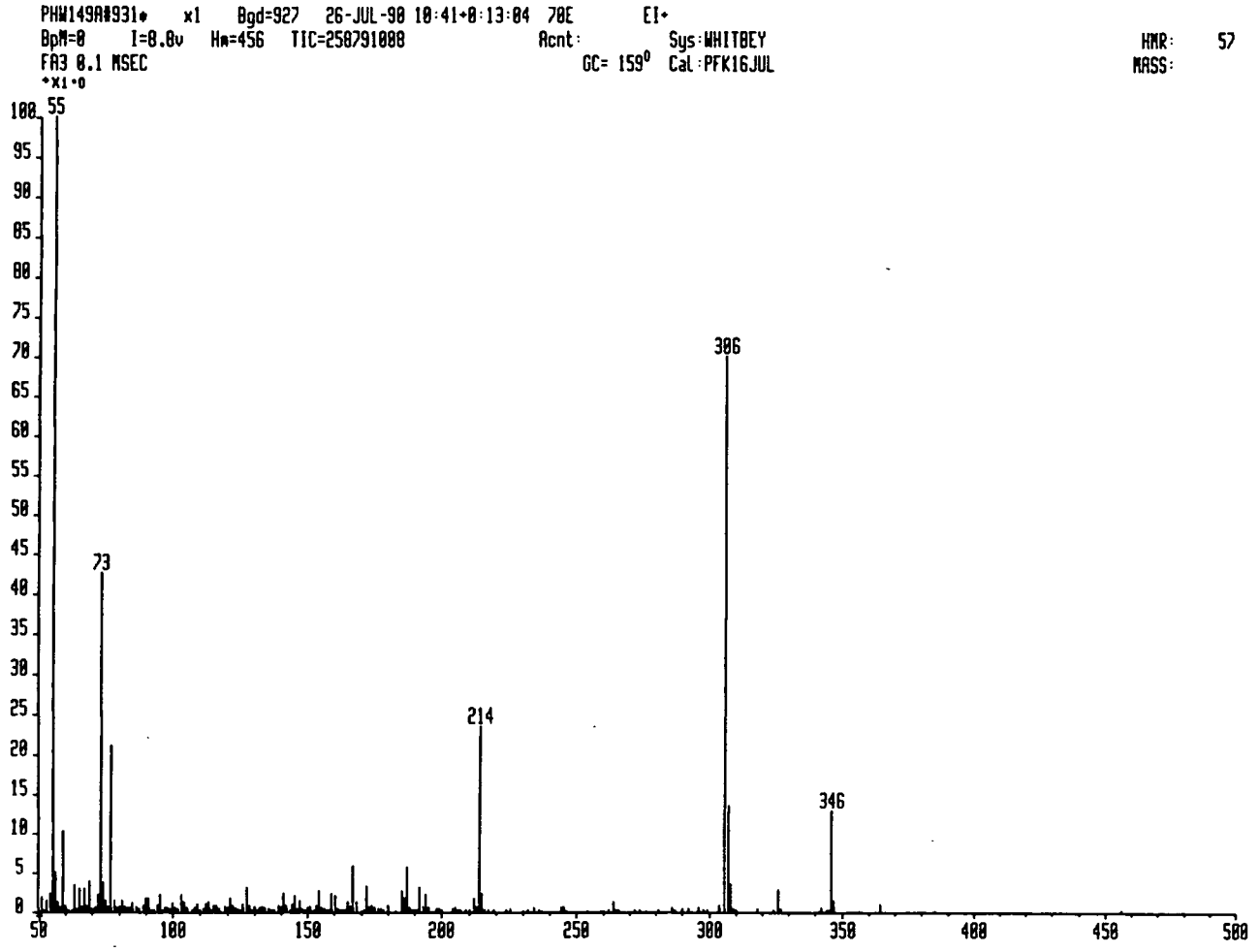
Mass	% Base	
41.04	5.57	
42.02	3.63	
43.02	100.00	
43.99	6.94	F
44.03	4.34	F
47.03	5.67	
51.02	2.02	
56.06	2.32	
57.07	1.68	
58.08	88.73	
59.07	3.58	
60.06	1.78	
69.01	6.94	
79.03	1.85	
100.08	33.75	
101.09	1.59	
119.01	1.15	
120.07	3.22	
128.92	3.34	
130.05	2.74	
130.93	3.18	
131.92	3.53	
133.92	1.11	
135.92	1.19	
148.04	1.30	
161.05	5.93	
170.07	3.82	
180.04	27.02	
181.03	1.72	
189.08	1.89	
190.09	2.20	
194.06	2.78	
236.07	1.06	
251.09	2.64	
252.12	0.28	

Mass Spectrum No.6 M.W. 307



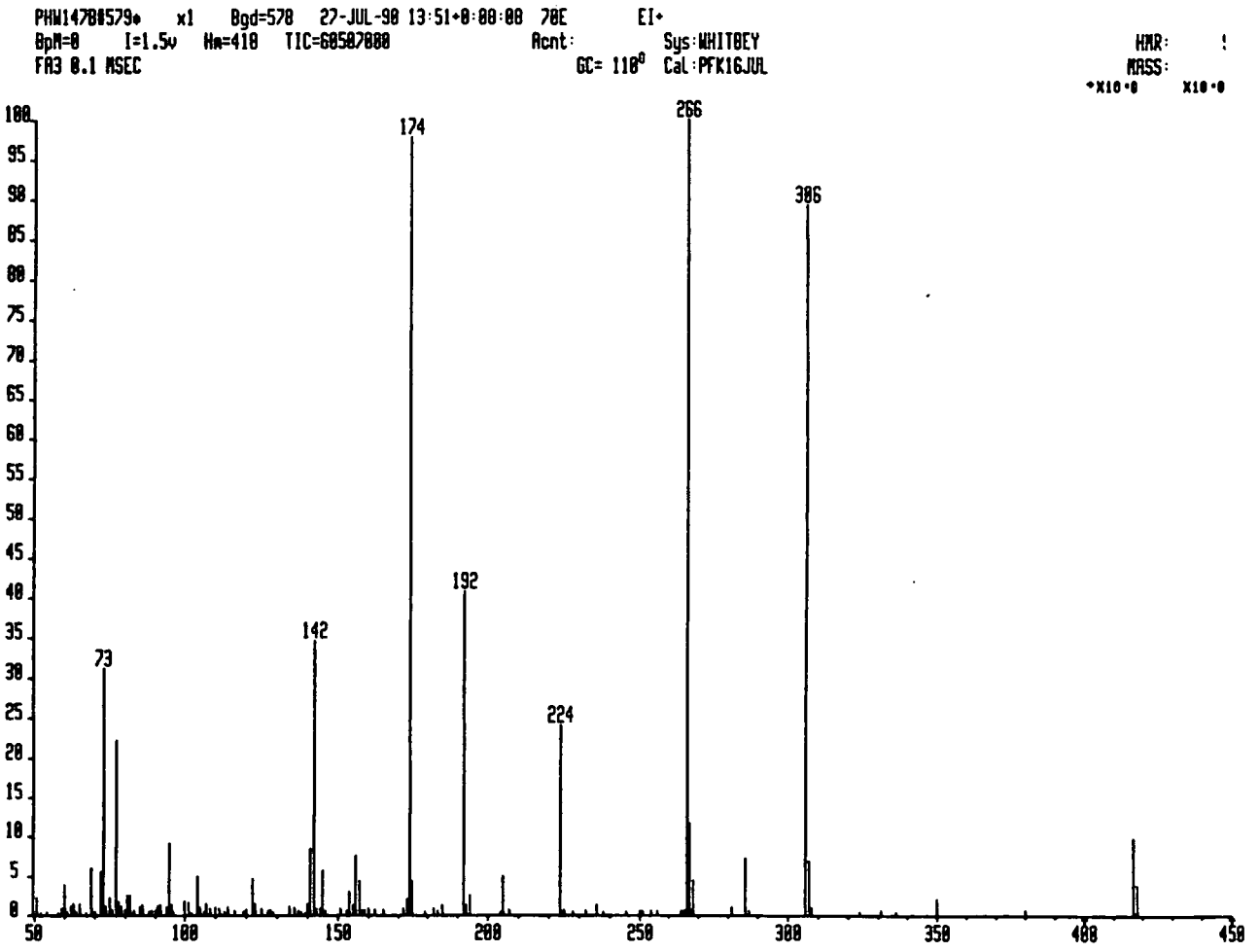
Mass	% Base		Mass	% Base	
41.01	20.61		89.96	1.64	
42.01	6.74	F	90.98	1.86	
42.97	8.55	F	94.96	1.42	F
43.98	5.06		100.00	1.95	
44.99	21.14		102.98	1.42	
45.99	1.27		103.97	5.02	
46.95	2.35	F	108.97	1.32	
47.00	1.37	F	111.99	1.66	
48.96	4.41		112.96	1.11	
50.98	1.84		120.96	1.03	
53.00	1.99		126.00	1.95	
54.01	3.27		126.97	1.23	
55.02	33.48		128.00	4.11	
56.03	2.35	F	141.95	2.70	
56.50	2.62		145.99	1.17	
56.99	2.83		147.96	2.05	
57.99	2.95		153.97	1.90	F
59.00	11.05		154.85	1.60	F
60.00	1.29		156.05	100.00	FO
62.97	6.49		157.03	42.87	F
64.99	1.31		158.03	13.56	
67.01	2.87		159.99	1.30	
68.01	1.32		167.94	1.11	
68.96	3.48	F	175.96	3.16	
69.03	8.38	F	190.97	4.75	
70.51	1.15		191.93	1.05	
70.99	1.18		195.95	5.66	
72.00	3.44		213.93	1.02	
73.00	100.00	O	291.91	14.66	
74.00	9.90		292.92	2.57	
74.99	3.99		305.94	0.59	
76.98	34.01		306.94	2.84	
77.98	2.97		307.94	0.56	
78.98	1.12		308.94	0.12	
80.94	2.53	F			
82.00	3.54				
84.02	4.77				
84.99	1.80				
85.99	3.26				

Mass Spectrum No.7 M.W. 457



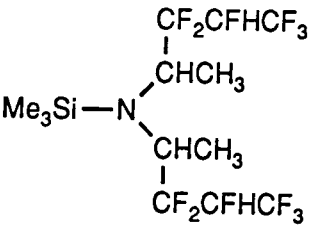
Mass	% Base				
55.07	100.00	245.08	0.64	345.08	0.16
56.08	5.04	246.07	0.05	346.06	12.92
59.05	10.19	254.02	0.05	347.05	1.37
73.06	42.58	259.07	0.05	356.09	0.06
77.04	21.06	260.01	0.07	364.06	0.87
167.06	5.72	262.03	0.16	385.13	0.06
187.07	5.67	264.07	1.18	456.12	0.22
200.05	0.20	265.08	0.13		
202.00	0.03	266.03	0.09		
204.08	0.37	272.11	0.11		
205.05	0.45	274.02	0.13		
206.07	0.08	276.03	0.07		
207.02	0.09	281.05	0.13		
209.00	0.11	286.04	0.48		
210.02	0.18	287.13	0.21		
212.05	1.64	288.12	0.03		
213.06	0.63	290.06	0.35		
213.40	0.08	292.03	0.33		
214.06	23.52	296.07	0.49		
215.08	2.21	297.56	0.03		
216.00	0.12	298.03	0.17		
217.05	0.10	299.06	0.13		
218.07	0.04	300.03	0.05		
219.07	0.12	304.01	0.74		
220.07	0.05	306.09	70.16 F		
224.08	0.12	307.10	13.41 F		
225.09	0.25	308.12	3.54 F		
226.07	0.04	308.59	0.07		
227.10	0.03	308.80	0.13		
230.06	0.06	309.13	0.25		
232.07	0.15	310.18	0.11		
233.07	0.05	318.03	0.28		
233.75	0.04	324.07	0.19		
234.07	0.40	326.05	2.80		
235.09	0.05	327.06	0.31		
236.03	0.09	340.98	0.06		
237.08	0.07	342.01	0.42		
244.07	0.50	344.07	0.11		

Mass Spectrum No.8 M.W. 417



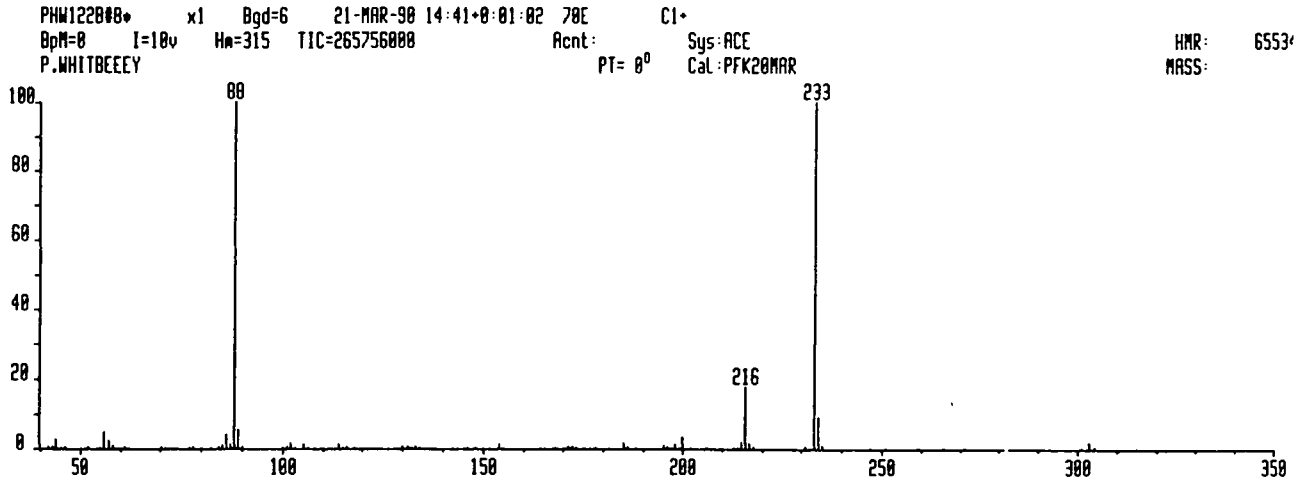
Mass	% Base
69.00	5.96
72.04	5.44
73.05	31.00
77.02	22.11
95.01	8.99
141.01	8.27
142.02	34.54
145.00	5.65
156.03	7.50
174.01	97.68
192.00	40.73
224.00	24.04
266.03	100.00
267.04	11.59
285.97	7.17
305.96	89.42
306.97	6.80
417.01	0.97
418.02	0.38

Mass Spectrum No.9 M.W. 445



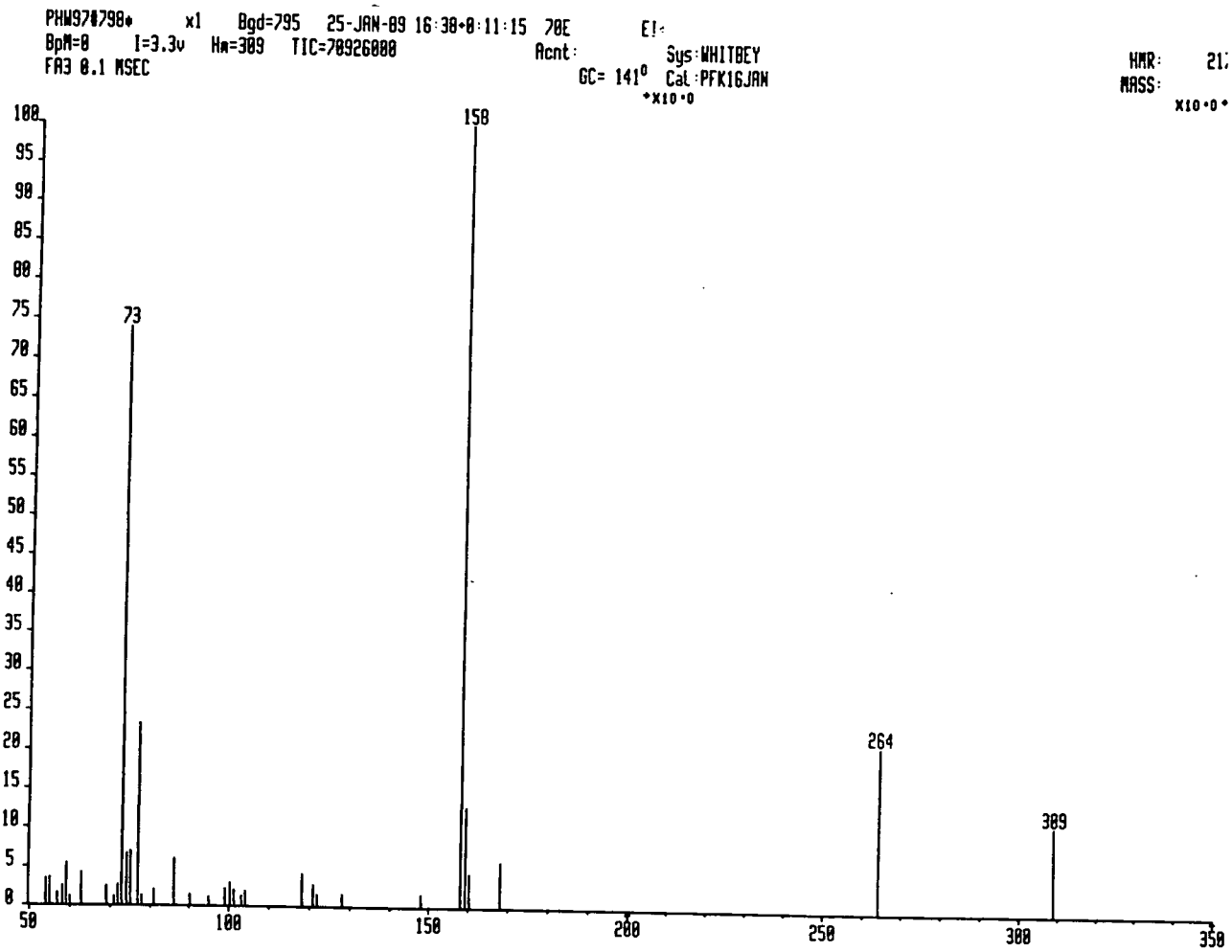
Mass	% Base				
51.00	7.19	121.03	1.99	336.06	0.57
53.02	0.45	122.03	0.92	338.04	2.51
54.02	2.95	127.02	0.49	351.06	0.78
55.02	1.20	128.01	3.23	352.06	1.71
56.03	1.38	132.06	2.63	445.16	0.94
57.01	1.88	136.04	7.38		
58.02	2.11	139.02	3.72		
59.02	9.39	139.98	0.88		
60.03	0.92	141.03	0.78		
62.00	0.99	142.08	1.08		
63.00	8.95	143.09	0.41		
64.00	0.73	144.07	0.57		
65.01	6.00	148.04	0.57		
66.02	0.82	150.99	1.17		
68.04	2.01	154.02	1.17		
68.99	7.44 F	156.03	20.70		
69.06	3.98 F	157.03	1.08		
70.05	2.61	159.02	9.43		
71.03	2.31	160.02	0.95		
72.03	4.85	163.07	0.46		
73.04	100.00 0	164.05	0.66		
74.04	10.71	168.04	2.63		
75.03	4.08	172.02	2.70		
76.01	2.23	173.03	0.84		
77.01	60.05	174.03	2.44		
78.02	4.36	176.05	2.91		
79.01	1.64	180.04	0.95		
80.99	4.33	181.06	0.47		
82.02	0.84	182.05	1.51		
85.03	0.49	183.06	0.64		
86.03	7.51	186.04	1.38		
87.04	1.08	188.04	0.83		
89.01	3.30	194.06	0.56		
90.00	2.67	200.06	3.28		
91.02	4.75	201.05	1.26		
92.02	2.13	202.06	100.00 0		
93.00	0.43	203.07	10.61		
95.00	7.97	204.04	1.81		
96.00	0.64	206.04	1.07		
97.03	0.98	218.04	2.27		
98.03	0.43	220.05	2.46		
100.05	23.77	224.04	0.52		
101.06	8.39	232.06	0.50		
102.05	0.83	233.07	0.84		
103.04	0.61	250.04	0.43		
104.03	4.34	252.05	12.76		
105.03	0.49	253.05	1.19		
106.04	0.62	260.09	0.85		
108.00	0.91	278.12	0.52		
109.02	7.27	288.06	0.40		
110.02	0.78	292.10	1.15		
112.05	0.67	294.09	84.78 F		
113.01	2.73	295.10	12.95 F		
114.07	4.55	296.10	3.17 F		
115.05	2.15	297.10	0.47		
116.04	4.69	306.07	0.58		
117.05	0.51	314.04	1.21		
118.05	3.31	332.06	0.62		
119.03	1.20	334.04	60.53 F		
120.05	1.02	335.06	6.60 F		

Mass Spectrum No.10 M.W. 215



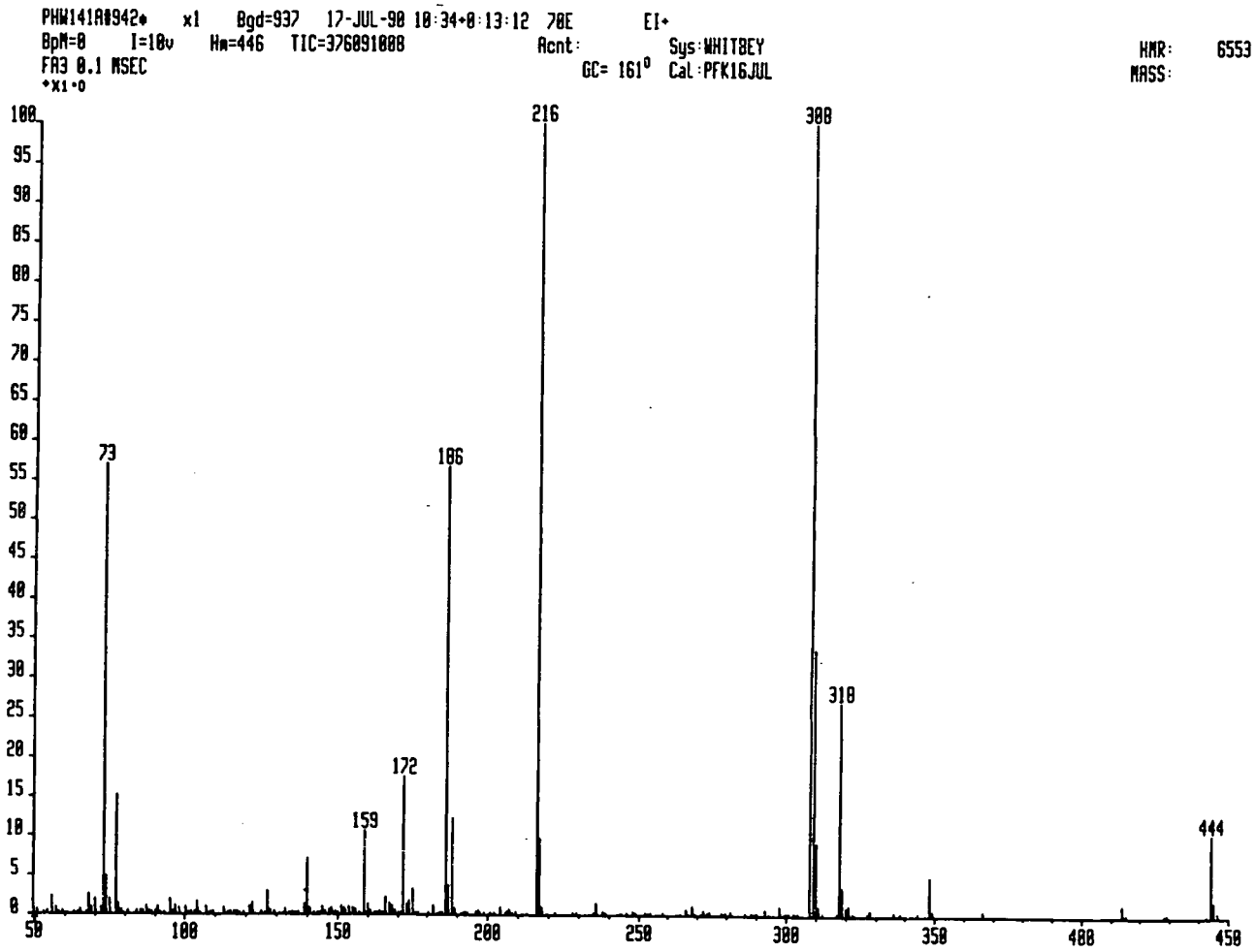
Mass	% Base	
21.92	9.75	
22.00	17.67	
22.06	17.11	
30.03	0.87	
35.06	85.76	
36.06	0.63	
42.04	0.39	
44.05	2.34	
56.05	4.54	
57.06	2.08	
58.07	0.71	
78.06	0.52	
85.05	0.84	
86.06	3.87	
87.07	1.09	
88.07	100.00	0
89.08	5.22	
90.07	0.36	
101.06	0.36	
102.09	1.48	
105.09	1.08	
114.05	0.95	
116.06	0.45	
131.07	0.49	
133.08	0.37	
154.03	0.96	
171.06	0.42	
185.01	1.31	
195.01	0.86	
196.02	0.33	
198.03	1.10	
200.00	3.26	
215.04	1.89	
216.02	17.67	
217.02	1.40	
233.06	100.00	0
234.05	9.10	
235.05	0.72	
303.07	1.72	

Mass Spectrum No.11 M.W. 309



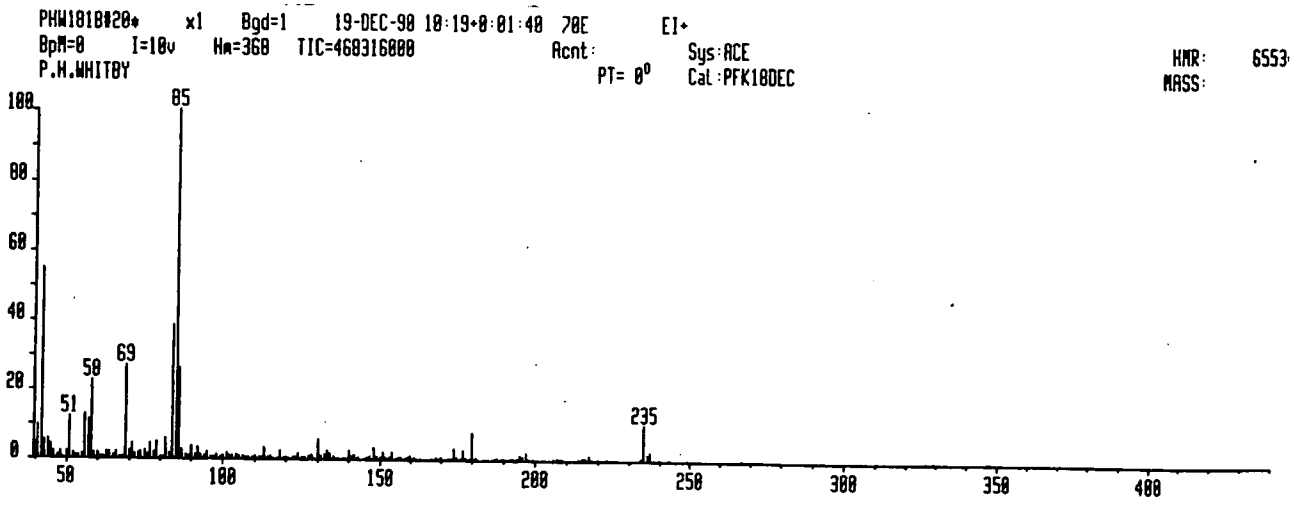
Mass	% Base
59.05	5.24
73.09	73.76
74.09	6.51
75.07	6.88
77.07	23.21
86.10	5.85
158.19	100.00
159.19	12.66
168.15	5.82
200.16	0.13
206.17	0.70
208.22	0.13
216.18	0.42
217.18	0.16
236.18	0.08
264.20	2.12
265.20	0.31
278.24	0.11
281.18	0.10
294.23	0.88
309.25	1.12

Mass Spectrum No.12 M.W. 459



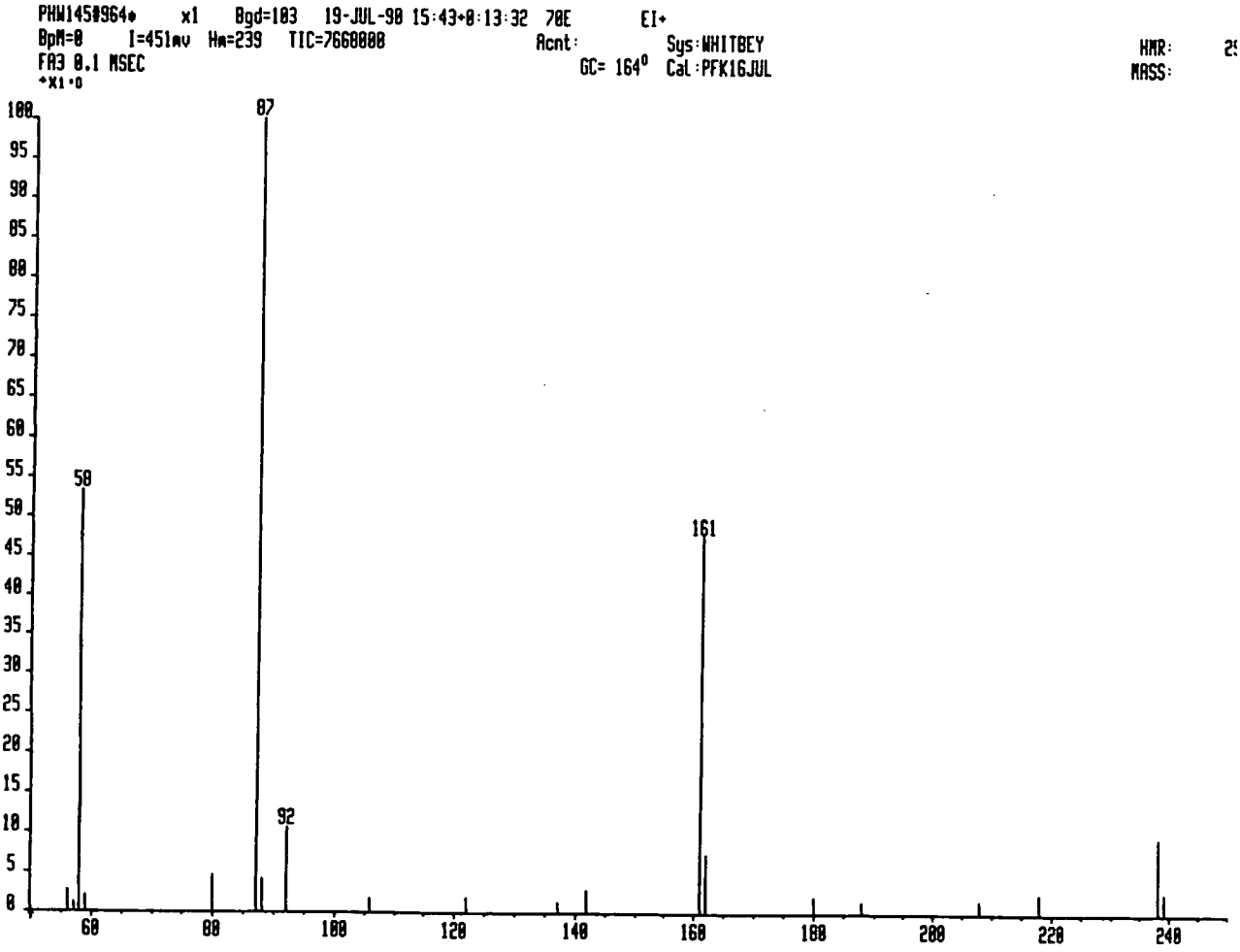
Mass	% Base		
56.06	2.18	348.12	4.86
68.06	2.36	414.14	1.41
70.04	1.77	415.16	0.09
73.06	56.79	428.17	0.16
74.06	4.75	429.17	0.13
75.05	1.82	442.31	0.05
77.04	15.00	444.16	10.26
78.04	1.24	445.16	1.86
95.03	1.79	446.18	0.53
97.04	1.12		
104.06	1.48		
122.05	1.40		
127.04	2.87		
139.05	1.22		
140.04	6.94		
151.35	1.03 F		
159.06	10.44		
160.04	1.27 F		
166.06	2.10		
167.07	1.38		
168.08	1.04		
172.05	17.48		
173.06	1.22		
174.07	1.72		
175.05	3.18		
182.06	1.05		
186.07	56.70		
187.08	3.69		
188.08	12.09		
216.10	100.00 0		
217.09	9.56		
236.08	1.42		
298.08	1.03		
308.17	100.00 F0		
309.13	33.66 F		
310.13	9.27		
318.10	26.97		
319.11	3.45		
321.11	1.25		

Mass Spectrum No.13 M.W. 236



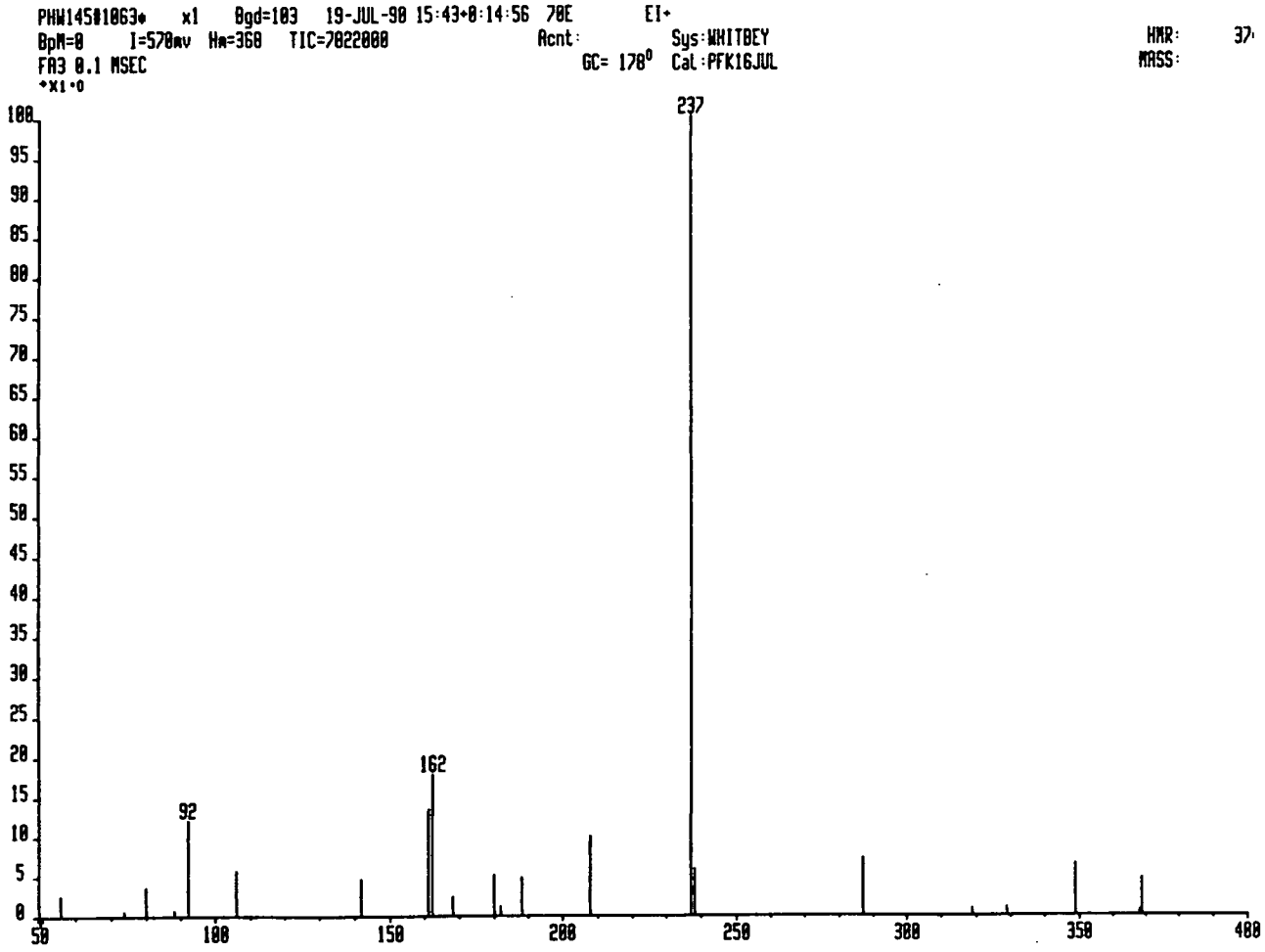
Mass	% Base				
20.01	2.40	89.01	0.57	195.98	0.78
26.01	1.49	89.99	3.54	196.96	1.96
27.01	5.66	91.00	0.92	215.97	0.36
28.02	82.79	92.00	3.21	216.97	1.02
29.02	33.20	92.97	0.92	233.95	0.47
30.03	85.39	93.97	0.58	234.95	10.16
30.99	5.13 F	94.99	1.75	235.96	1.28
31.02	2.16 F	97.03	0.33	236.96	1.97
32.00	0.81	98.00	0.98		
33.01	1.56	99.00	0.39		
35.97	0.39	99.97	0.79		
37.00	0.39	100.99	1.27		
38.00	0.78	101.98	0.85		
39.01	1.73	103.00	0.63		
40.01	4.16	104.00	0.91		
41.02	9.38	104.99	0.82		
42.02	54.76	105.98	0.85		
43.02	5.14	106.99	0.40		
44.00	5.49	107.98	0.40		
45.01	3.96	109.98	0.78		
46.00	1.90	111.05	0.39		
46.99	0.60	112.96	3.15		
48.01	1.66	113.98	0.33		
49.98	1.65	114.99	0.82		
50.99	11.72	117.97	2.01		
52.00	1.32	118.99	0.39		
53.01	0.78	119.97	0.46		
54.01	0.78	121.98	0.40		
55.02	1.02	123.97	1.36		
56.01	12.50	126.98	0.78		
57.02	10.94	127.97	1.17		
58.01	22.68	129.99	5.41		
59.02	1.56	130.96	0.86		
60.01	1.38	131.96	1.02		
61.01	0.41	132.98	2.02		
62.99	1.95	133.98	1.56		
63.99	1.75	134.99	0.64		
65.01	0.78	139.97	2.18		
66.00	1.95	140.97	0.66		
68.01	0.39	141.98	0.97		
68.98	26.68	145.98	0.32		
70.00	2.16	146.99	0.58		
71.03	4.30	147.97	3.20		
72.01	0.99	148.98	0.87		
73.02	1.38	149.97	0.39		
73.99	1.70	150.95	1.81		
74.99	2.13	152.97	0.39		
75.99	1.17	153.97	1.80		
76.99	4.30	156.97	0.39		
77.99	1.78	159.00	0.39		
79.00	4.54	159.97	0.74		
80.01	0.39	167.96	0.39		
81.01	0.39	169.97	0.39		
81.98	5.60	173.97	2.73		
83.00	1.59	174.96	0.40		
84.00	38.16	176.96	2.54		
85.04	100.00 O	179.96	7.42		
86.02	26.25	180.96	0.39		
87.02	2.54	187.95	0.39		
88.00	1.17	194.97	0.90		

Mass Spectrum No.14 M.W. 238



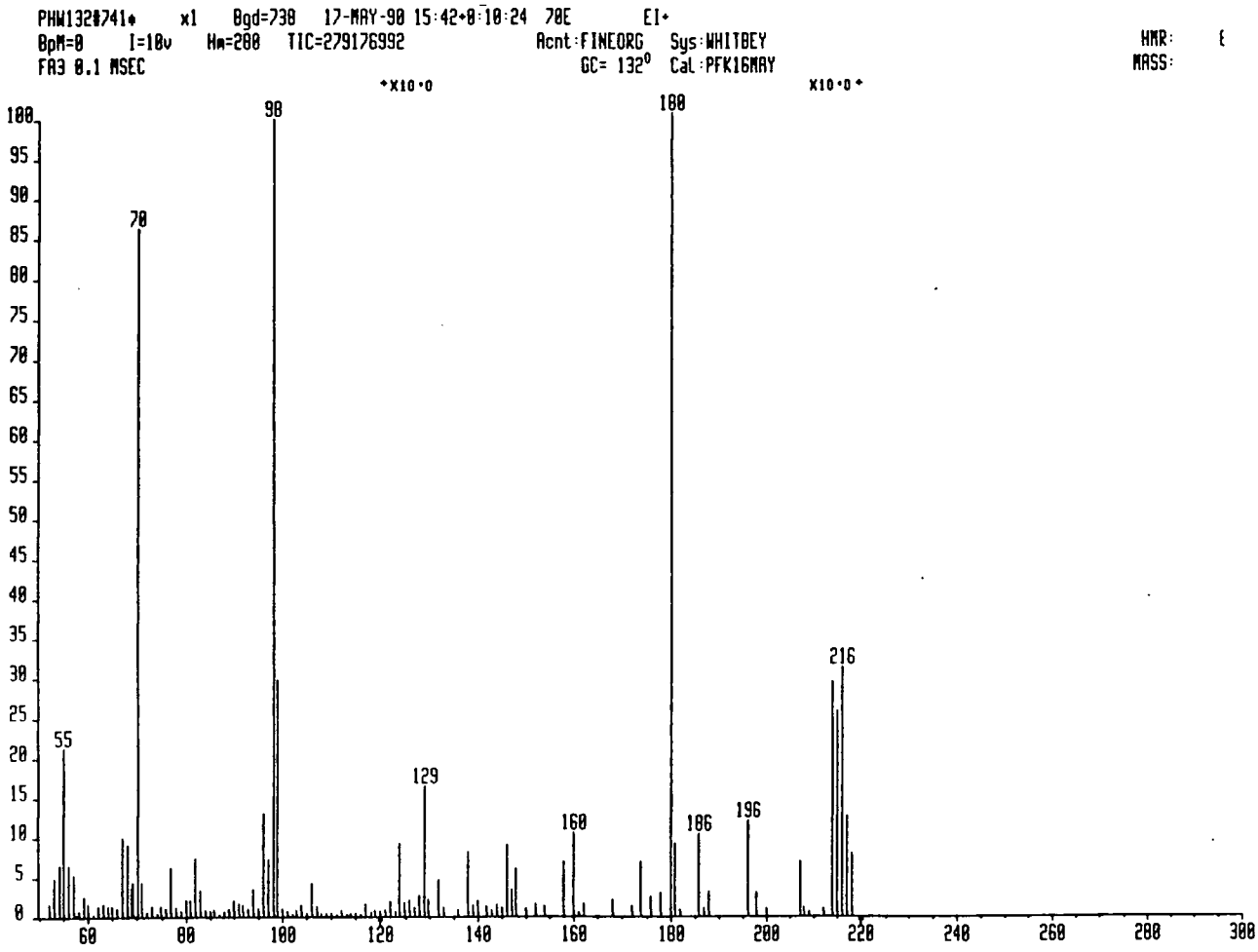
Mass	% Base
56.01	2.57
57.05	1.12
58.03	53.25
59.03	1.89
80.02	4.60
87.04	100.00
88.05	4.06
92.02	10.42
106.00	1.69
122.01	1.79
137.04	1.25
142.01	2.67
161.00	47.60
162.01	7.24
180.01	1.96
187.99	1.32
207.98	1.49
218.02	2.44
238.01	9.40
239.02	2.64

Mass Spectrum No.15 M.W. 388



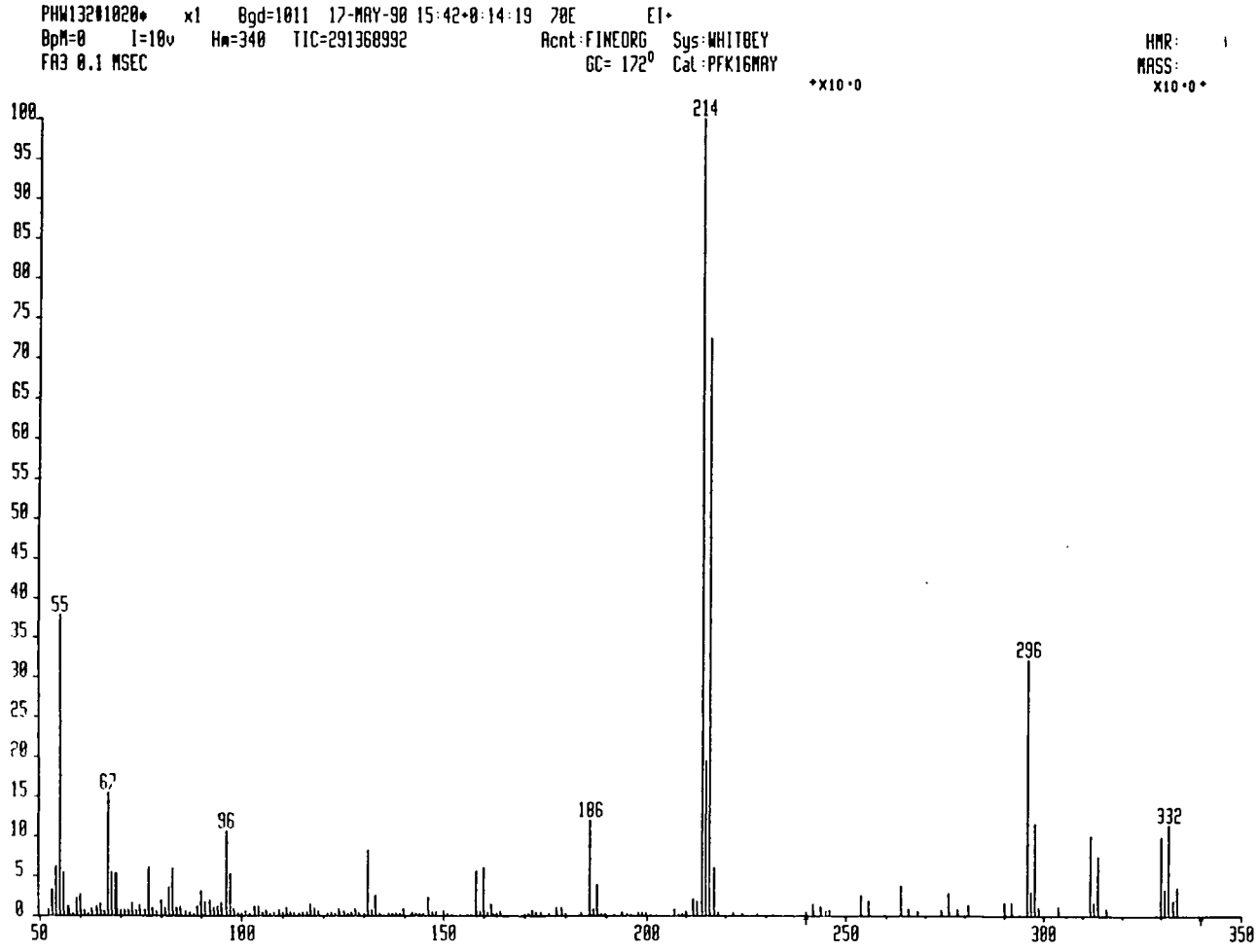
Mass	% Base
56.01	2.49
80.02	3.48
92.02	11.95
106.00	5.67
142.01	4.52
161.00	13.37
162.01	17.67
167.99	2.30
180.00	4.95
182.02	1.10
187.98	4.63
207.97	9.92
237.00	100.00
238.00	5.72
286.99	7.17
348.96	6.39
368.97	4.55

Mass Spectrum No.16 M.W. 215.5



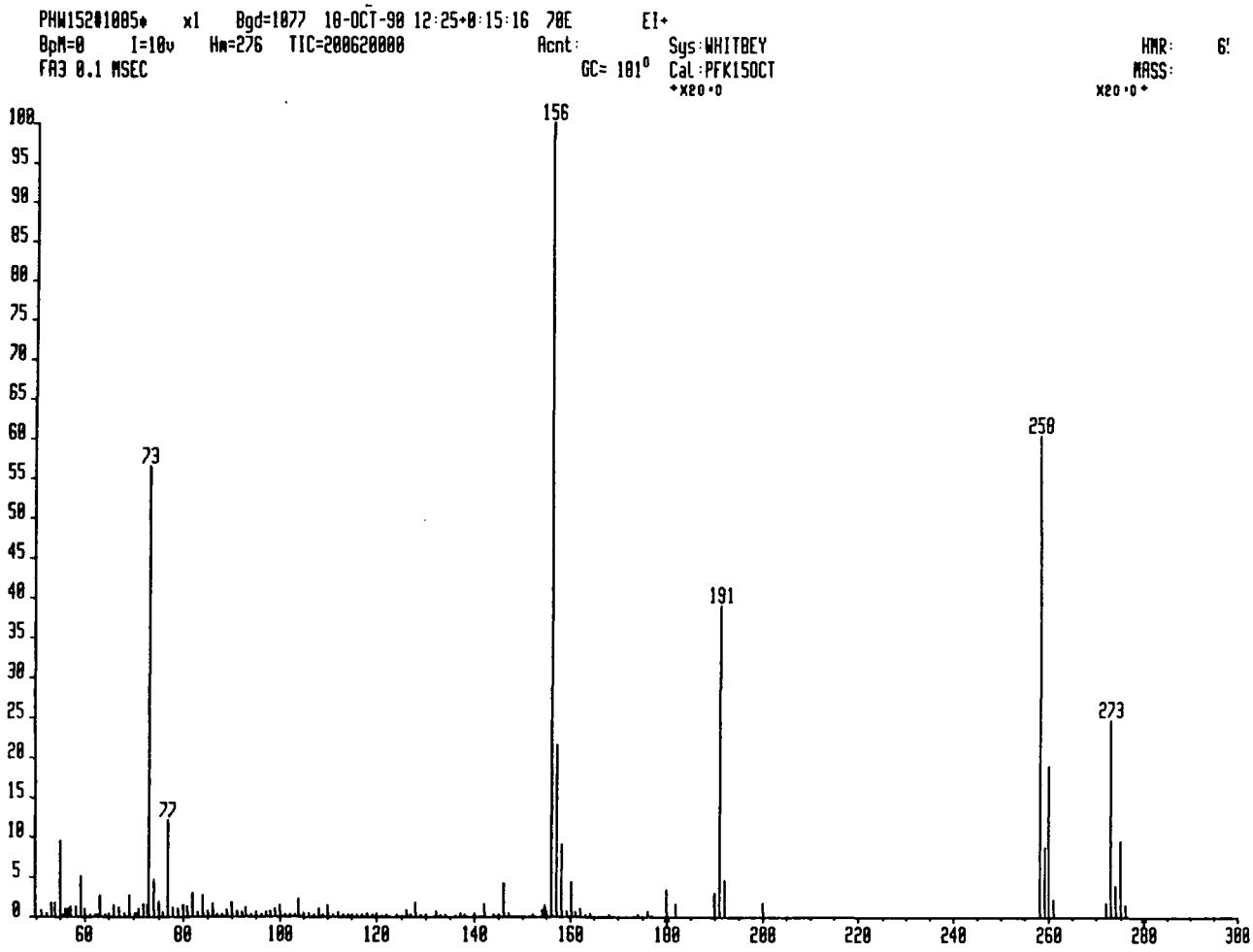
Mass	% Base	
54.07	6.43	
55.08	21.25	
56.08	6.37	
57.08	5.19	F
66.96	9.79	F
68.02	8.94	
70.03	86.21	
76.98	6.10	
82.02	7.20	F
96.03	12.90	
96.99	7.16	F
98.06	100.00	FO
99.04	29.69	
179.98	11.91	
206.94	0.69	
207.94	0.10	
208.96	0.05	
211.96	0.10	
212.97	0.05	
213.97	2.94	
214.97	2.57	
215.97	3.13	
216.97	1.26	
217.99	0.78	
280.97	0.04	

Mass Spectrum No.17 M.W. 332



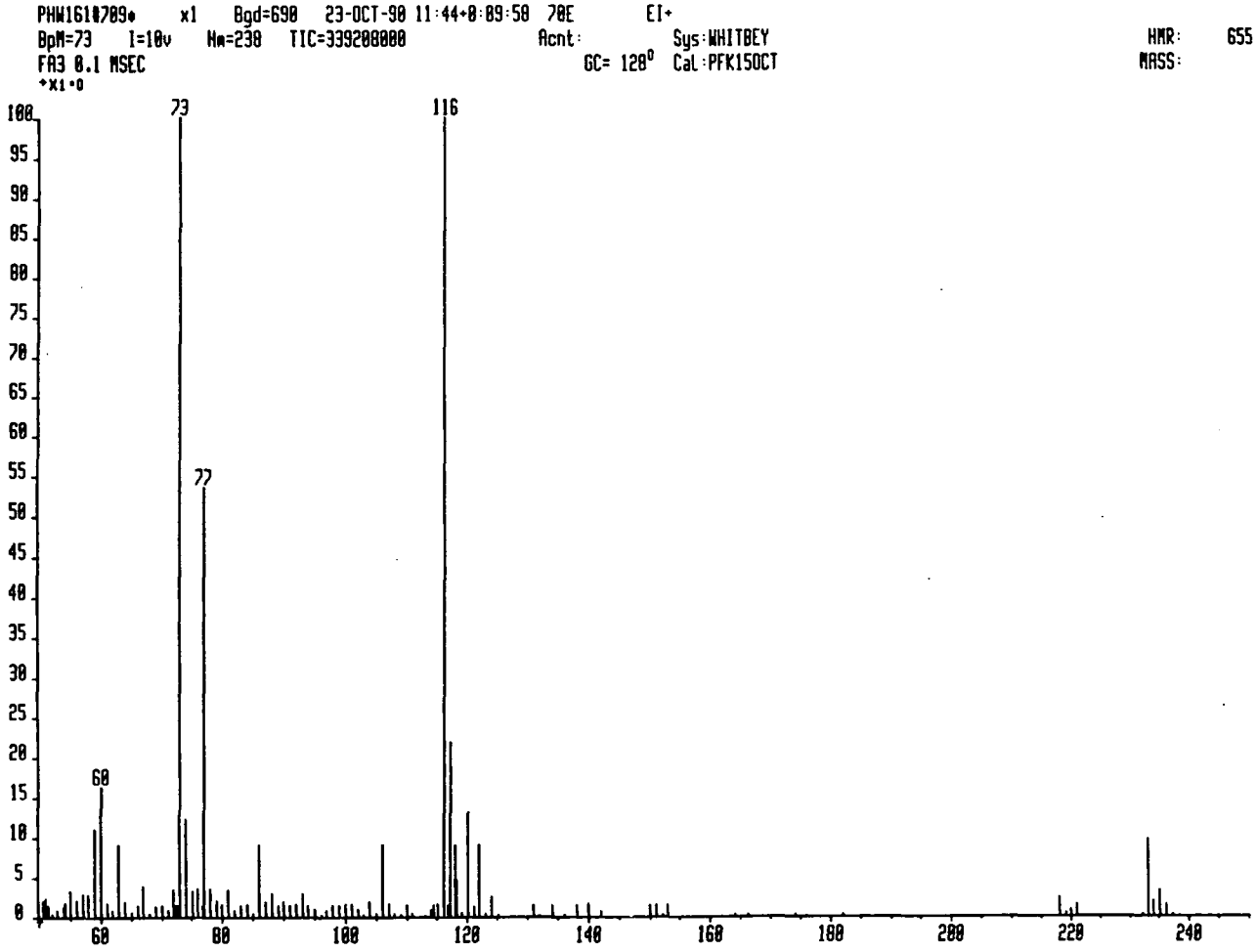
Mass	% Base			Mass	% Base	
54.08	6.11			241.94	0.14	
55.09	37.66			243.96	0.11	
56.09	5.30			244.95	0.05	
66.96	15.25	F		245.95	0.06	
67.04	6.57	F		248.93	0.04	
68.03	5.29			253.92	0.24	
68.95	5.10	F		255.91	0.18	
69.04	5.15	F		257.88	0.04	
76.98	5.95			259.93	0.03	
83.02	5.74			261.97	0.04	
96.03	10.45			263.95	0.37	
97.04	5.12			265.93	0.08	
130.89	7.96			267.91	0.05	
157.93	5.42			269.90	0.05	
159.95	5.90			273.89	0.06	
185.92	11.84			275.90	0.27	
200.94	0.06			277.91	0.08	
201.95	0.03			280.96	0.12	
206.95	0.72			281.94	0.04	
207.92	0.15			289.89	0.16	
208.96	0.11			291.92	0.15	
209.94	0.47			295.94	3.22	
210.29	0.03			296.96	0.28	
210.51	0.03			297.93	1.14	
211.82	2.02	F		298.93	0.10	
212.83	1.61	F		303.85	0.10	
213.95	100.00	F0		311.89	0.98	
214.97	19.41	F		312.92	0.16	
215.97	72.37	F		313.90	0.73	
216.39	0.04			314.90	0.04	
216.97	5.95			315.92	0.08	
217.98	0.29			329.92	0.96	
221.93	0.32			330.92	0.32	
223.93	0.20			331.92	1.12	
227.93	0.11			332.93	0.18	
231.95	0.05			333.92	0.35	
235.93	0.04			340.92	0.03	
239.92	0.31					
240.93	0.05					

Mass Spectrum No.18 M.W. 273.5



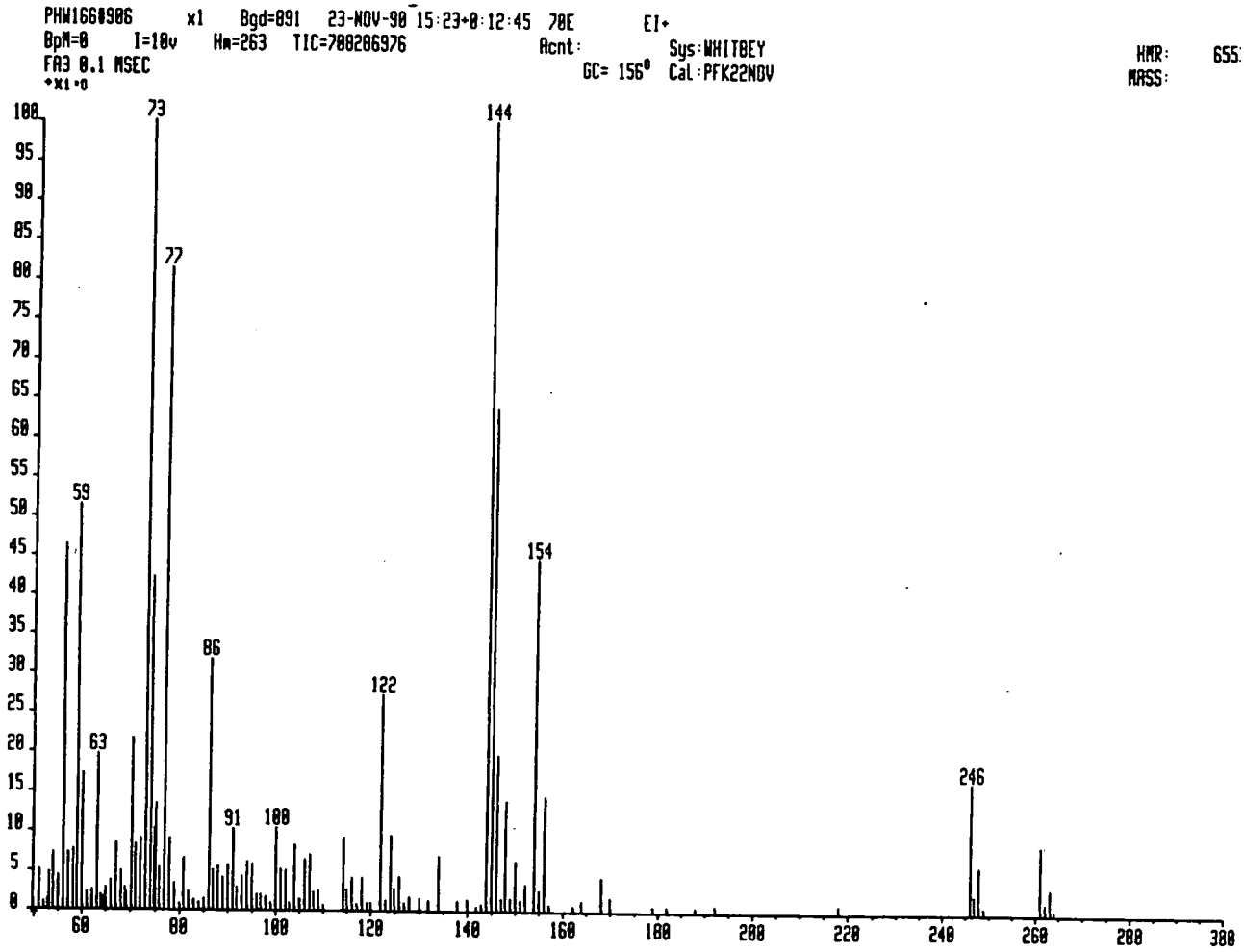
Mass	% Base	
55.05	9.37	
59.03	5.07	
73.05	56.47	F
77.03	12.03	
156.12	100.00	FO
157.13	21.49	
158.13	8.98	
200.05	0.08	
218.07	0.05	
258.07	3.04	
259.08	0.43	
260.06	0.95	
261.07	0.11	
272.09	0.09	
273.10	1.23	
274.10	0.19	
275.10	0.47	
276.10	0.07	

Mass Spectrum No.19 M.W. 233.5



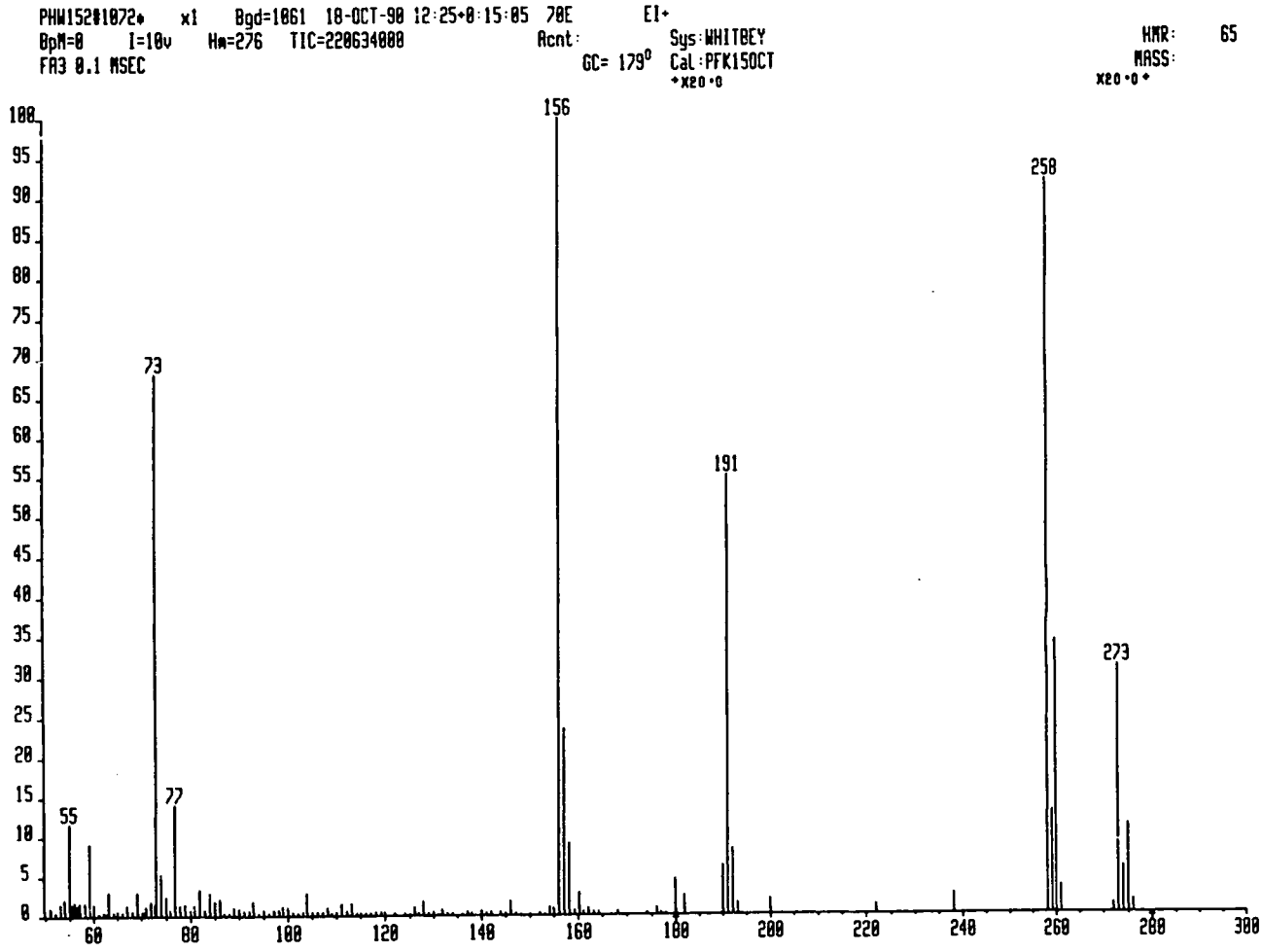
Mass	% Base	
59.06	10.86	
60.05	16.21	
63.03	8.98	
73.07	100.00	FO
74.07	12.08	
77.05	53.49	F
86.08	8.98	
106.09	8.98	
116.14	100.00	FO
117.14	21.79	
118.12	8.98	F
120.12	12.96	
122.08	8.98	
216.14	0.03	
218.12	2.27	
219.12	0.24	
220.12	0.82	
221.07	1.37	
232.14	0.11	
233.14	9.55	
234.15	1.81	
235.14	3.18	
236.16	1.37	
237.14	0.08	

Mass Spectrum No.20 M.W. 261.5



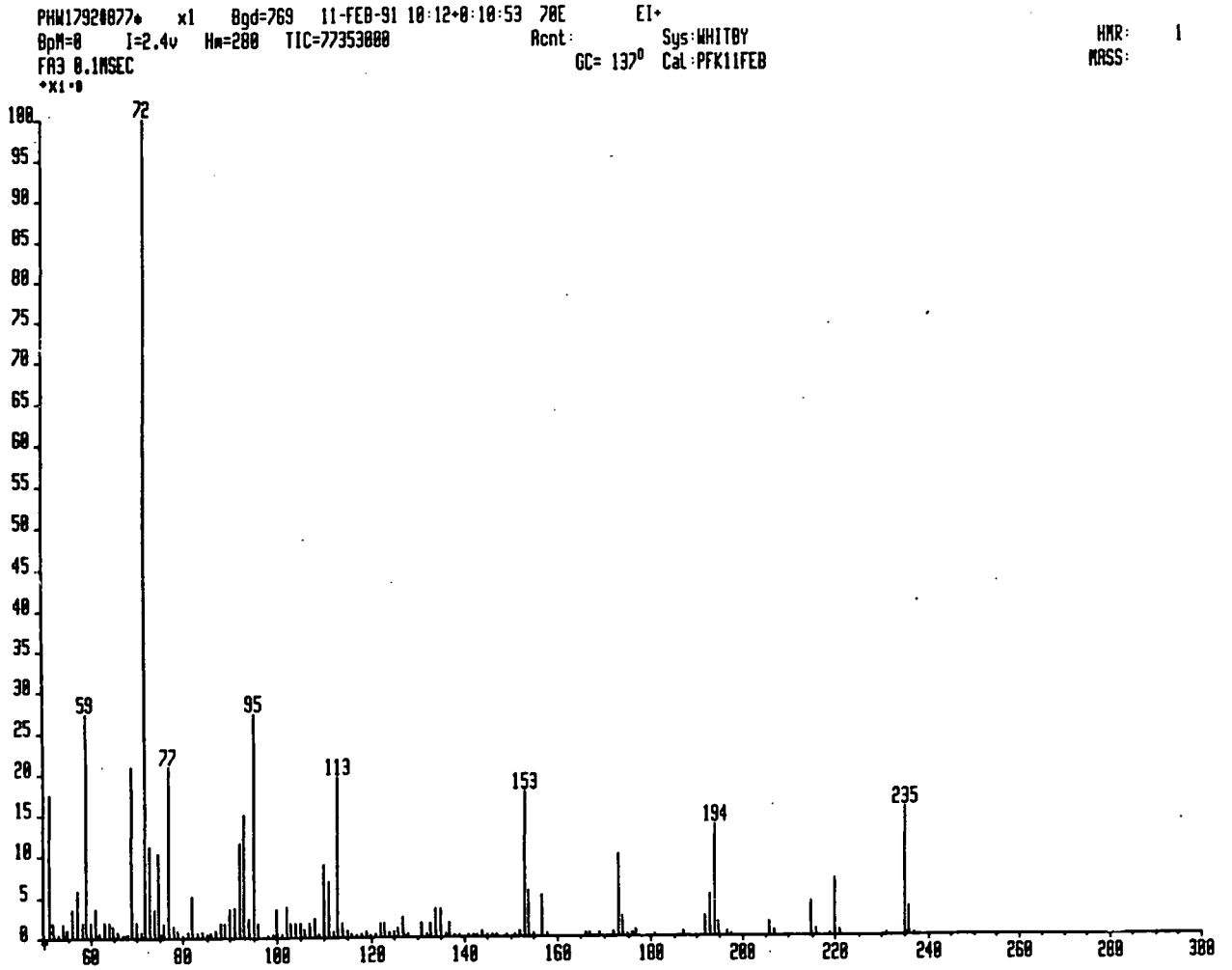
Mass	% Base		
50.99	1.55	94.97	1.55
53.01	1.18	95.95	0.52
54.02	1.82	96.95	0.37
55.01	1.21	97.98	0.34
56.03	11.95	100.02	2.25
57.01	1.87	101.02	0.92
58.01	2.14	102.00	1.08
59.02	13.56	103.99	1.81
60.01	4.14	106.00	1.25
61.00	0.52	106.97	1.55
61.97	0.52	107.97	0.52
62.98	4.61	108.97	0.52
63.98	0.38	114.04	1.97
64.99	0.67	115.04	0.52
66.01	1.03	116.04	0.82
66.97	2.23	118.00	0.70
68.02	1.27	121.97	5.69
68.98	0.64	123.97	1.77
70.03	5.42	124.95	0.36
71.01	1.99	125.94	0.74
72.03	2.59	134.02	1.03
73.02	84.21	144.06	100.00
74.02	10.41	145.06	13.96
75.00	3.35	146.06	4.17
75.98	1.18	148.04	2.99
76.99	19.31	150.00	1.22
77.99	2.25	151.99	0.66
78.98	0.78	153.95	8.37
80.97	1.62	154.95	0.39
81.99	0.52	155.94	2.54
86.01	6.95	167.97	0.66
87.00	1.05	245.96	2.62
88.02	1.21	246.96	0.34
88.99	0.87	247.96	0.89
89.98	1.16	260.98	1.26
91.00	2.12	262.98	0.36
91.99	0.63		
92.96	1.19		
93.97	1.45		

Mass Spectrum No.21 M.W. 275.5



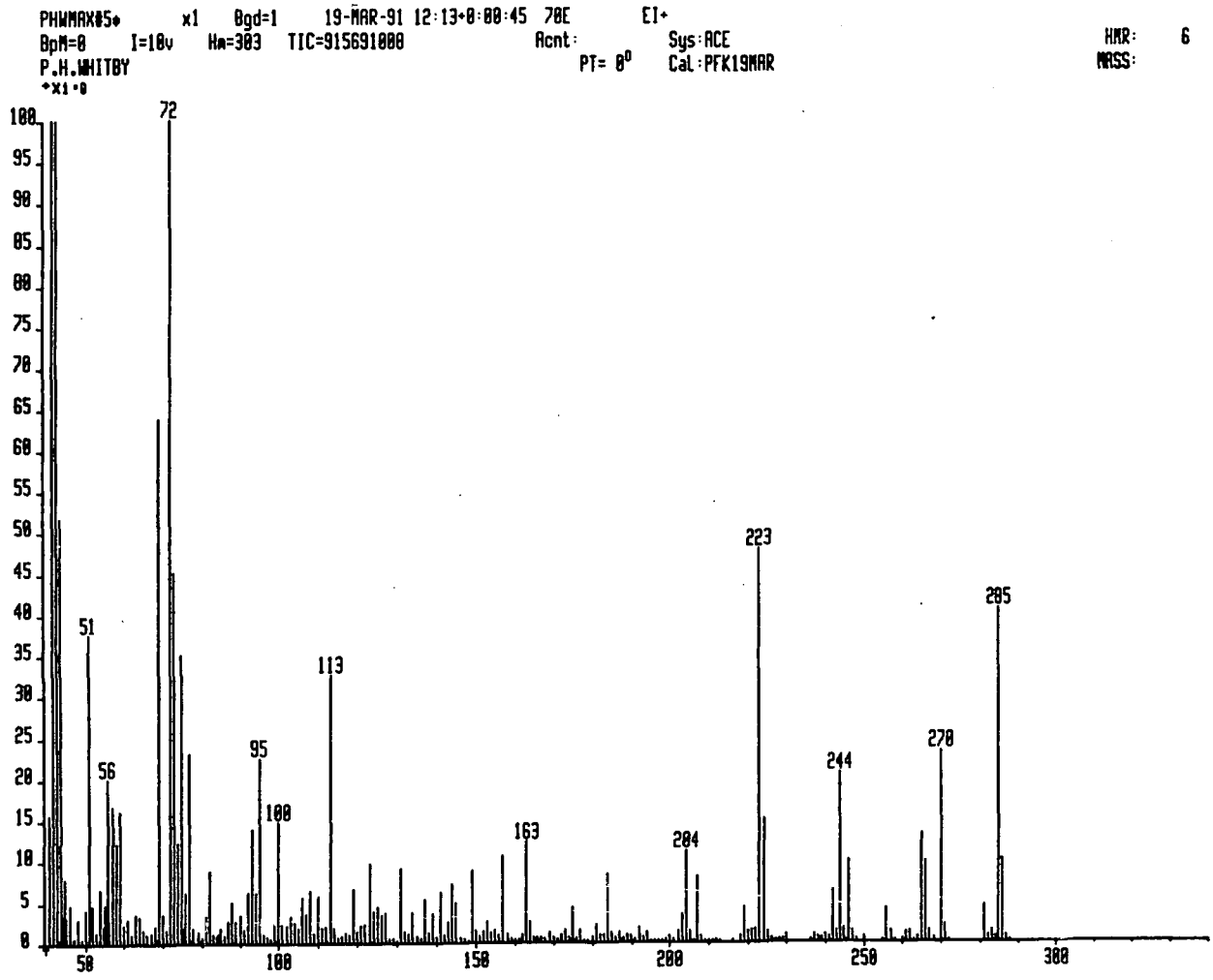
Mass	% Base	
55.05	11.51	
59.03	8.98	
73.05	67.97	F
74.05	5.22	
77.03	13.93	
156.13	100.00	FO
157.13	23.45	
158.13	8.98	
200.07	0.09	
205.13	0.03	
206.13	0.03	
222.12	0.06	
238.14	0.12	
258.08	4.61	
259.08	0.65	
260.08	1.71	
261.08	0.17	
272.10	0.06	
273.10	1.56	
274.10	0.29	
275.10	0.55	
276.11	0.08	

Mass Spectrum No.22 M.W. 235



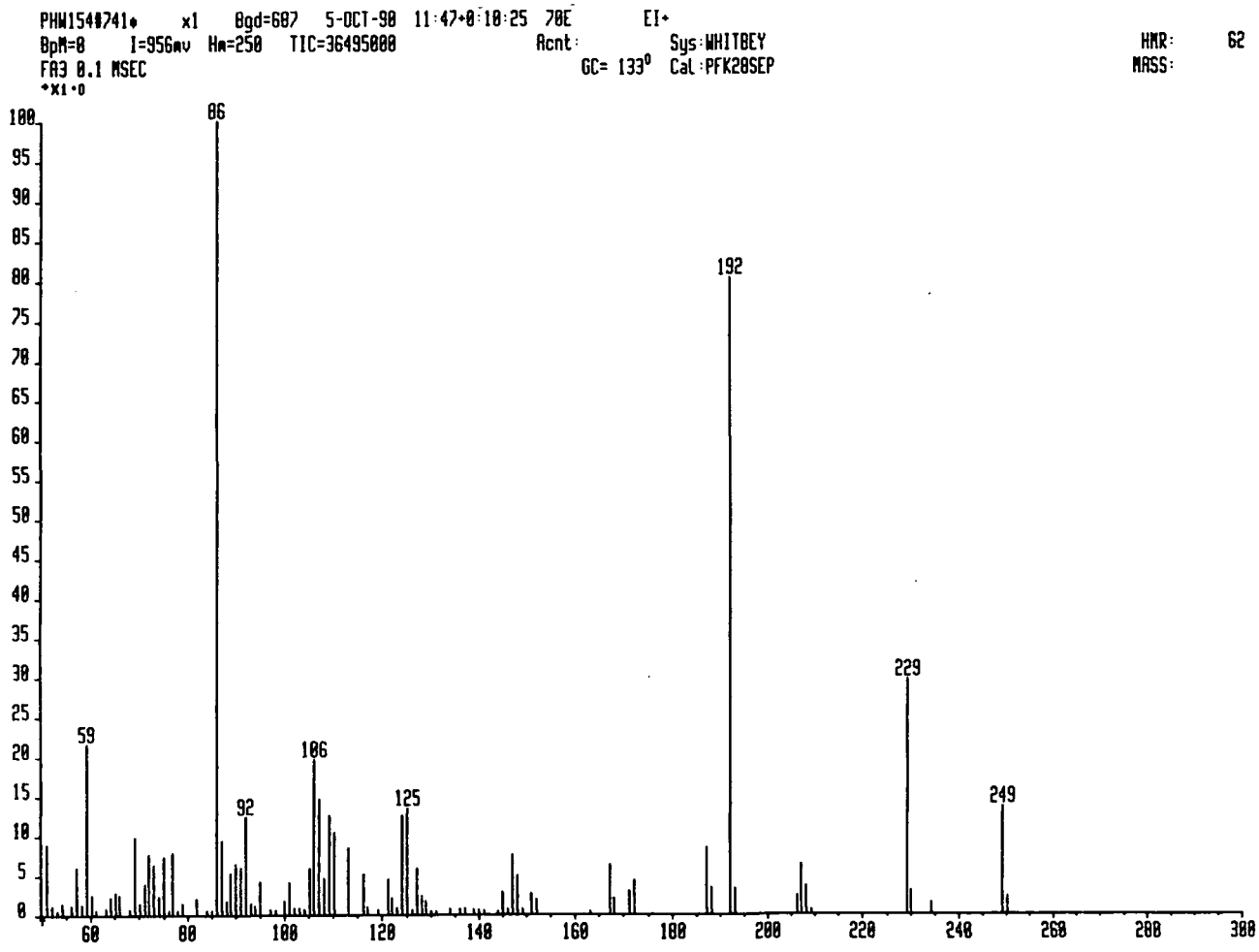
Mass	% Base
50.95	17.39
56.96	5.70
58.98	27.12
68.93	20.76
71.97	100.00
72.97	11.05
74.93	10.20
76.94	20.76
91.94	11.38
92.94	14.95
94.92	27.12
109.92	8.69
110.93	6.65
112.90	19.38
152.89	17.50
153.89	5.54
172.88	9.97
193.90	13.47
219.88	6.87
230.83	0.10
230.90	0.10
234.90	15.45
235.46	0.08
235.91	3.32
236.92	0.21

Mass Spectrum No.23 M.W. 285



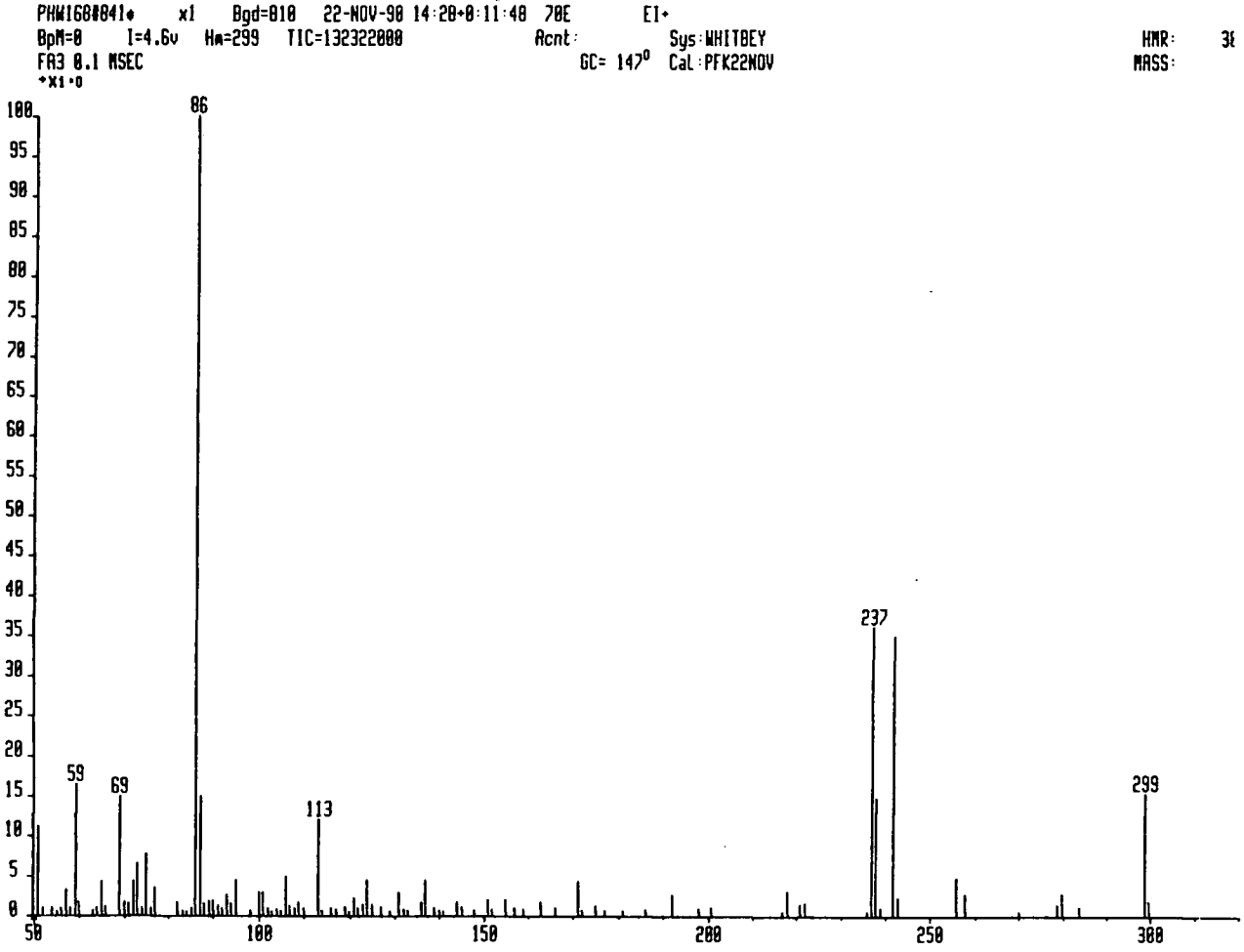
Mass	% Base		Mass	% Base	
41.03	15.58	F	143.98	7.16	
42.00	100.00	FO	149.00	8.79	
42.03	25.21	F	156.98	10.51	
43.01	100.00	O	162.98	12.26	
44.01	51.68	F	183.99	8.34	
45.01	7.86	F	203.99	11.15	
51.01	37.55		206.97	8.02	
54.03	6.52		222.99	47.92	
56.01	20.07	F	224.00	15.03	
57.01	16.67	F	241.99	6.31	
57.07	6.29	F	244.00	20.53	
58.02	12.18	F	246.04	9.86	F
59.03	16.10		265.00	13.15	
68.99	63.73	F	266.00	9.72	
72.04	100.00	O	269.97	23.22	
73.04	45.04		280.97	4.37	
74.01	12.24		281.97	0.66	
75.00	35.05		282.96	1.38	
76.01	6.15		284.00	0.54	
77.01	23.04		285.00	40.66	
81.99	8.70	F	286.01	10.10	
88.00	5.03		287.01	0.72	
92.01	6.07		287.99	0.11	
92.99	13.85				
93.99	6.09				
94.99	22.42	F			
99.98	14.69				
105.99	5.51				
108.00	6.43				
110.01	5.63				
112.98	32.55				
118.99	6.61				
123.01	9.56				
130.98	8.99				
136.98	5.26				
141.00	6.17				

Mass Spectrum No.24 M.W. 249



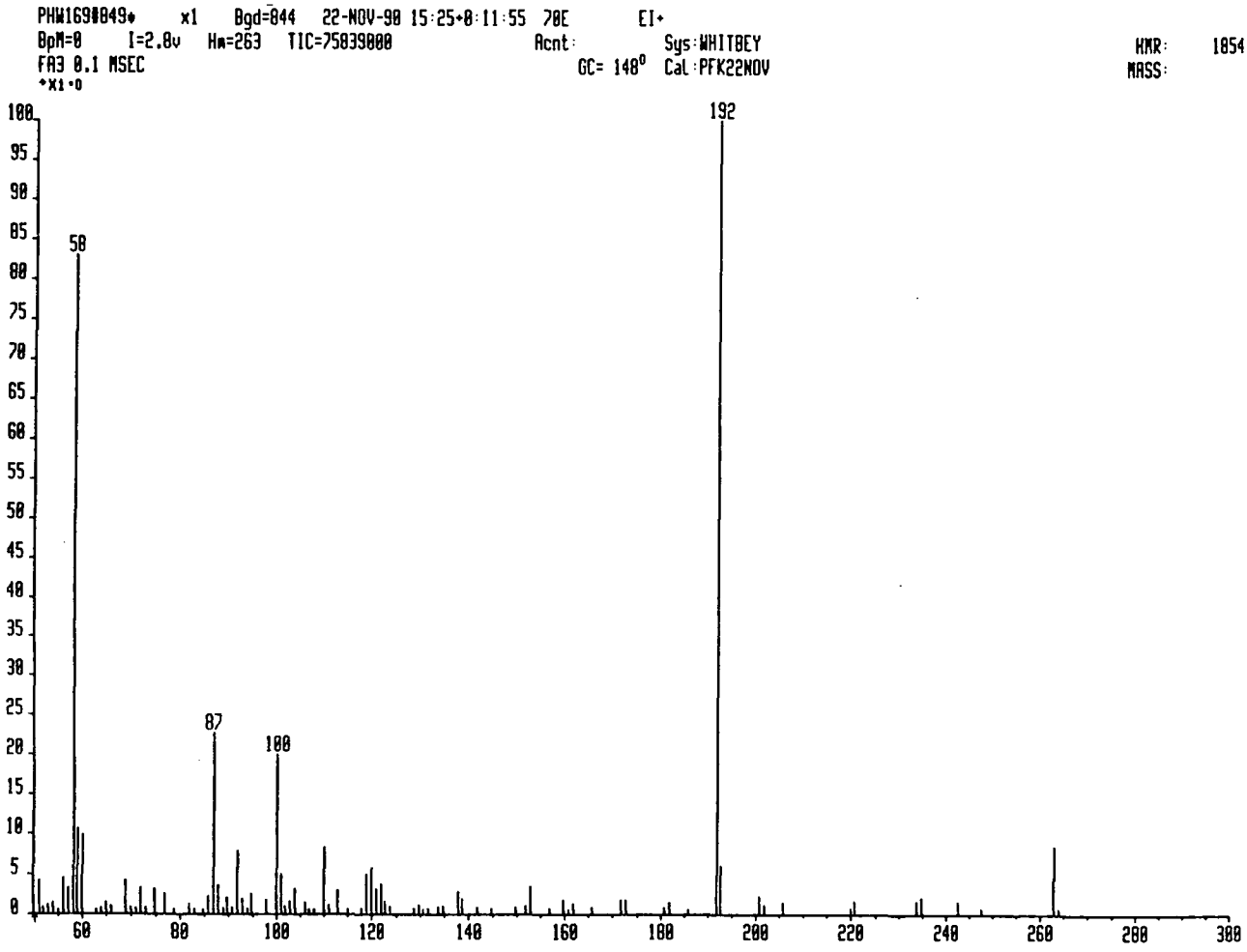
Mass	% Base
51.04	8.73
57.07	5.86
59.08	21.50
69.05	9.64
72.09	7.55
73.10	6.27
75.07	7.20
77.07	7.77
86.11	100.00
87.11	9.29
89.08	5.15
90.09	6.37
91.10	5.87
92.09	12.34
105.11	5.81
106.12	19.47
107.13	14.57
109.10	12.50
110.10	10.23
113.08	8.38
124.13	12.46
125.13	13.33
127.11	5.83
147.14	7.48
167.16	6.21
187.16	8.31
192.14	80.26
207.18	6.21
229.20	29.48
249.21	13.50
250.22	2.17

Mass Spectrum No.25 M.W. 299



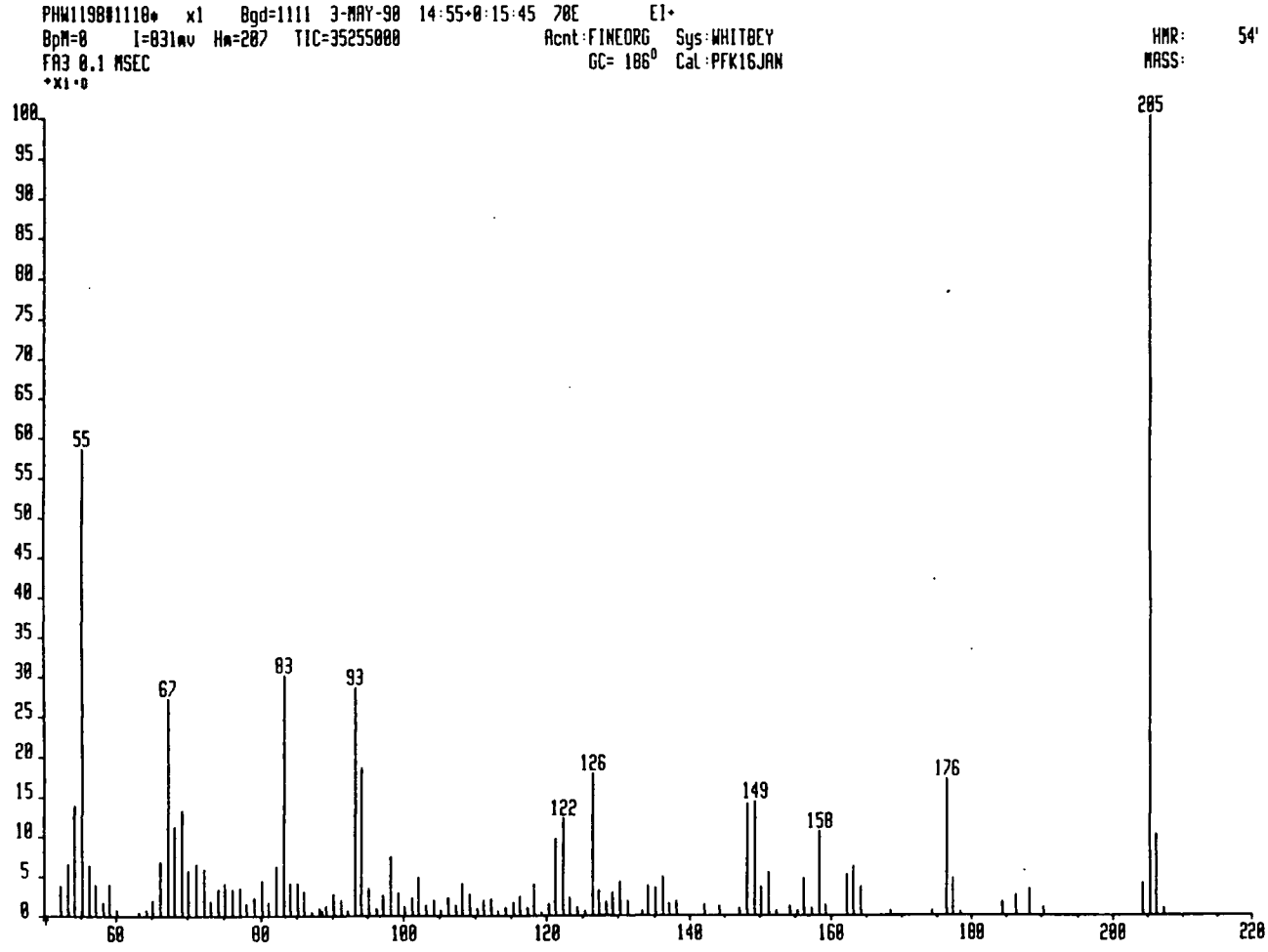
Mass	% Base				
50.97	11.05	94.93	4.36	147.91	0.66
51.99	0.84	97.97	0.55	150.88	2.04
54.00	0.84	99.92	2.94	151.88	0.75
55.00	0.40	100.93	2.95	154.89	1.96
55.99	0.88	101.94	0.84	155.89	0.31
56.99	3.23	102.94	0.50	156.86	0.96
57.98	0.89	103.95	0.75	158.87	0.77
58.99	16.43	104.95	0.64	162.86	1.69
59.95	1.69	105.95	4.86	165.88	0.84
60.97	0.36	106.96	1.14	170.87	4.26
62.97	0.60	107.94	0.84	171.88	0.55
63.97	0.84	108.94	1.69	174.85	1.14
64.97	4.22	109.94	0.84	176.86	0.63
65.97	1.13	112.92	12.01	177.88	0.38
67.99	0.37	113.93	0.55	180.85	0.54
68.94	14.79	115.95	0.97	185.87	0.74
69.97	1.61	116.94	0.75	191.84	2.53
70.97	1.50	118.91	1.12	197.84	0.84
71.98	4.22	119.91	0.41	200.82	1.06
72.99	6.55	120.92	2.19	216.84	0.51
73.97	0.92	121.93	0.85	217.84	3.02
74.95	7.59	122.92	1.36	220.82	1.34
75.95	6.84	123.92	4.43	221.81	1.49
76.96	3.49	124.91	1.33	222.83	0.31
80.95	0.35	126.90	0.99	235.80	0.43
81.94	1.72	128.79	0.40	236.80	36.00
82.96	0.58	130.87	2.91	237.80	14.65
83.97	0.47	131.86	0.75	238.81	0.94
84.98	0.84	132.90	0.64	241.76	34.78
85.99	100.00	133.90	0.38	242.77	2.31
86.99	14.91	134.91	0.39	255.79	4.73
87.97	1.50	135.91	1.61	257.81	2.70
88.95	1.80	136.91	4.40	269.84	0.41
89.95	1.89	138.89	0.98	278.79	1.32
90.96	1.24	139.89	0.58	279.81	2.72
91.95	0.84	140.89	0.44	283.77	1.08
92.92	2.53	143.87	1.70	298.76	15.34
93.94	1.51	144.88	1.00	299.77	1.88

Mass Spectrum No.26 M.W. 263



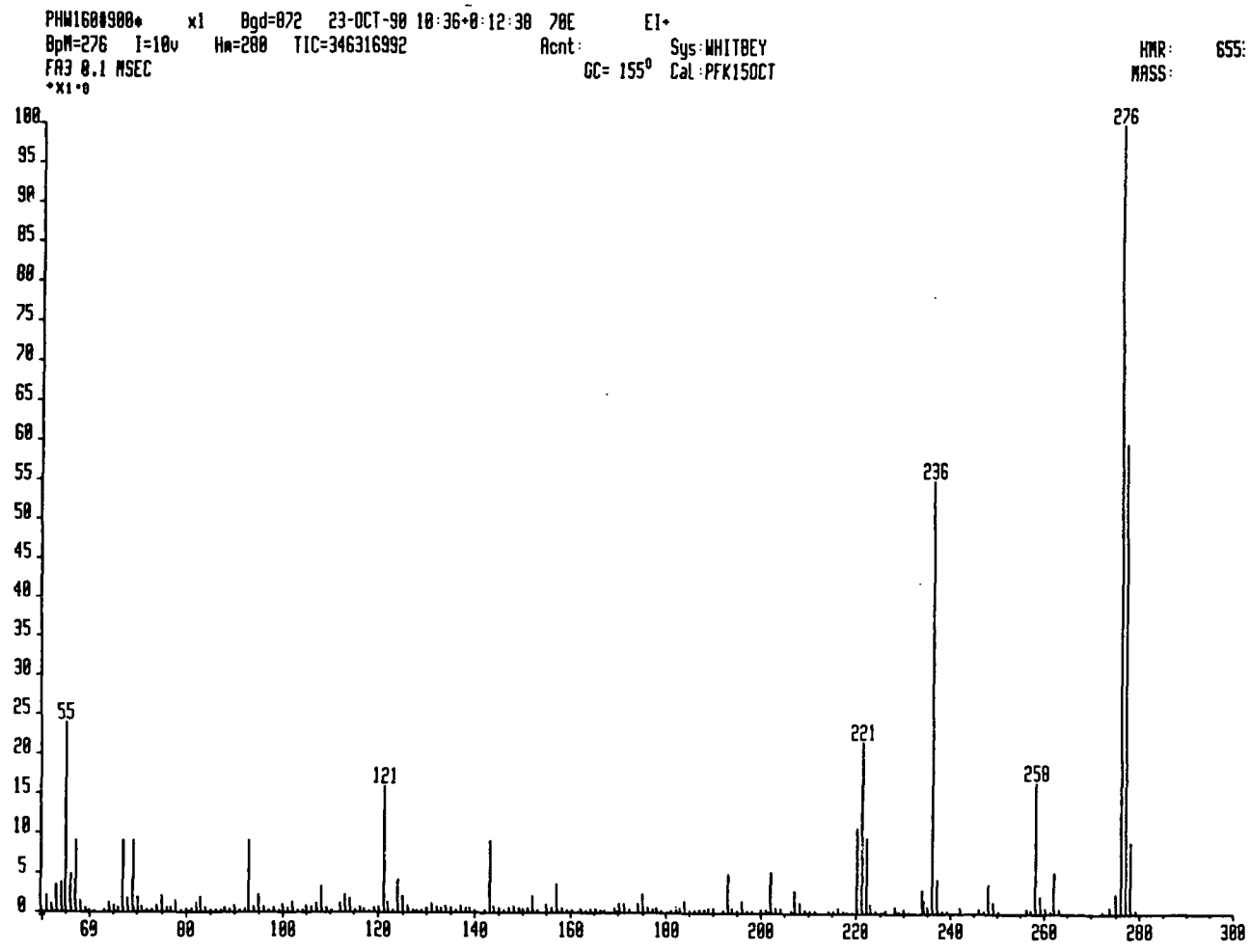
Mass	% Base				
50.95	4.14	97.93	1.67	160.85	0.52
51.96	0.80	99.94	19.87	161.85	1.26
52.97	0.99	100.94	4.84	165.83	0.79
53.98	1.38	101.91	0.85	171.80	1.72
54.98	0.44	102.90	1.51	172.80	1.63
55.98	4.46	103.91	3.09	180.83	0.80
56.97	3.19	104.91	0.33	181.82	1.40
57.99	82.88	105.91	1.43	185.80	0.42
58.97	10.46	106.88	0.44	191.77	100.00
59.97	9.73	107.88	0.41	192.77	5.98
60.96	0.37	108.89	0.36	200.78	2.19
62.93	0.53	109.89	8.15	201.80	1.01
63.94	0.56	110.90	1.00	205.77	1.38
64.94	1.38	112.87	2.92	219.78	0.56
65.94	0.93	114.90	0.50	220.78	1.53
68.91	4.14	117.90	0.57	233.74	1.56
69.93	0.75	118.90	4.89	234.74	1.91
70.94	0.57	119.91	5.64	242.74	1.53
71.95	3.12	120.90	3.04	243.76	0.37
72.96	0.82	121.88	3.59	247.72	0.66
73.95	0.38	122.88	1.49	262.73	8.28
74.92	3.06	123.88	0.91	263.75	0.60
76.93	2.37	128.73	0.53		
78.92	0.46	129.89	1.07		
81.91	1.22	130.73	0.47		
82.93	0.56	131.73	0.65		
84.90	0.45	132.85	0.37		
85.95	2.19	133.85	0.83		
86.95	22.61	134.87	0.84		
87.94	3.42	137.87	2.76		
88.93	0.59	138.86	1.75		
89.91	2.04	141.87	0.70		
90.92	0.69	144.83	0.60		
91.91	7.73	149.86	0.72		
92.91	1.86	151.82	0.97		
93.88	0.58	152.82	3.34		
94.88	2.36	156.80	0.67		
96.89	0.36	159.81	1.73		

Mass Spectrum No.27 M.W. 205



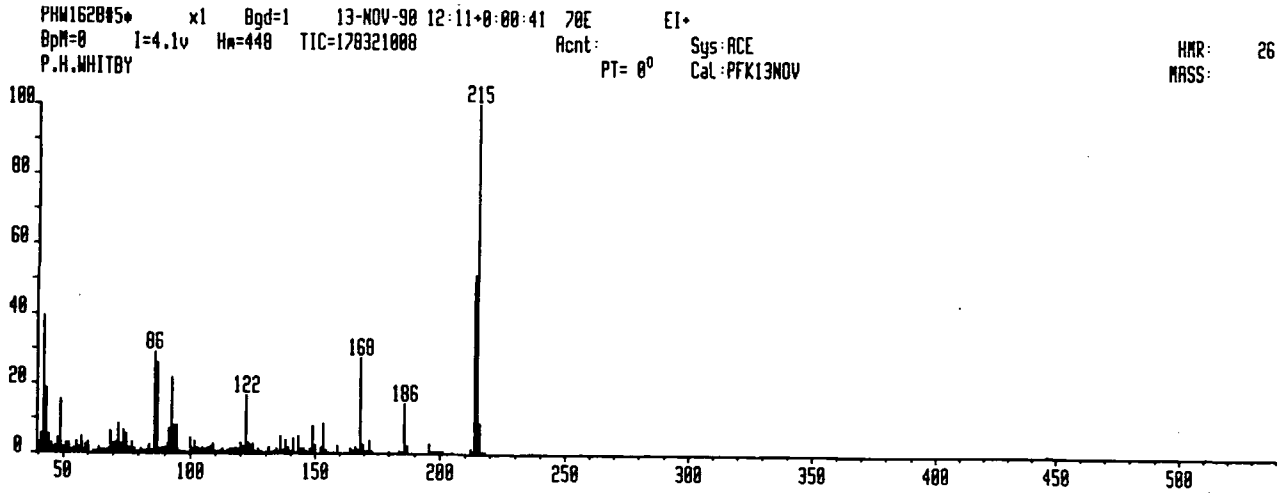
Mass	% Base						
52.13	3.63	91.23	1.89	129.26	2.68	207.35	0.70
53.15	6.39	92.24	0.48	130.27	4.02		
54.15	13.83	93.20	28.42	131.26	1.63		
55.16	58.42	94.21	18.44	133.26	0.50		
56.17	6.17	95.21	3.32	134.26	3.63		
57.14	3.83	96.24	0.77	135.26	3.38		
58.14	1.54	97.25	2.39	136.26	4.64		
59.16	3.83	98.25	7.32	137.28	1.38		
60.16	0.66	99.26	2.73	138.30	1.67		
63.16	0.37	100.25	1.08	142.29	1.16		
64.17	0.61	101.23	2.13	144.29	1.10		
65.18	1.87	102.23	4.73	147.27	0.77		
66.19	6.70	103.24	1.19	148.28	13.94		
67.20	27.19	104.25	1.74	149.28	14.22		
68.20	11.06	105.26	0.55	150.27	3.43		
69.22	13.19	106.28	2.15	151.28	5.25		
70.18	5.63	107.23	1.25	152.28	0.42		
71.18	6.40	108.23	3.96	154.32	1.12		
72.19	5.72	109.25	2.59	155.32	0.39		
73.20	1.61	110.26	0.75	156.32	4.53		
74.17	3.19	111.27	1.76	157.31	0.83		
75.17	3.98	112.28	1.93	158.33	10.46		
76.18	3.19	113.27	0.48	159.34	1.21		
77.19	3.36	114.25	0.90	162.31	5.06		
78.21	1.43	115.25	1.50	163.29	6.11		
79.23	2.07	116.25	2.28	164.30	3.56		
80.22	4.31	117.25	0.90	168.35	0.51		
81.22	1.58	118.26	3.72	174.32	0.50		
82.25	6.06	119.23	0.33	176.32	17.01		
83.26	30.04	120.23	1.34	177.32	4.57		
84.25	3.98	121.23	9.56	178.34	0.31		
85.22	3.87	122.23	12.18	184.33	1.52		
86.22	2.84	123.24	2.11	186.34	2.35		
87.22	0.35	124.26	0.90	188.34	3.25		
88.21	0.75	125.28	0.46	190.32	0.88		
88.71	0.50	126.29	17.69	204.34	4.00		
89.21	1.05	127.28	2.97	205.35	100.00		
90.21	2.53	128.26	1.56	206.36	9.98		

Mass Spectrum No.28 M.W. 277



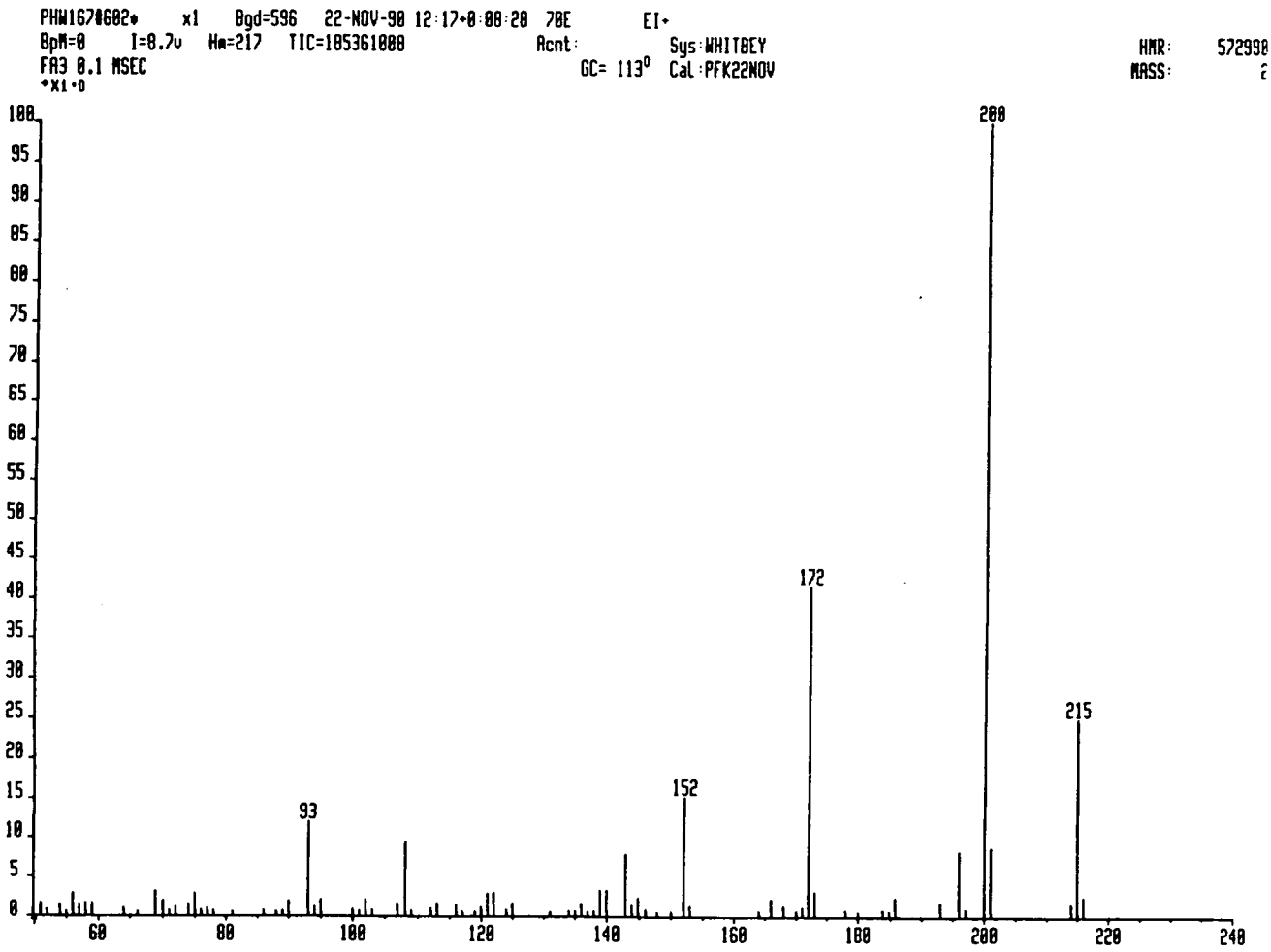
Mass	% Base	
55.09	23.81	
57.09	8.98	
67.09	8.98	
69.02	8.98	F
69.05	5.14	F
69.11	8.98	F
93.06	8.98	
121.09	15.70	
143.09	8.98	
202.11	5.17	
220.11	10.55	F
221.13	21.49	F
222.14	9.40	
236.15	55.01	F
250.16	0.18	
254.14	0.03	
256.18	0.42	
257.18	0.24	
257.61	0.02	
258.19	16.32	
259.19	2.07	
260.16	0.62	
261.16	0.21	
262.16	5.09	
263.16	0.50	
272.14	0.14	
272.43	0.02	
273.94	0.76	F
275.22	2.37	F
276.18	100.00	FO
277.20	59.65	F
278.21	8.98	
279.22	0.32	

Mass Spectrum No.29 M.W. 215



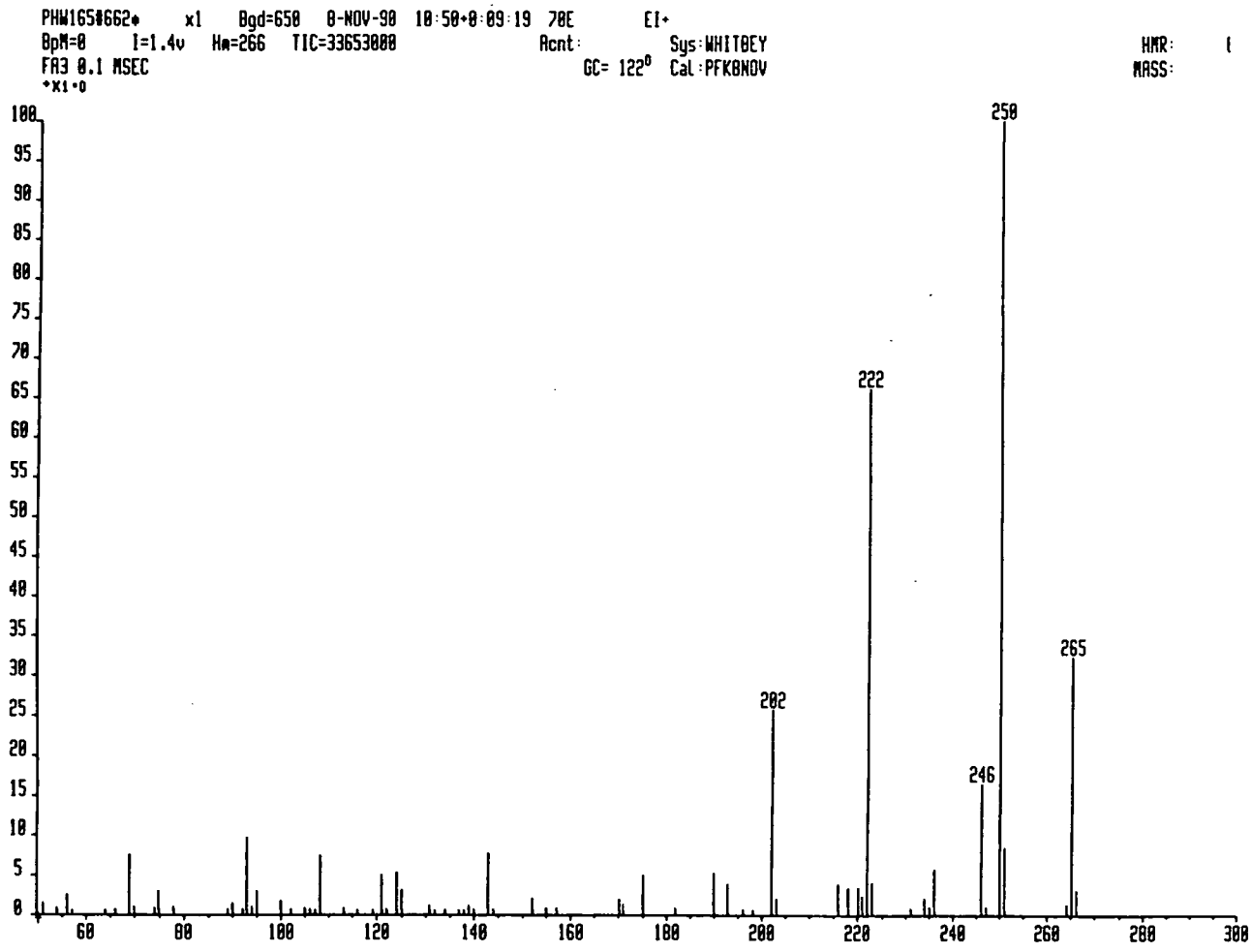
Mass	% Base				
40.03	2.53	93.02	21.35	187.07	1.94
41.04	5.31	94.06	7.95	196.07	2.68
42.04	38.75	95.04	7.73	198.04	0.46
43.05	18.36	96.05	0.43	201.06	0.35
44.05	4.84	97.12	0.40	212.05	1.06
45.03	2.55	100.02	4.20	213.07	0.52
46.02	1.31	101.04	0.95	214.06	51.05
47.02	1.74	102.03	3.14	215.07	100.00
48.02	3.96	103.04	1.39	216.07	8.60
49.02	14.91	104.05	1.22	217.08	0.50
50.01	1.43	105.03	1.34		
51.02	2.67	106.06	1.03		
52.03	2.39	107.03	1.56		
53.04	0.60	108.03	1.91		
54.05	0.95	109.04	2.48		
55.02	2.14 F	112.01	0.58		
55.07	2.70 F	113.03	1.12		
56.02	1.21	115.07	0.64		
56.07	1.53	116.06	1.04		
57.03	2.68	117.06	0.96		
57.08	4.33	118.07	1.46		
58.04	0.61	119.03	0.95		
59.05	2.01	120.05	3.02		
60.04	2.92	121.04	1.67		
63.04	0.35	122.04	16.57		
64.03	1.42	123.05	2.86		
65.05	0.63	124.02	2.08		
66.04	0.85	125.03	2.61		
67.07	0.72	126.04	0.36		
68.02	0.95	127.04	0.92		
68.07	0.45	128.08	0.36		
68.54	0.95	131.02	1.38		
69.01	5.95	134.05	0.95		
69.09	1.24	135.07	0.51		
70.03	2.37	136.07	4.55		
70.09	0.53	137.06	0.67		
71.03	2.89	138.03	3.57		
71.10	0.97	139.05	1.40		
72.05	8.22	140.05	0.48		
73.05	2.68	141.05	3.97		
74.02	6.25	143.02	4.77		
75.02	5.28	144.03	0.95		
76.03	1.44	145.04	1.17		
77.05	2.85	146.06	0.31		
78.03	1.24	148.06	1.15		
80.03	0.49	149.05	7.63		
81.02	0.95	150.05	2.01		
81.09	0.52	152.04	1.57		
82.03	0.48	153.04	8.05		
83.03	0.32	154.05	0.70		
83.10	0.64	159.04	1.70		
84.04	2.17	164.06	0.95		
85.07	0.74	165.06	0.41		
86.06	28.90	166.06	1.38		
87.07	25.75	167.06	0.76		
88.06	0.96	168.06	27.24		
89.04	1.60	169.07	2.01		
90.04	1.42	171.03	0.48		
91.05	2.56	172.04	3.27		
92.05	6.94	186.06	14.00		

Mass Spectrum No.30 M.W. 215



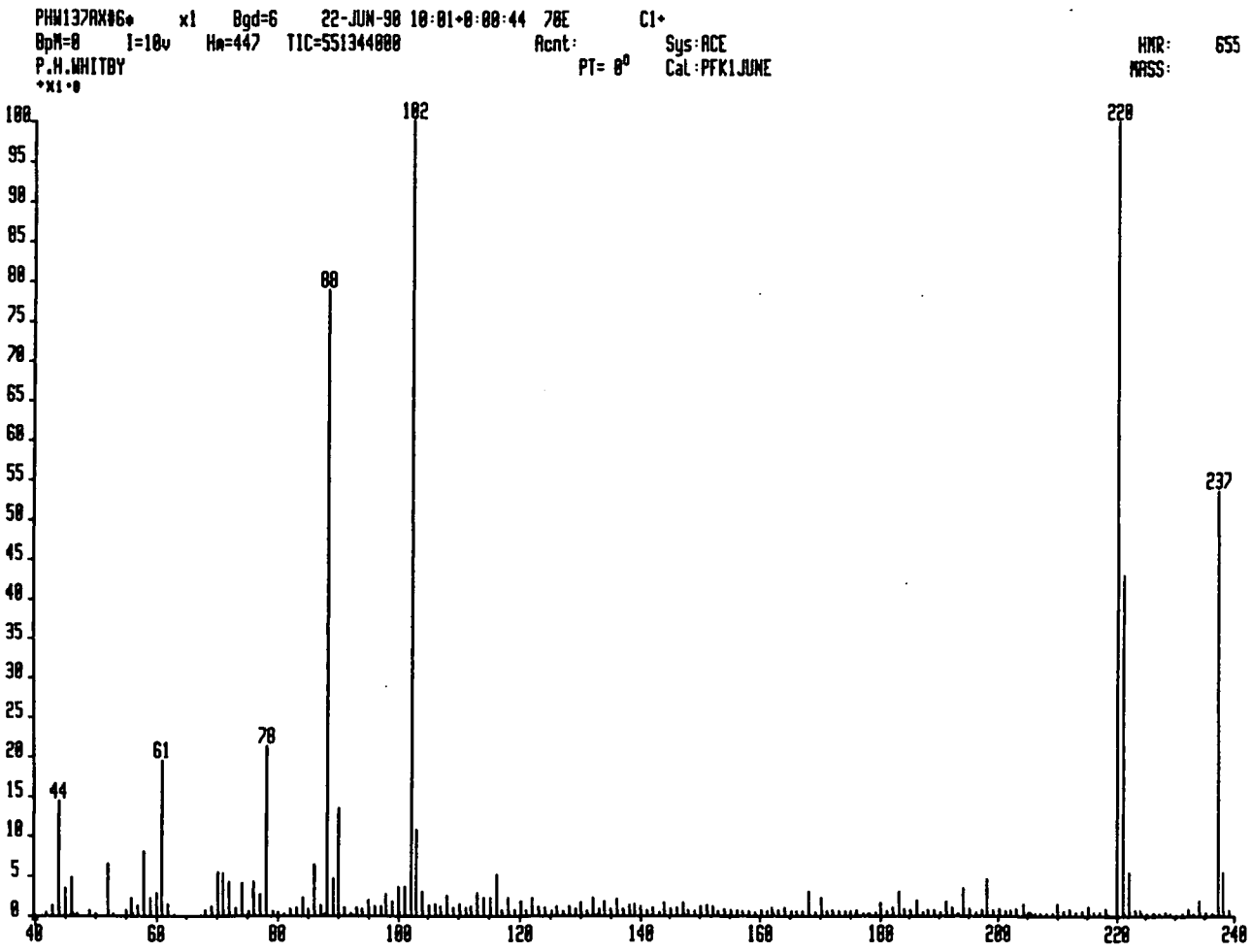
Mass	% Base				
51.01	1.48	117.02	0.52	196.03	8.19
52.02	0.70	118.99	0.50	197.03	0.89
54.04	1.44	119.99	1.12	199.98	100.00
55.03	0.45	121.00	2.78	200.98	8.63
56.05	2.79	122.00	2.85	202.00	0.31
57.02	1.34	123.98	0.69	214.00	1.56
58.01	1.46	124.98	1.48	215.01	24.87
59.02	1.57	130.95	0.50	216.02	2.45
64.01	0.89	133.99	0.65		
66.02	0.45	135.00	0.60		
68.99	3.10	136.00	1.59		
70.01	1.88	137.00	0.45		
71.02	0.64	137.97	0.55		
72.02	1.00	138.97	3.14		
74.00	1.34	139.98	3.13		
75.00	2.74	142.95	7.67		
76.00	0.57	143.97	1.34		
77.01	0.95	144.97	2.33		
78.01	0.58	146.00	0.71		
80.99	0.46	147.93	0.49		
86.02	0.59	150.00	0.52		
87.03	0.34	151.97	15.05		
88.00	0.46	152.97	1.24		
89.00	0.67	156.97	0.34		
90.00	1.75	163.99	0.58		
92.98	11.87	165.99	2.07		
93.99	1.06	166.99	0.32		
94.99	1.97	168.01	1.28		
100.02	0.71	169.96	0.58		
101.01	0.54	170.98	1.06		
102.00	1.97	171.97	41.47		
103.01	0.76	172.98	3.00		
106.99	1.47	178.00	0.75		
108.00	9.17	180.00	0.45		
109.00	0.63	183.97	0.74		
111.99	0.98	184.98	0.64		
112.99	1.45	185.98	2.33		
116.02	1.38	193.01	1.69		

Mass Spectrum No.31 M.W. 265



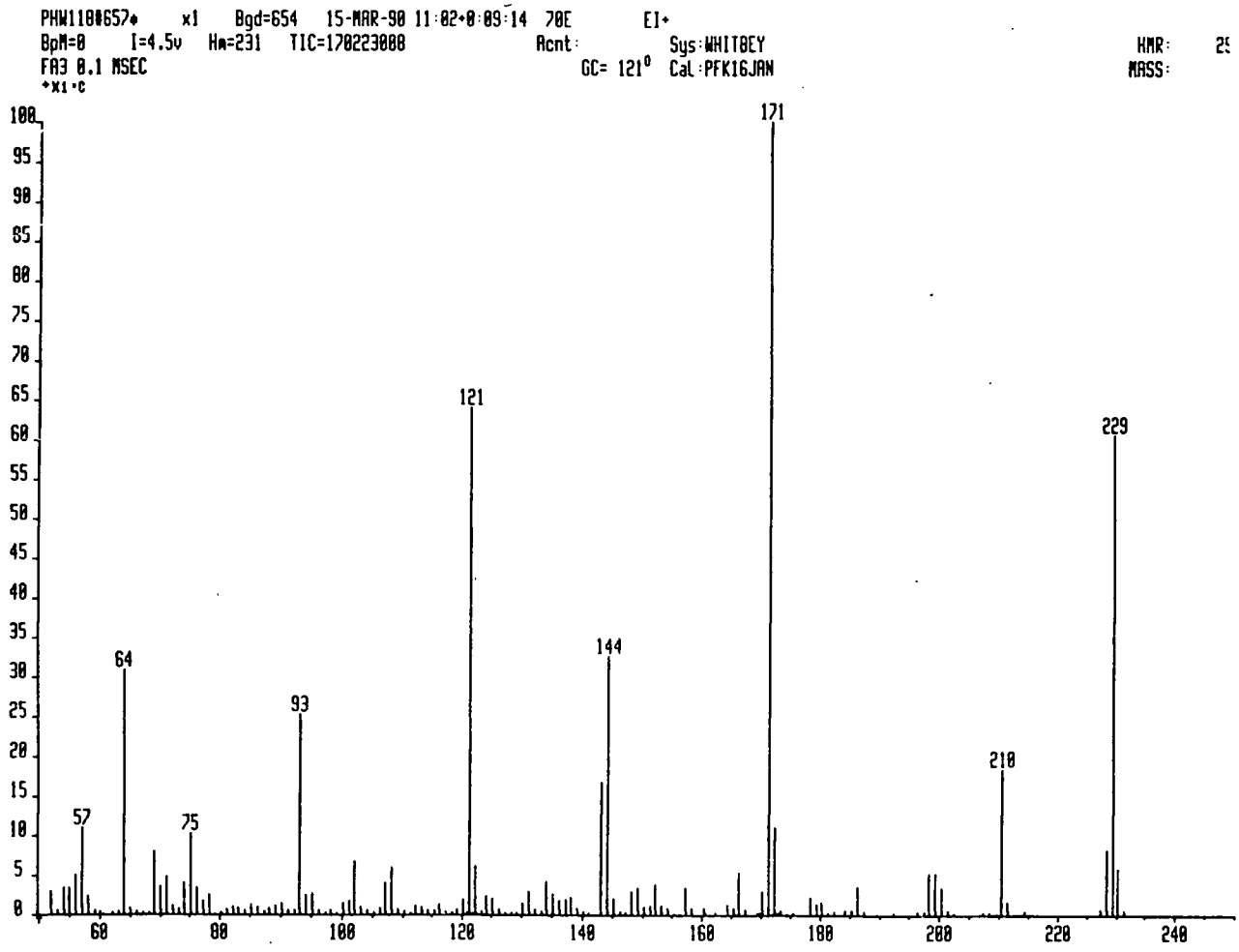
Mass	% Base
55.98	2.42
68.97	7.35
75.00	2.89
93.00	9.55
95.02	2.89
108.01	7.20
121.02	4.92
124.01	5.14
125.02	3.08
143.00	7.63
175.02	4.86
190.03	5.16
193.02	3.77
202.03	25.64
216.06	3.73
218.08	3.34
220.04	3.34
221.05	2.31
222.04	66.34
223.06	3.96
230.08	0.20
231.09	0.75
234.06	2.02
235.08	0.94
236.06	5.53
246.10	16.43
247.13	0.97
250.07	100.00
251.08	8.39
264.09	1.15
265.08	32.25
266.11	3.08

Mass Spectrum No.32 M.W. 219



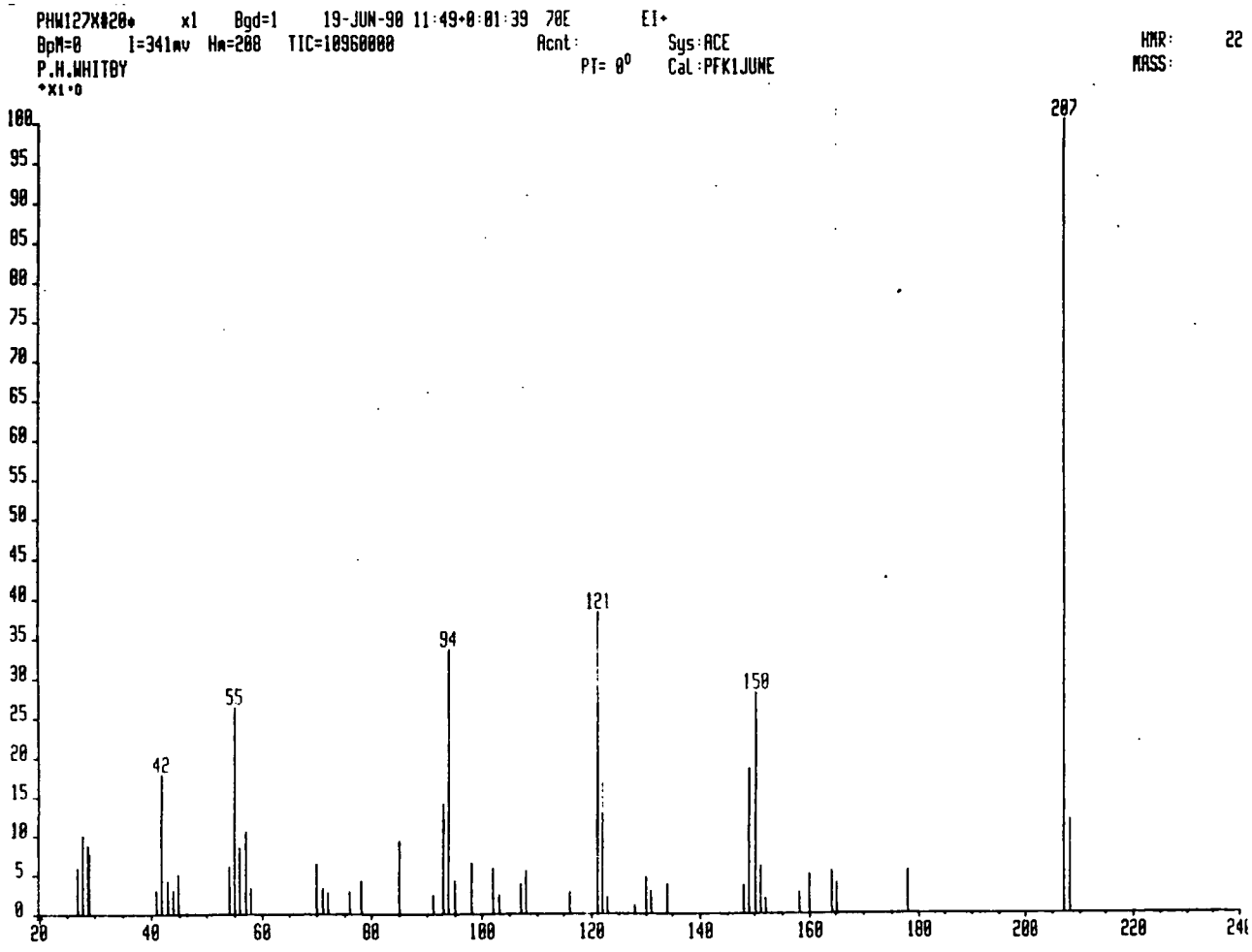
Mass	% Base				
43.97	14.25	216.21	0.24	241.19	0.18
52.04	6.33	216.98	0.07	241.26	0.15
58.04	7.82	217.19	0.25		
61.03	19.46	218.19	0.79		
70.08	5.25	218.28	0.15		
71.09	5.17	218.54	0.05		
78.10	21.24	220.20	100.00 FO		
86.10	6.20	221.15	42.99 F		
88.11	78.79	221.42	0.08		
90.10	13.28	222.03	0.04		
102.15	100.00 0	222.16	5.25		
103.13	10.63	223.16	0.65		
200.19	0.72	224.14	0.56		
201.19	0.41	224.28	0.09		
202.10	0.07	225.16	0.20		
202.18	0.53	226.15	0.14		
203.17	0.70	226.24	0.13		
204.34	1.30	226.32	0.09		
205.01	0.09	227.17	0.04		
205.22	0.38	227.23	0.14		
205.44	0.26	228.22	0.28		
205.59	0.04	228.28	0.11		
205.63	0.05	229.21	0.14		
205.69	0.13	230.22	0.07		
205.85	0.04	231.22	0.13		
206.18	0.13	232.18	0.71		
207.17	0.13	233.19	0.19		
208.15	0.20	234.17	1.89		
209.19	0.09	235.19	0.26		
209.29	0.06	236.20	0.17		
210.15	1.42	236.41	0.07		
211.17	0.48	236.46	0.05		
211.88	0.06	236.57	0.07		
212.18	0.69	237.18	53.58		
213.16	0.31	237.47	0.06		
213.25	0.07	238.19	5.33		
214.18	0.38	239.20	0.67		
215.19	1.05	240.24	0.21		

Mass Spectrum No.33 M.W. 229



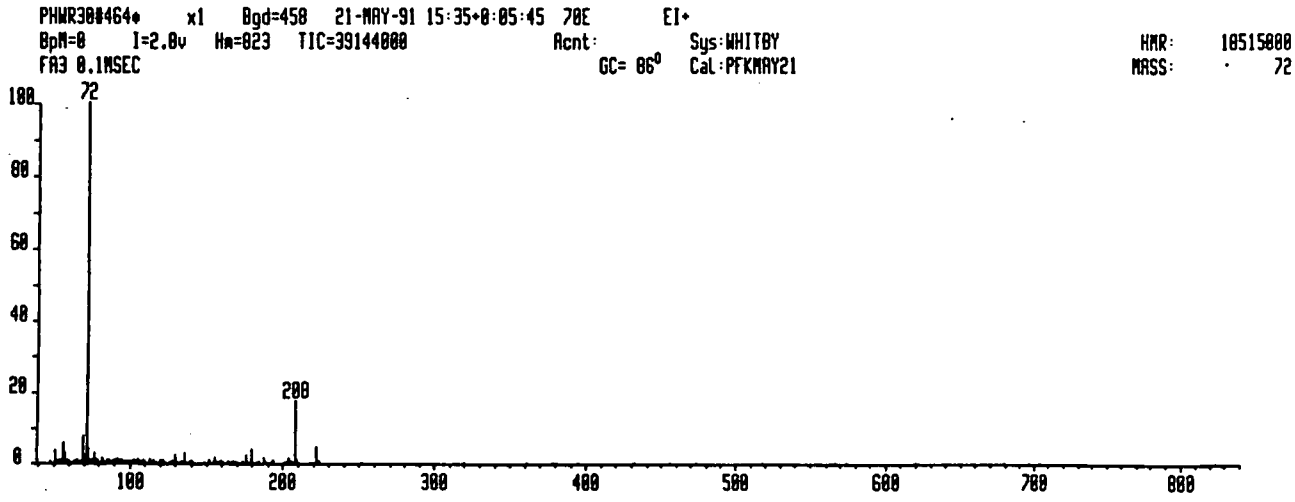
Mass	% Base
57.14	10.92
64.13	30.79
69.12	7.81
75.15	10.09
93.17	25.21
102.21	6.59
108.21	5.85
121.22	63.94
122.22	6.06
143.23	16.68
144.24	32.60
166.30	5.25
171.28	100.00
172.29	10.87
198.34	5.11
199.35	5.09
210.38	18.40
227.41	0.64
228.39	8.23
229.40	60.58
230.41	5.76
231.43	0.39

Mass Spectrum No.34 M.W. 207



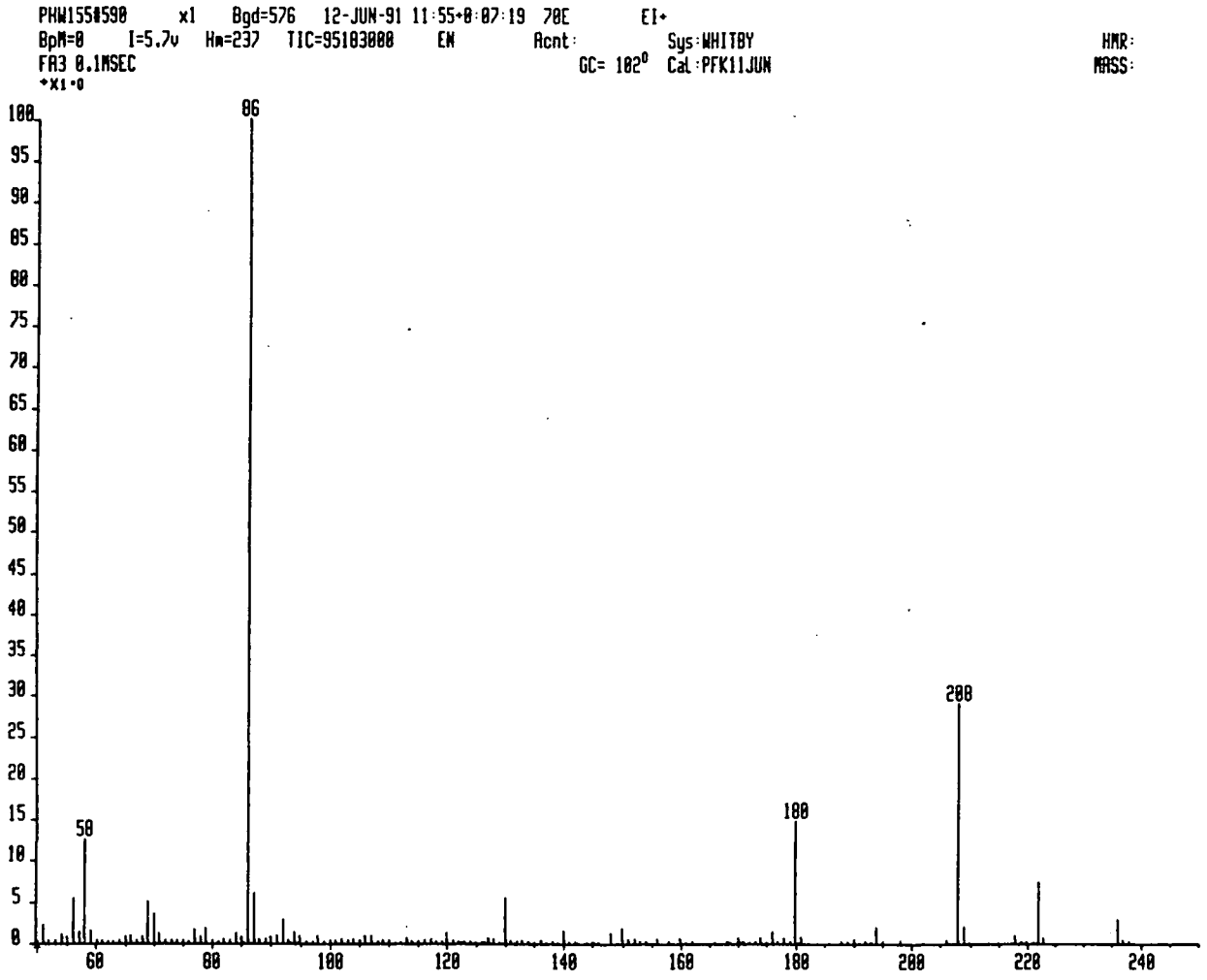
Mass	% Base
41.95	17.74
53.99	5.90
55.01	26.27
56.02	8.27
57.01	10.28
70.04	6.26
85.08	9.07
93.04	13.99
94.05	33.51
98.08	6.34
102.06	5.63
108.07	5.23
121.07	38.20
122.07	16.89
149.08	18.50
150.10	28.06
151.09	5.85
164.10	5.32
178.14	5.23
207.15	100.00
208.16	11.75

Mass Spectrum No.35 M.W. 223



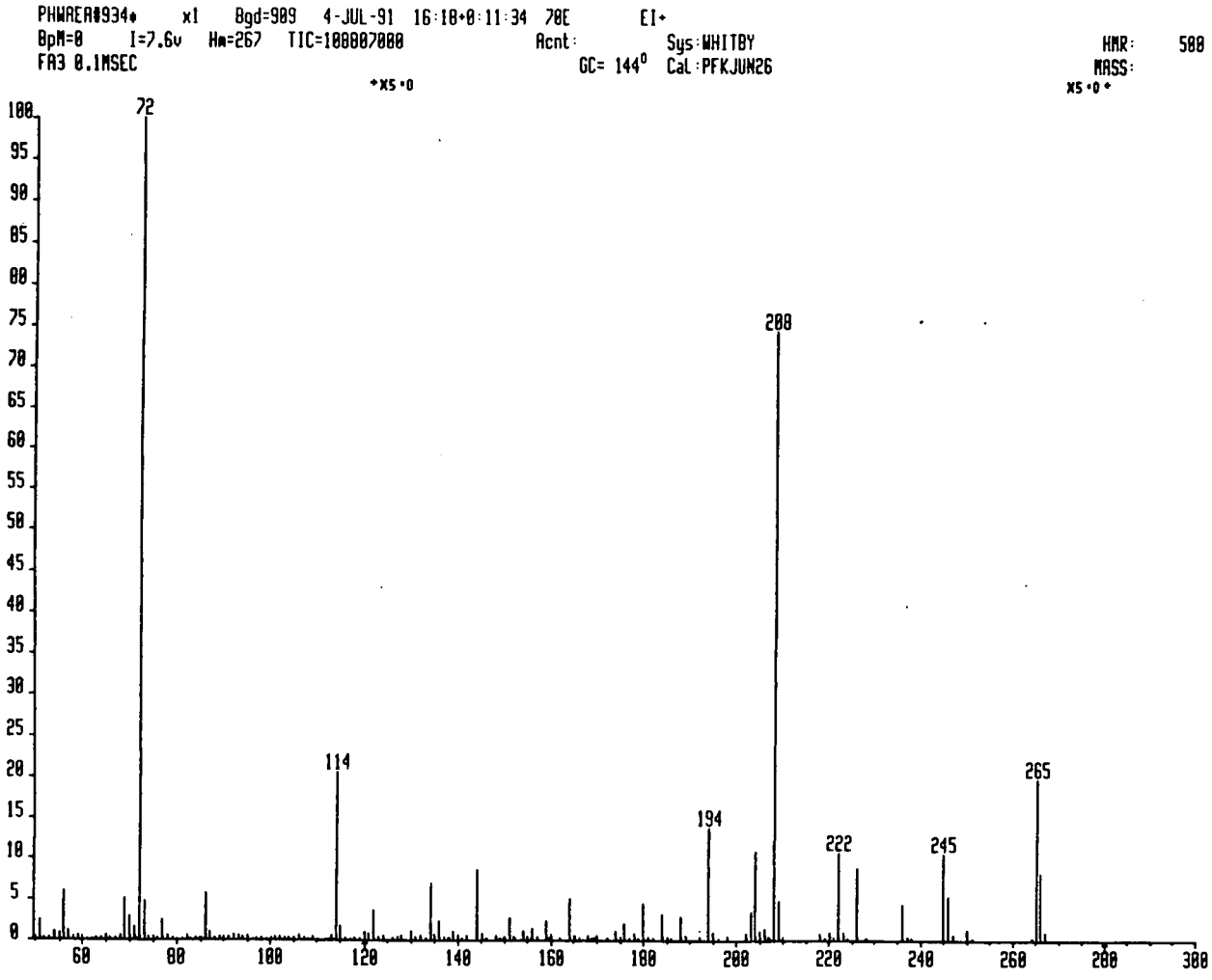
Mass	% Base		
48.01	0.44	209.00	1.03
50.99	3.36	221.99	4.43
54.02	0.84	223.01	0.48
55.03	0.60	224.00	0.33
56.03	5.34		
57.03	2.87		
59.01	0.77		
60.01	0.43		
65.01	0.65		
66.00	0.43		
68.98	7.63		
70.03	1.74		
71.05	1.94		
72.06	100.00		
73.06	4.23		
74.02	0.74		
75.01	1.04		
76.99	2.85		
78.00	0.78		
79.00	0.63		
81.98	1.22		
86.01	0.56		
87.02	0.55		
88.03	0.35		
89.00	0.46		
89.99	0.62		
91.01	0.66		
92.01	1.15		
93.01	0.93		
94.02	0.55		
94.99	0.81		
98.01	0.44		
101.02	0.51		
103.05	0.79		
106.02	1.02		
107.02	0.41		
108.99	0.74		
112.97	0.87		
116.00	0.64		
120.02	0.63		
121.01	0.31		
122.04	0.71		
129.99	2.11		
136.00	2.76		
138.98	0.32		
139.96	0.58		
150.95	0.58		
155.98	1.37		
158.98	0.46		
159.97	0.47		
164.02	0.37		
173.99	0.32		
176.00	2.02		
179.96	3.80		
183.98	0.32		
187.98	1.30		
193.97	0.70		
202.00	0.30		
204.01	1.24		
207.98	17.49		

Mass Spectrum No.36 M.W. 237



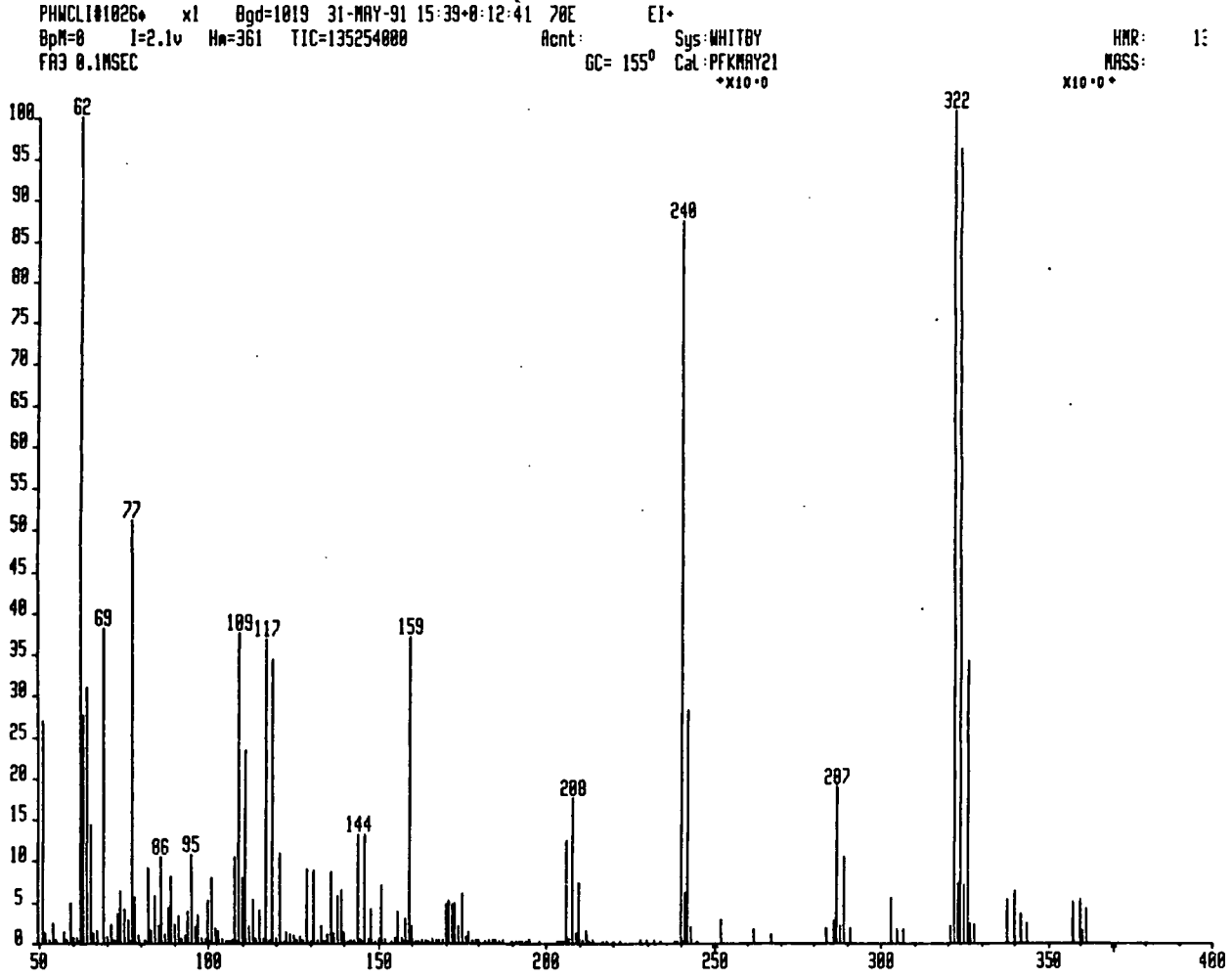
Mass	% Base	
51.04	2.18	
56.07	5.36	
57.06	1.33	
58.07	12.60	
59.05	1.40	
68.97	5.01	
70.03	3.46	
71.03	1.18	
76.97	1.63	
78.97	1.81	
84.02	1.15	
86.04	100.00	
87.04	5.93	
91.98	2.71	
93.98	1.32	
119.98	1.21	
129.95	5.36	
139.93	1.52	
147.93	1.11	
149.95	1.68	
175.93	1.31	
179.90	14.69	M
193.91	1.96	
207.90	29.04	M
208.91	1.93	
220.89	0.05	
221.30	0.05	
221.90	7.30	
222.90	0.59	
235.93	2.76	
236.93	0.34	
237.95	0.13	

Mass Spectrum No.37 M.W. 265



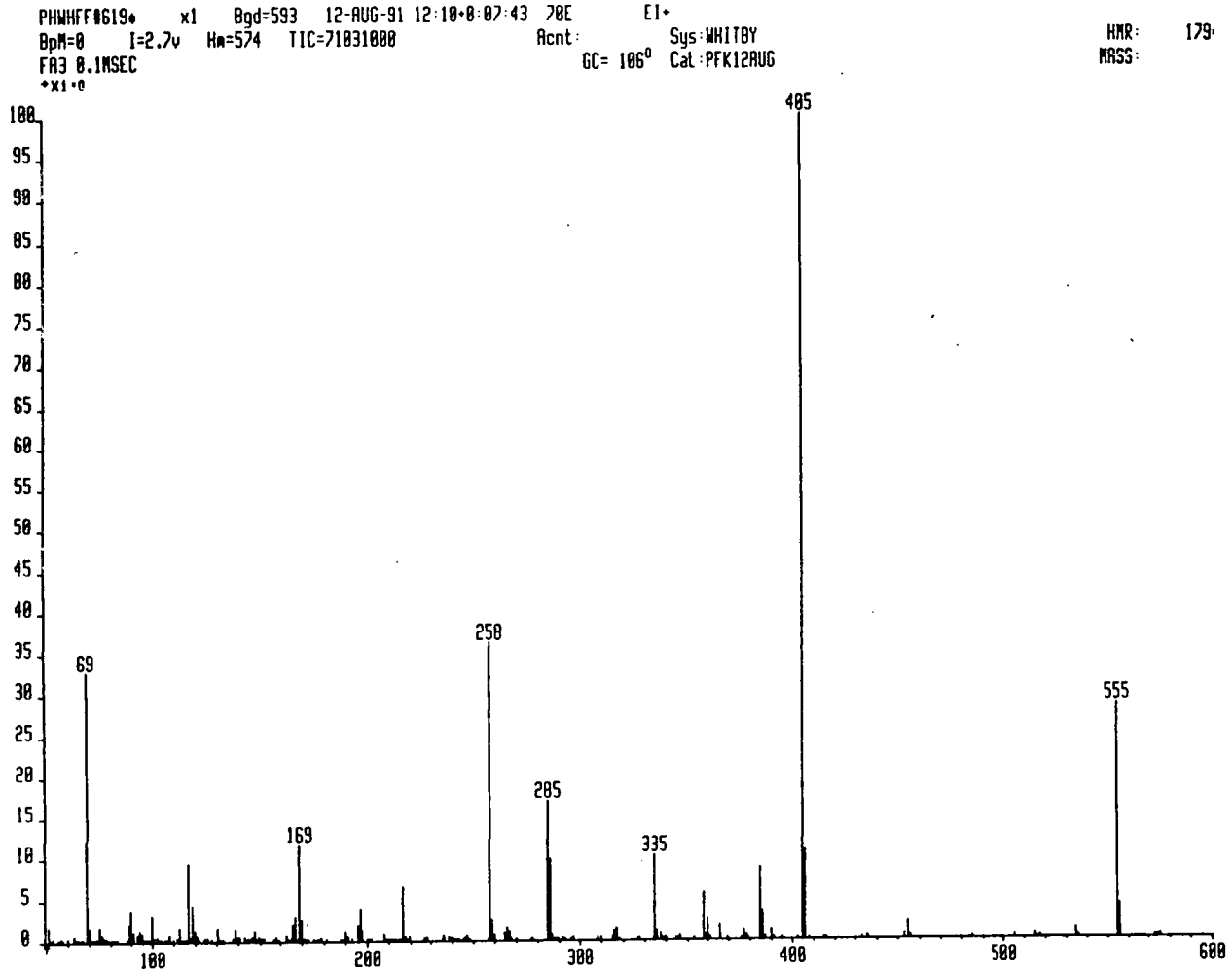
Mass	% Base
51.01	2.29
56.05	5.85
57.05	1.08
69.00	4.92
70.06	2.75
71.07	1.41
72.08	100.00
73.08	4.62
77.02	2.28
86.06	5.52
114.10	20.49
115.09	1.58
134.07	1.38
144.08	1.69
194.03	2.75
204.07	2.17
208.04	14.87
222.04	2.14
226.07	1.74
245.08	2.12
246.09	1.06
265.08	3.94
266.08	1.63

Mass Spectrum No.38 M.W. 324.5



Mass	% Base				
48.97	3.16	118.89	34.37	302.83	0.54
50.99	26.92	120.88	10.76	304.87	0.17
54.03	2.40	128.88	8.98	306.86	0.16
59.02	4.76	130.88	8.75	320.81	0.21
61.97	100.00	132.89	2.10	321.84	10.13
62.99	27.55	135.94	8.57	322.83	0.72
63.97	30.99	137.94	5.66	323.83	9.62
65.00	14.25	138.98	6.46	324.84	0.70
68.98	38.14	143.88	13.12	325.84	3.41
71.01	2.14	145.88	13.11	326.88	0.24
72.96	3.46	147.87	4.04	327.80	0.22
73.97	6.22	150.98	6.98	337.80	0.52
74.98	4.11	155.88	3.84	339.81	0.63
75.97	2.82	157.88	2.98	341.78	0.35
77.00	51.09	158.98	37.10	343.79	0.23
78.01	5.49	159.94	2.02	357.79	0.50
81.93	9.06	169.90	4.71	359.81	0.52
83.92	5.71	170.90	5.15	360.85	0.14
84.94	2.11	171.89	4.69	361.79	0.41
85.96	10.31	172.89	4.87		
87.97	4.30	173.89	2.10		
89.00	8.06	174.93	6.04		
90.00	2.19	205.83	12.40		
91.01	3.15	207.82	17.46		
93.93	3.73	209.83	7.26		
94.99	10.65	239.93	87.51		
97.00	3.29	240.94	6.08		
99.98	5.11	241.93	28.18		
100.99	7.86	251.92	0.27		
107.93	10.36	261.93	0.16		
108.94	37.53	266.98	0.10		
109.92	7.93	283.90	0.17		
110.92	23.38	285.89	0.27		
111.92	2.05	286.89	1.88		
112.94	5.20	287.90	0.21		
114.99	4.00	288.88	1.04		
116.88	36.81	290.89	0.17		

Mass Spectrum No.39 M.W. 574



Mass	% Base				
48.98	0.52	149.95	0.48	357.90	5.57
50.98	1.58	157.96	0.46	358.91	0.52
53.00	0.36	162.95	0.57	359.91	2.51
60.01	0.32	165.97	1.95	365.89	1.68
62.99	0.54	166.98	2.99	376.89	0.95
68.97	32.74	168.94	11.70	377.90	0.50
69.99	1.50	169.96	2.54	384.88	8.57 F
74.98	1.64	189.97	1.05	385.91	3.32 F
75.98	0.70	190.96	0.42	386.92	0.35
76.98	0.43	195.95	1.75	389.90	1.03
88.98	1.85	196.97	3.73	404.88	100.00 F
89.99	3.59	197.97	1.11	405.96	10.87 F
90.99	1.02	207.95	0.69	434.91	0.35
92.97	0.74	216.95	6.44	452.90	0.39
93.97	1.21	217.95	0.46	454.92	2.08
94.98	0.88	219.93	0.37	515.31	0.38
99.96	3.14	227.92	0.34	534.90	0.96
100.98	0.36	235.95	0.53	554.87	28.54 F
101.99	0.41	237.93	0.47	555.99	4.01 F
107.97	0.67	246.93	0.55		
111.96	0.34	257.92	36.18		
112.96	1.46	258.93	2.54		
116.99	9.33	259.94	0.57		
117.99	0.46	264.94	0.93		
118.96	4.21	265.94	1.45		
119.97	1.13	266.95	1.08		
120.98	0.62	284.92	16.87 F		
124.97	0.35	285.94	9.83 F		
125.97	0.33	286.94	0.78		
130.96	1.42	314.91	0.36		
138.97	1.27	315.92	1.03		
139.97	0.46	316.93	1.25		
140.98	0.45	334.92	10.26		
142.95	0.42	335.92	1.06		
145.97	0.35	337.90	0.70		
146.98	0.40	339.91	0.31		
147.98	1.19	346.91	0.37		

APPENDIX FOUR

Colloquia, Conferences and Induction Course

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:-

(1) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(2) lectures organised by Durham University Chemical Society;

(3) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

(4) details of the postgraduate induction course.

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS.
OCTOBER 1988 - SEPTEMBER 1991

(Those attended are marked *)

18.10.88 Dr. J. Dingwall (Ciba Geigy)

* *Phosphorous Containing Amino Acids: Biologically Active Natural and Unnatural Products*

24.11.88 Drs. R.R. Baldwin and R.W. Walker (Hull University)

Combustion: Some Burning Problems

2.12.88 Dr. G. Hardgrove (St. Olaf College, USA)

Polymers in the Physical Chemistry Laboratory

25.1.89 Dr. L. Harwood (Oxford University)

Synthetic Approaches to Phorbols Via Intramolecular Furan Diels-Alder Reactions:

Chemistry Under Pressure

2.2.89 Prof. L.D. Hall (Addenbrooke's Hospital, Cambridge)

* *NMR - A Window to the Human Body*

9.2.89 Prof. J.E. Baldwin (Oxford University)

* *Recent Advances in the Bioorganic Chemistry of Penicillin Biosynthesis*

15.2.89 Dr. A.R. Butler (St. Andrews University)

* *Cancer in Linxiam: The Chemical Dimension*

16.2.89 Prof. B.J. Aylett (Queen Mary College, London)

Silicon Based Chips: The Chemist's Contribution

1.3.89 Dr. R.J. Errington (Newcastle University)

Polymetalate Assembly in Organic Solvents

15.3.89 Dr. R. Aveyard (Hull University)

Surfactants at your Surface

20.4.89 Dr. M. Casey (Salford University)

Sulphoxides in Stereoselective Synthesis

27.4.89 Dr. D. Crich (University College, London)

* *Some Novel Uses of Free Radicals in Organic Synthesis*

11.5.89 Dr. J. Frey (Southampton University)

Spectroscopy of the Reaction Path: Photodissociation Raman Spectra of NOCl

10.9.89 Prof. J.I.G. Cadogan (B.P.)

From Pure Science to Profit

17.10.89 Dr. F. Palmer (Nottingham University)

* *Thunder and Lightning*

25.10.89 Prof. C. Floriani (Lausanne University, Switzerland)

Molecular Aggregates - A Bridge Between Homogeneous and Heterogeneous Systems

1.11.89 Dr. J.P.S. Badyal (Durham University)

Breakthroughs in Heterogeneous Catalysis

9.11.89 Prof. N.N. Greenwood (Leeds University)

Novel Cluster Geometries in Metalloborane Chemistry

10.11.89 Prof. J.E. Bercaw (California Institute of Technology)

* *Synthetic and Mechanistic Approaches to Ziegler-Natta Polymerisation of Olefins*

13.11.89 Dr. J. Becher (Odense University)

* *Synthesis of New Macrocyclic Systems using Heterocyclic Building Blocks*

16.11.89 Dr. D. Parker (Durham University)

* *Macrocycles, Drugs and Rock 'n' Roll*

29.11.89 Prof. D.J. Cole-Hamilton (St. Andrews University)

New Polymers from Homogeneous Catalysis

30.11.89 Dr. M.N. Hughes (King's College, London)

A Bug's Eye View of the Periodic Table

4.12.89 Dr. D. Graham (B.P. Research Centre)

How Proteins Absorb on Interfaces

6.12.89 Dr. R.L. Powell (ICI)

* *The Development of CFC Replacements*

7.12.89 Dr. A. Butler (St. Andrews University)

* *The Discovery of Penicillin: Facts and Fancies*

13.12.89 Dr. J. Klinowski (Cambridge University)

Solid State NMR Studies of Zeolite Cages

15.12.89 Prof. R. Huisgen (Universitat Munchen)

* *Recent Mechanistic Studies of [2+2] Additions*

24.1.90 Dr. R.N. Perutz (York University)

Plotting the Course of C-H Activations with Organometallics

31.1.90 Dr. U. Dyer (Glaxo)

Synthesis and Conformation of C-Glycosides

1.2.90 Prof. J.H. Holloway (Leicester University)

Noble Gas Chemistry

7.2.90 Dr. D.P. Thompson (Newcastle University)

The role of Nitrogen in Extending Silicate Crystal Chemistry

8.2.90 Rev. R. Lancaster (Kimbolton Fireworks)

* *Fireworks - Principles and Practice*

12.2.90 Prof. L. Lunazzi (University of Bologna)

Application of Dynamic NMR to the Study of Conformational Isomerism

14.2.90 Prof. D. Sutton (Simon Fraser University, Vancouver B.C.)

Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium

15.2.90 Prof. L. Crombie (Nottingham University)

The Chemistry of Cannabis and Khat

21.2.90 Dr. C. Bleasdale (Newcastle University)

* *The Mode of Action of some Anti-tumour Agents*

22.2.90 Prof. D.T. Clark (ICI Wilton)

Spatially Resolved Chemistry using Nature's Paradigm in the Advanced Materials Area

28.2.90 Dr. R.K. Thomas (Oxford University)

Neutron Reflectometry from Surfaces

1.3.90 Dr. J.F. Stoddart (Sheffield University)

* *Molecular Lego*

8.3.90 Dr. A.K. Cheetham (Oxford University)

Chemistry of Zeolite Cages

21.3.90 Dr. I. Powis (Nottingham University)

Spinning off in a huff: Photodissociation of Methyl Iodide

23.3.90 Prof. J.M. Bowman (Emory University)

Fitting Experiment with Theory in Ar-OH

9.7.90 Prof. L.S. German (USSR Academy of Sciences - Moscow)

* *New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes*

9.7.90 Prof. V.E. Platonov (USSR Academy of Sciences - Novosibirsk)

* *Polyfluoroindanes: Synthesis and Transformation*

9.7.90 Prof. I.N. Rozhkov (USSR Academy of Sciences - Moscow)

* *Reactivity of Perfluoroalkyl Bromides*

11.10.90 Dr. W.A. MacDonald (ICI Wilton)

Materials for the Space Age

24.10.90 Dr. M. Bochmann (U.E.A.)

Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls

26.10.90 Prof. R. Soulen (South Western University, Texas)

* *Preparation and Reactions of Bicycloalkenes*

31.10.90 Dr. R. Jackson (Newcastle University)

* *New Synthetic Methods: a-aminoacids and Small Rings*

1.11.90 Dr. N. Logan (Nottingham University)

Rocket Propellants

6.11.90 Dr. P. Kocovsky (Uppsala)

* *Stereo-controlled Reactions Mediated by Transition and Non-Transition Metals*

7.11.90 Dr. D. Gerrard (B.P.)

Raman Spectroscopy for Industrial Analysis

7.11.90 Dr. W. Dolbier (Gainsville, Florida)

* *Rearrangements of bis CF_3 Vinyl Aromatics: a Route to 1,3,5-Hexatrienes*

8.11.90 Dr. S.K. Scott (Leeds University)

Clocks, Oscillations and Chaos

14.11.90 Prof. T. Bell (SUNY, Stony Brook)

* *Functional Molecular Architecture and Molecular Recognition*

21.11.90 Prof. J. Pritchard (Queen Mary and Westfield College, London)

Copper Surfaces and Catalysts

28.11.90 Dr. B.J. Whitaker (Leeds University)

Two-dimensional Velocity Imaging of State-selected Reaction Products

29.11.90 Prof. D. Crout (Warwick University)

* *Enzymes in Organic Synthesis*

5.12.90 Dr. P.G. Pringle (Bristol University)

Metal Complexes with Functionalised Phosphines

13.12.90 Prof. A.H. Cowley (University of Texas)

New Organometallic Routes to Electronic Materials

15.1.91 Dr. B.J. Alder (Lawrence Livermore Labs., California)

Hydrogen in all its Glory

17.1.91 Dr. P. Sarre (Nottingham University)

Comet Chemistry

23.1.91 Prof. J.S. Higgins (Imperial College, London)

Rheology and Molecular Structure of Ionomer Solutions

24.1.91 Dr. P.J. Sadler (Birkbeck College, London)

Design of Inorganic Drugs: Precious Metals, Hypertension and HIV

30.1.91 Prof. E. Sinn (Hull University)

New Results in High T_c Superconductivity

31.1.91 Dr. D. Lacey (Hull University)

* *Liquid Crystals*

6.2.91 Dr. R. Bushby (Leeds University)

* *Biradicals and Organic Magnets*

14.2.91 Dr. M.C. Petty (Durham University)

Molecular Electronics

20.2.91 Prof. B.L. Shaw (Leeds University)

New Chemistry with Transition Metal Multihydrides

28.2.91 Dr. J. Brown (Oxford University)

Can Chemistry Provide Catalysts Superior to Enzymes?

6.3.91 Dr. C.M. Dobson (Oxford University)

NMR Studies of Dynamics in Molecular Crystals

7.3.91 Dr. J. Markham (ICI Pharmaceuticals)

DNA Fingerprinting

24.4.91 Prof. R.R. Schrock (MIT)

Metal-ligand Multiple Bonds and Metathesis Initiators

25.4.91 Prof. T. Hudlicky (Virginia Polytechnic Institute)

* *Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products*

20.6.91 Prof. M.S. Brookhart (University of North Carolina)

Olefin Polymerisations, Oligomerisations and Dimerisations Using Electrophilic Late Transition Metal Catalysts

29.7.91 Dr. M.A. Brimble (Massey University, New Zealand)

* *Synthetic Studies Towards the Antibiotic Griseusin-A*

Research Conferences Attended

Dec 88	Royal Society of Chemistry Perkin Division, One Day Meeting,York University.
April 1989	North East Graduate Symposium, Durham University.
Aug 89	European Symposium on Fluorine Chemistry, Leicester University.
15.12.89	Royal Society of Chemistry Perkin Division, One Day Meeting, Durham University.
7.3.90	SCI Graduate Symposium, York University.
2.4.90	North East Graduate Symposium, Newcastle University.
Sept 91	13th International Symposium on Fluorine Chemistry, Ruhr Universität, Bochum, Germany.

First Year Induction Course

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisation - Dr. E.J.F. Ross

Safety Matters - Dr. M.R. Crampton

Electrical Appliances - Mr. B.T. Barker

Chromatography and Microanalysis - Mr. T.F. Holmes

Atomic Absorptiometry and Inorganic Analysis - Mr. R. Coult

Library Facilities - Mr. R.B. Woodward

Mass Spectrometry - Dr. M. Jones

Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews

Glass-blowing Techniques - Mr. R. Hart and Mr. G. Haswell

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