The synthesis and properties of some polyesters containing a perfluoroether link

Reeves, Neil

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TO TERRY.

UNIVERSITY OF DURHAM

A THESIS

entitled

THE SYNTHESIS AND PROPERTIES OF SOME POLYESTERS CONTAINING A PERFLUOROETHER LINK

Submitted by

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(GRADUATE SOCIETY)

A candidate for the degree of Doctor of Philosophy

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ACKNOWLEDGEMENTS

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Assistance from members of the technical staff, particularly Mr. L. Chadwick and Mr. D. Hunter, is greatly appreciated. The author would also like to thank the Ministry of Technology for a maintenance grant and for the facilities made available for analyses.

MEMORANDUM

The work described in this thesis was carried out in the Chemistry Laboratories of the University of Durham between September 1967 and May 1970. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

Part of this work has been the subject of the following publications:

N. Reeves, W.J. Feast and W.K.R. Musgrave,
J. Chem. Soc. (D), 1970, 67.

W.J. Feast, W.K.R. Musgrave and N. Reeves,
J. Chem. Soc. (C), accepted for publication.

SUMMARY

A new synthesis of perfluoro-oxydiacetic acid is described. The halogen exchange method for the preparation of polyfluoroaliphatic compounds from polychloroaliphatic compounds is extended to perchloro-2,5-dihydrofuran; the fluorination of which produces perfluoro- and 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofurans, which on oxidation give perfluoro-oxydiacetic acid. Several chlorofluoro-2,5-dihydrofurans obtained as by-products are also characterised and some reactions of chlorofluoro-2,5-dihydrofurans with nucleophiles investigated.

The reactions of perfluoro-oxydiacetic acid and some of its derivatives are studied, particularly with regard to halodecarboxylation. It is found that the molecule undergoes fragmentation in preference to halodecarboxylation.

The preparation of 2,2,4,4-tetrafluoro-3-oxapentane diol and its polymerisation with three aromatic diacid chlorides to produce polyesters is also described. The physical properties of these polyesters are compared to the analogous polyesters prepared from hexafluoropentane diol, the effect of replacement of a difluoromethylene link by an ether link causing a reduction in the thermal stability of the polymer and producing a small increase in the value of the glass transition temperature.

ERRATA

Page 24, line 2.	For permanhanate read permanganate.
Page 106, line 16.	For J_{AX}, 7·5 Hz and J_{BX}, 4·6 Hz, read J_{BX}, 7·5 Hz and J_{AX}, 4·6 Hz.
Page 157.	No. 26 should read: 2,2,4-Trichloro-5,5-difluoro-3-methoxy-2,5-dihydrofuran.

CONTENTS

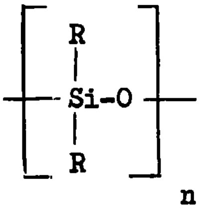
Chapter I. Synthesis of perfluoro-oxydiacetic acid.

Chapter II. Reactions of perfluoro-oxydiacetic acid and its derivatives.

Chapter III. The fluorination of perchloro-2,5-dihydrofuran, and reactions of some chlorofluoro-2,5-dihydrofurans with nucleophiles.

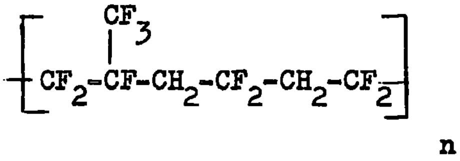
GENERAL INTRODUCTION

A great variety of polymeric materials are known both natural and synthetic, and these materials are used for many different purposes ranging from food and clothing through to lubricants, engineering components, structural and decorative materials. One area in which modern technology has need for a material is in the thermally stable elastomer range. A lot of work is currently being carried out to find improvements in or replacements for the materials which are at present being used, i.e. organopolysiloxanes



$$\left[\begin{array}{c} R \\ | \\ -\mathrm{Si}-O- \\ | \\ R \end{array}\right]_n$$

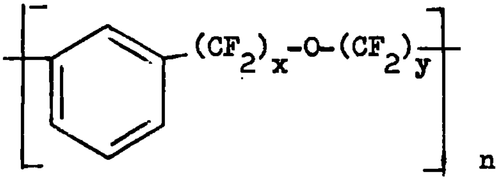
and the copolymer of hexafluoropropene and vinylidene fluoride (Viton A)



$$\left[CF_2-\overset{\displaystyle CF_3}{\overset{|}{C}}F-CH_2-CF_2-CH_2-CF_2 \right]_n$$

Any material which showed superior hydrolytic stability (over the Silicones) and/or thermal stability (over Viton A) would be of value.

Although numerous elastomers have been developed, a material having elastomeric properties from below room temperature to 250°C, and being thermally stable above 250°C is still sought. The primary aim of this research work was the synthesis of polyethers of the structure (I).



(I)

(where x and y are odd)

Theoretical considerations based on knowledge of the thermal stability and elastomeric properties of known polymers leads to the hypothesis that the incorporation of an ether link into a perfluoroalkylene linked aromatic polymer may produce a polymer with the above sought after properties.

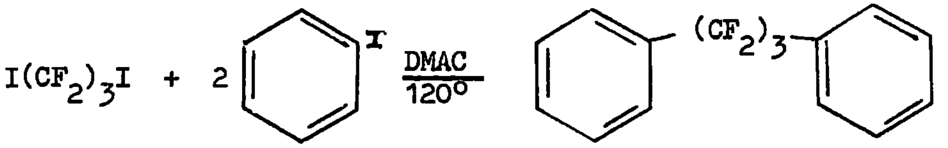
For the production of polymers of type (I), the synthesis of possible precursors had to be investigated. The initial objective was the synthesis of di-iodides of the type

$$I(CF_2)_xO(CF_2)_yI \qquad (x,y = 1,3 \text{ etc.})$$

(II)

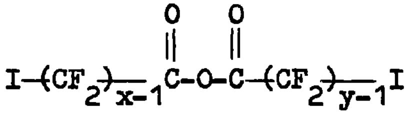
since the projected polymerisation was to be of the polycondensation type with meta-iodo substituted benzenes via a copper coupling reaction[1] devised by workers at R.A.E. Farnborough Materials Department.

For example:



72%. Ref.1.

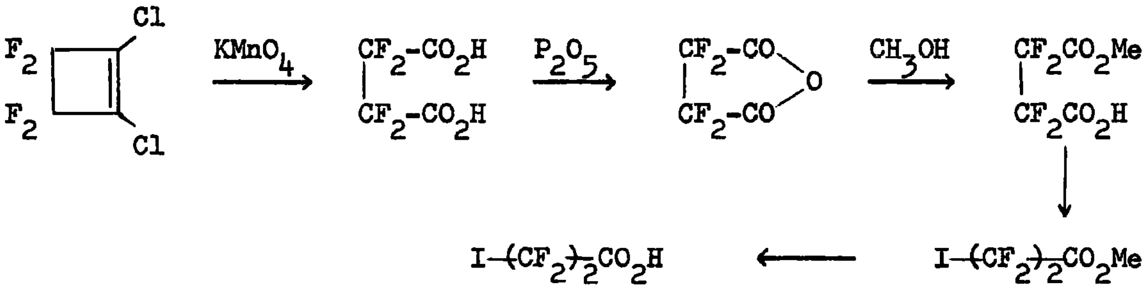
Initially, the reaction of anhydrides with sulphur tetrafluoride was investigated, since a possible method of preparation of (II) was the fluorination of anhydrides of the type



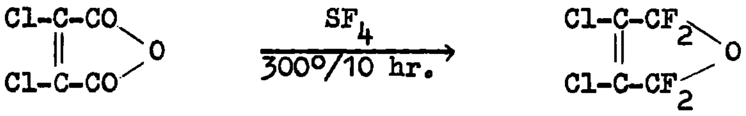
$$I\text{-}(CF_2)_{x-1}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CF_2)_{y-1}I$$

(III)

using sulphur tetrafluoride. The preparation of these anhydrides was envisaged from the intermolecular dehydration of ω-iodoperfluoro-acids, for example, I $(CF_2)_2CO_2H$, these being synthesised via the following scheme:[2]



An analogous sequence can be written for perfluoroadipic acid to give $I\text{-}(CF_2)_4CO_2H$; however the dehydration of perfluoroadipic acid to give the cyclic anhydride could not be achieved, although claimed in the patents literature,[3] which on hindsight is reasonable since this would involve the formation of a seven membered ring, and is difficult even in the 'hydrocarbon' case. At the same time the reaction of trifluoroacetic anhydride with sulphur tetrafluoride was studied, over a wide temperature range both with and without boron trifluoride as catalyst, the only product being trifluoroacetyl fluoride. According to the literature[4], the only anhydride which retains the C-O-C link on fluorination with sulphur tetrafluoride is dichloromaleic anhydride, the product of the reaction being 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV).

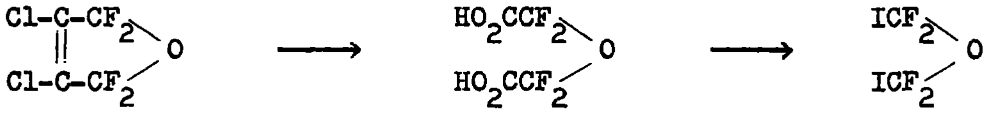


(IV)

46%[4]

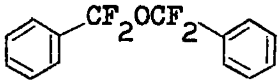
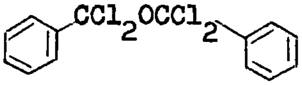
Other anhydrides produce either acyl fluorides or bis(trifluoromethyl) derivatives. Hence alternative syntheses were sought for compounds of type (II).

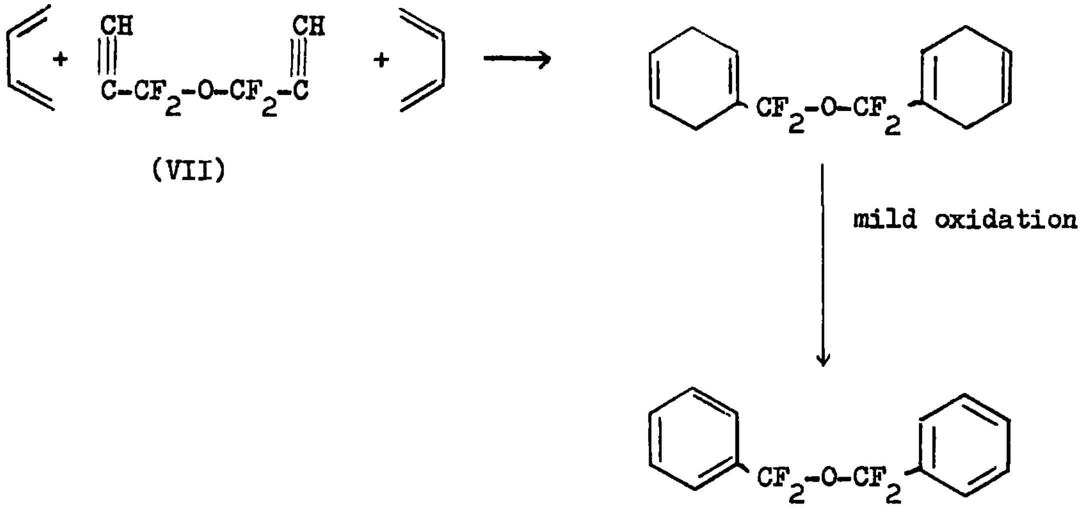
A possible route was oxidation of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) to give perfluoro-oxydiacetic acid (V), which it was hoped would give 1,3-di-iodotetrafluoro-2-oxapropane (VI) (i.e. II, x = y = 1) on decarboxylation in the presence of iodine.



(IV) (V) (VI)

The oxidation of (IV) to (V) was achieved quite smoothly the problems encountered in the synthesis, and oxidation, of (IV) being described in Chapter I. Decarboxylation of the acid (V) by Hunsdiecker's method[5] did not produce (VI) and alternative possible syntheses of (VI) from (V) were attempted but no trace of (VI) was found. This work is described in Chapter II.

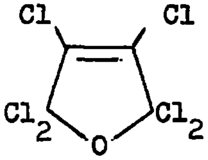
However, derivatives of (V) could be used in the formation of polymers, so the effect of substituting a -CF$_2$-O-CF$_2$- link for a -CF$_2$-CF$_2$-CF$_2$- link in the polymer backbone could be investigated. The synthesis of a model compound  was also attempted; the first attempt involving the reaction of benzoic anhydride with phosphorus pentachloride. This was to be followed by antimony trifluorodichloride but the first step involving the formation of  did not take place; it resulted in cleavage of the C-O-C bond, the product being benzoyl chloride. An alternative possible synthesis was via a Diels Alder reaction:



The synthesis of the diacetylene (VII) was envisaged as proceeding through a diketone $CH_3COCF_2OCF_2COCH_3$, but all attempts to prepare this diketone failed. Alternative syntheses of (VII) via Wittig reactions on the diacyl chloride of (V) also failed.

Due to the failure of all routes to prepare precursors for polymers of type (I), it was decided to prepare polyesters incorporating the $-CF_2-O-CF_2-$ link, since this would show the effect of this link on polymer properties, particularly on the glass transition temperature, although the thermal stability of the polyesters could not be expected to be as good as that expected of polymers of structure (I). The diol of perfluoro-oxydiacetic acid was prepared and used for the preparation of polyesters by polycondensation with diacid chlorides, this being described in Chapter IV. Polyesters derived from 2,2,3,3,4,4-hexafluoropentane-1,5-diol are known in the literature[6], and the physical and thermal properties of the polyesters prepared from 3-oxa-2,2,4,4-tetrafluoropentane-1,5-diol are compared to those from 2,2,3,3,4,4-hexafluoropentane-1,5-diol in Chapter V.

The remaining chapter, Chapter III, deals with the products isolated from the fluorination of perchloro-2,5-dihydrofuran



This work was instigated to find an alternative synthesis of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran, Chapter I describes the difficulties encountered in trying to reproduce the original preparation.[4]

CHAPTER I.

SYNTHESIS OF PERFLUORO-OXYDIACETIC ACID.

Introduction.

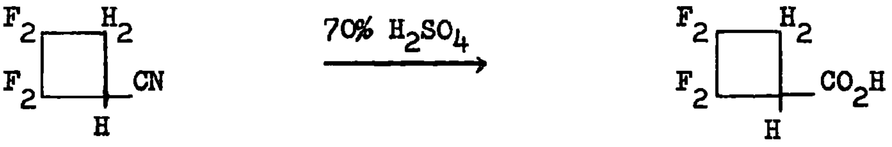
Decarboxylation of the appropriate dicarboxylic acid in the presence of iodine seemed a reasonable synthetic route for the preparation of highly fluorinated diiodides with the general formula (II), and indeed

$$I-(CF_2)_x-O-(CF_2)_y-I$$

(II)

the synthesis of 3-oxa-1,5-diiodooctafluoropentane (II, x = y = 2) from perfluorooxydipropionic acid has been reported[7], although no yield was given. Several alternative methods for effecting the replacement of the carboxyl function of a fluorinated acid by an iodine atom have been established, and the main difficulty would appear to be the synthesis of the dibasic acids.

Generally, the preparation of fluorinated acids involves either introduction of fluorine into acids or their derivatives, or oxidation of fluorinated olefins. Less general methods involve hydrolysis of fluorinated amides[8] or nitriles[9]; for example



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The usual method of introducing fluorine into acids involves electrochemical fluorination which is the electrolysis at high current density, but low voltage (5-7 volts), of a solution of the organic compound in anhydrous hydrogen fluoride. Hydrogen is liberated at the cathode and the organic material is fluorinated at the anode by an unknown mechanism. This method has not been used a great deal for the fluorination of dibasic acids, but the electrochemical fluorination of oxydipropionyl fluoride gives perfluorooxydipropionyl fluoride:[7,10]

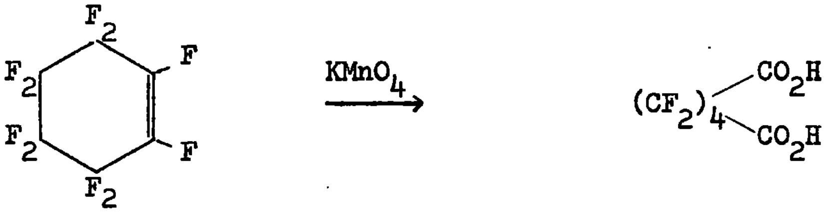
$$O(CH_2CH_2COF)_2 \longrightarrow O(CF_2CF_2COF)_2 \qquad 3{\cdot}7\%^{\,10}$$

However the practical difficulties involved with this method, and the low yields usually obtained, made this route unattractive.

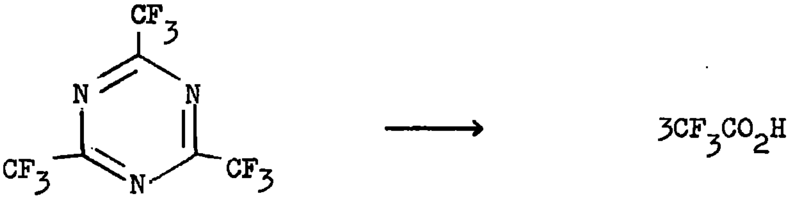
It has been found that oxidation of fluorinated olefins produces fluoroacids,[11] the main problem being the availability of the olefin. For example, perfluoropropionic acid may be prepared by the following route:[12]

$$C_2F_5I + H_2C{:}CF_2 \longrightarrow C_2F_5CH_2CF_2I \longrightarrow C_2F_5CH{:}CF_2 \longrightarrow C_2F_5CO_2H$$

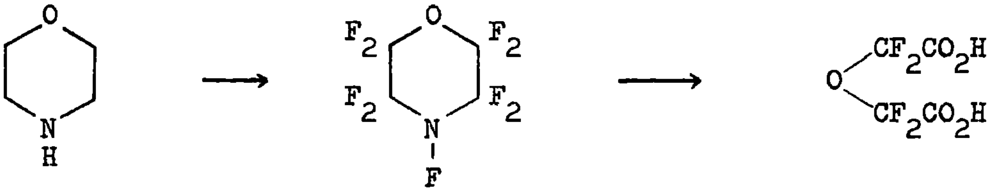
This method is used extensively for the synthesis of dibasic acids, by oxidation of cyclic olefins, for example:[13]



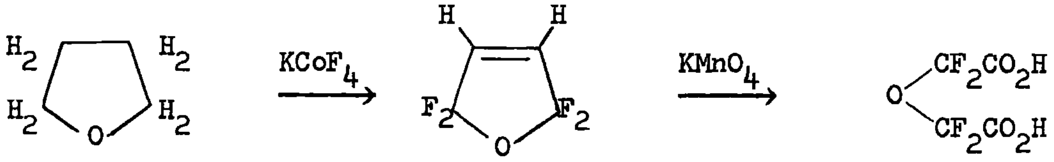
Specific methods of preparation for particular acids have been devised, as in the hydrolysis of tris(trifluoromethyl) triazines to give trifluoroacetic acid:[14]



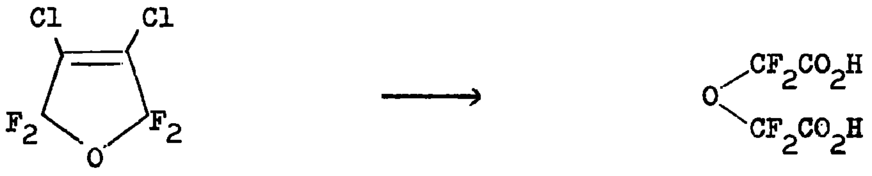
The synthesis of perfluoro-oxydiacetic acid has been reported via hydrolysis of perfluoro-N-fluoromorpholine, itself prepared by electrochemical fluorination of morpholine in 8% yield:[15]



The oxidation of 2,2,5,5-tetrafluoro-2,5-dihydrofuran also affords perfluoro-oxydiacetic acid, the furan derivative being formed in 3·5% yield from the fluorination of tetrahydrofuran with potassium tetrafluorocobaltate;[16] this method was published after the commencement of this work.

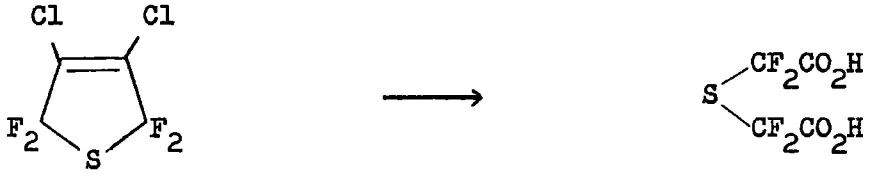


Greenwald et al., have reported the oxidation of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) to give perfluoro-oxydiacetic acid,[17]



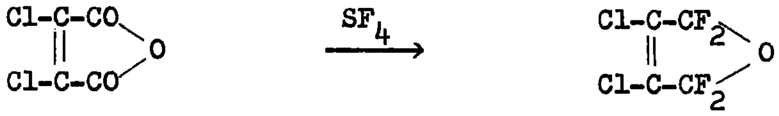
(IV)

although no experimental conditions or yields are given. The oxidation of the sulphur analogue 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrothiophen to give perfluorothiodiglycolic acid was reported in the patent



literature.[18]

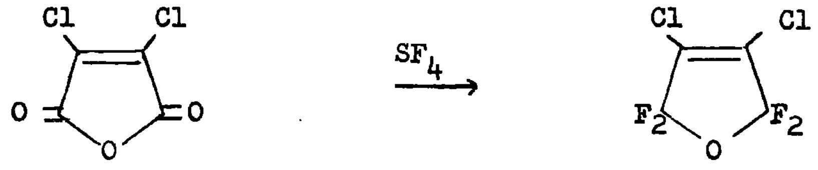
It was decided to prepare perfluoro-oxydiacetic acid from the oxidation of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV), the latter being prepared by the method of Hasek et al.[4], from the fluorination of dichloromaleic anhydride. This chapter relates the difficulties in obtaining reproducible yields for the fluorination stage. Because of



these difficulties an alternative synthesis of (IV) involving the fluorination of perchloro-2,5-dihydrofuran (dealt with in Chapter III) was developed. The latter was prepared via the cyclisation of perchlorocrotonyl chloride.[19]

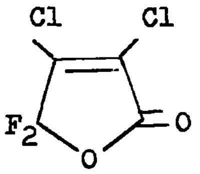
Discussion.

In the previously reported reaction of dichloromaleic anhydride with sulphur tetrafluoride[4], only one product 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) was mentioned.

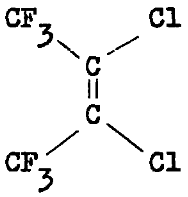


(IV)

Upon repeating this reaction the number of major products isolated varied from one to four depending on the reaction conditions used (Table 1). Treatment of dichloromaleic anhydride with sulphur tetrafluoride, prepared by Tullock's method[20], and using short reaction times and low sulphur tetrafluoride to anhydride ratios, yielded 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (VIII), as the only product. On the other hand, with longer reaction times and high molar ratios of reactants, the products were mixtures of *cis*- and *trans*-2,3-



(VIII)



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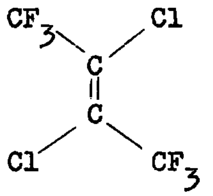
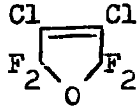
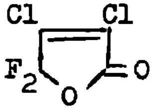
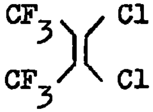
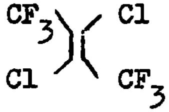
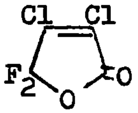
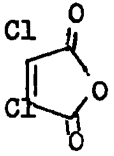


(X)

Table 1.

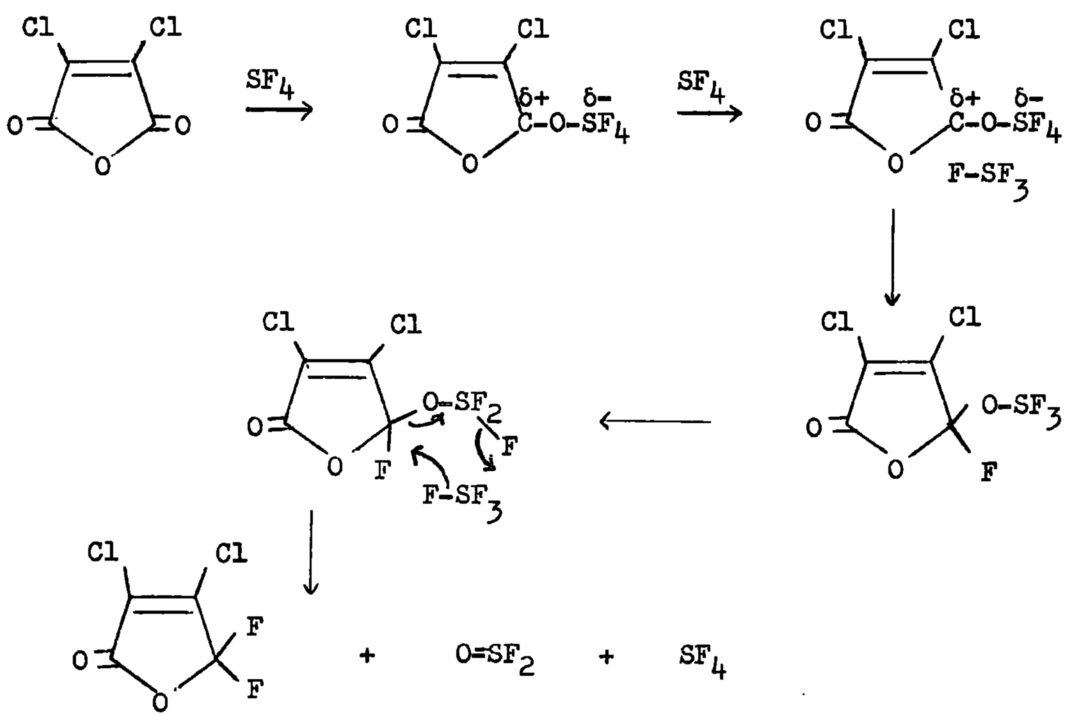
Run No.	Moles SF_4	Moles anhyd.	SF_4: anhyd.	Bomb size mls.	Temp. ^oC	Time hrs.	% yield[a]	Product %			
											
1	0·29	0·12	2·4:1	150	290	13	51	-	100	-	-
2	0·17	0·04	4·3:1	50	300	15	44	-	100	-	-
3	1·13	0·20	5·6:1	500	300	20	66	-	90	-	-
4	0·77	0·12	6·3:1	500	300	51	76	51	35	14	
5	0·97	0·18	5·4:1	800	300	64	62	29	22	44	
6	1·16	0·18	6·4:1	800	300	71	74	55	-	45	
7	1·19	0·18	6·6:1	800	300	72	73	53	-	47	
8	1·12	0·18	6·2:1	800	300	63	75	49	-	51	
 + SF_4											
9	0·16	0·03	5·3:1	50	290	22	34	37	63	-	-
10	0·61	0·08	7·7:1	500	300	86	72	23	40	17	20
 + SOF_2											
11	1·0	0·10	10·0:1	500	290	63	57	24	16	48	4

[a] Total yield of all products w.r.t. anhydride consumed.

dichlorohexafluorobut-2-enes (IX, X), 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV), and 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (VIII). The products were separated by preparative scale gas-liquid chromatography, and the structures of (IV) and (VIII) confirmed by spectroscopic data; thus both (IV) and (VIII) had only one type of ^{19}F resonance at -91·3 p.p.m. and -80·5 p.p.m. respectively from hexafluorobenzene; infra-red spectroscopy showed $>C=C<$ absorbtions at 1668 and 1640 cm^{-1} for (IV) and (VIII) respectively, with $>C=O$ at 1856 cm^{-1} for (VIII), and mass spectrometry indicated correct molecular weight, isotope and breakdown patterns expected for (IV) and (VIII). Further, both had correct elemental analysis, and alkaline hydrolysis gave dichloromaleic acid. The characterisation of (IX) and (X) was by mass and infra-red spectroscopies, the geometry being assigned on the basis of a carbon-carbon double bond stretching frequency (1610 cm^{-1}) observed in the infra-red spectrum of one isomer, the cis, and not the other. The carbon-carbon stretching mode would produce a change in dipole moment, and hence be infra-red active, for the cis isomer, but no change in dipole moment would occur for this mode in the trans isomer.

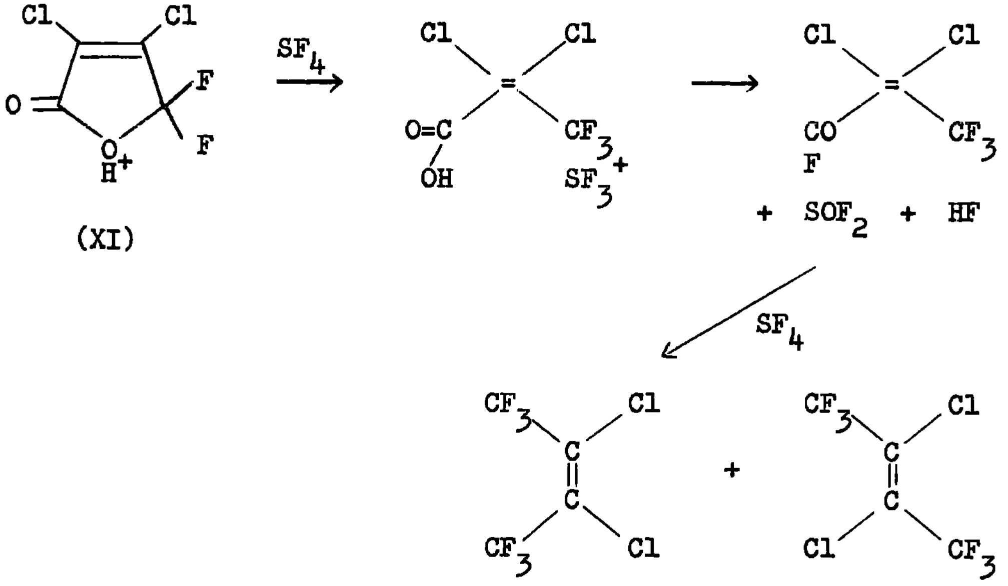
Blake and Schaar have reported a detailed investigation of the reaction of sulphur tetrafluoride with dichloromaleic anhydride,[21] emphasising the 'paramount importance' of pressure and the earlier authors are critizised for not reporting full experimental details, and consequently involving latter workers in unnecessary labour to find optimum conditions. The results in Table 1 suggest that this amounts to over-emphasis of the importance of pressure by comparison with other variables such as molar ratio of reactants, purity of sulphur tetrafluoride, temperature, and duration of reaction. From Blake and Schaar's investigation, it would seem that a change in molar ratio of anhydride to sulphur tetrafluoride from 1 to 2•32 to 1 to 2•34 together with a calculated pressure variation of 0•6%, should result in increase in the yields of ether (IV) by a factor of 2•7, and a change in the yield of lactone (VIII) by a factor 0•7, (see Reference 21, Table 1, runs 2 and 3) when all other parameters were held constant. In the present work the observed pressure never exceeded ca. 40 Ats. for the experiments listed in Table 1, even though the calculated pressures were in the range 50-160 Ats., and despite working at temperatures expected to be well above the critical temperatures of the gaseous materials. This observation casts doubt on the apparent reaction pressure dependance reported by Blake and Schaar. A possible explanation for the low observed pressure, after carefully excluding instrumental or manipulative errors, is that complex formation may have taken place between the reactants and effectively removed some of the volatile materials from the gas phase. Well characterised complexes of sulphur tetrafluoride have been obtained, albeit under very different conditions.[22,23] For example, the action of sulphur tetrafluoride on germanium dioxide, GeO_2, gives a product which analyses for the formula $GeF_4.2SF_4$.[22]

The mechanism for the fluorination previously put forward[21] postulates the formation of the lactone (VIII) as a reaction intermediate which is then further fluorinated, the formation of (VIII) being catalysed by hydrogen fluoride. Although no hydrogen fluoride was added, and the presence of dichloromaleic acid could not be detected by infra-red spectroscopy, the dichloromaleic anhydride may have contained trace amounts of the parent acid, and this could have provided sufficient hydrogen fluoride, by reaction with sulphur tetrafluoride, to act as a catalyst. From the results in Table 1 it can be seen that the lactone (VIII) could be fluorinated to the ether (IV) with sulphur tetrafluoride, albeit in low yield. Also, significant quantities of *cis*- and *trans*-2,3-dichlorohexafluorobut-2-enes were isolated, which were not mentioned by earlier workers. A possible mechanism to account for all the products isolated, could be fluorination of one carbonyl of the anhydride as postulated by Hasek et al.,[4] to give the lactone (VIII):



(VIII)

Protonation of the ether oxygen of (VIII) could then occur by any catalytic amount of hydrogen fluoride present, to give an intermediate (XI), which could react further with sulphur tetrafluoride in either of two ways: either by fluorination of the second carbonyl as suggested by Blake and Schaar[21] to give the ether (IV), or attack by sulphur tetrafluoride on the fluorinated carbon to produce a ring opened intermediate containing a carboxylic acid group. This could react further with sulphur tetrafluoride to produce cis-dichlorohexafluorobut-2-ene, which then isomerises under reaction conditions to give the cis/trans mixture isolated.

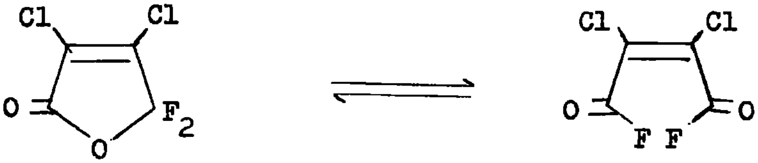


(XI)

(IX)

(X)

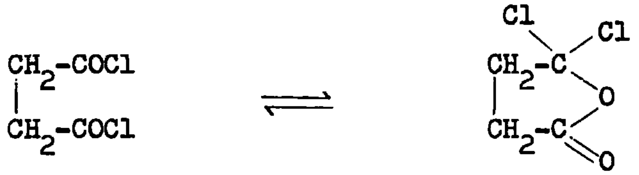
A further possible mechanism to account for the formation of (IX) and (X), is that the lactone (VIII) exists in equilibrium with a ring opened tautomer (XII).



(VIII)

(XII)

This ring opened tautomer would react with sulphur tetrafluoride to produce (IX) and (X), but no evidence exists to suggest this equilibrium, although equilibria of this type have been shown in non-fluorinated compounds.[24,25] For example, succinyl chloride has been shown to react partly in the cyclic form:[25]

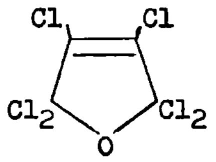


To account for the formation of the furan (IV), direct fluorination of the lactone (VIII) must have occurred with sulphur tetrafluoride as suggested by Blake and Schaar[21], but the overall mechanism of the reaction is not as straightforward as previously suggested.

In a series of some forty experiments it was found that product yields were erratic even for reactions which were carried out under apparently identical conditions and despite exercising considerable care to avoid manipulative errors. As a result of this observation the purity of the sulphur tetrafluoride used was carefully assessed and, not unexpectedly, it was found to be contaminated with thionyl fluoride. Samples were checked by mass and infra-red spectrometric analysis, after taking care to dry thoroughly the vessels and cells and then flush them out several times with the mixture to be analysed so as to remove traces of adsorbed mixture. It was found that there was a wide variation in purity, from cylinder to cylinder, of sulphur tetrafluoride purchased, and also in the quality of the reagent prepared from sulphur dichloride and sodium fluoride, in acetonitrile.[20] The variations in quality were so great that some of the earlier experiments may have been carried out with almost pure thionyl fluoride. Accordingly, one reaction (Table 1, run 11) was carried out using thionyl fluoride which contained less than 5% sulphur tetrafluoride. More fluorinated product than could arise from the trace amounts of the sulphur tetrafluoride was obtained, and cis-2,3-dichlorohexafluorobut-2-ene was the major product. Thus, thionyl fluoride can effect the fluorination of dichloromaleic anhydride to the ether (IV), lactone (VIII), and cis-2,3-dichlorohexafluorobut-2-ene (IX), but is less effective than sulphur tetrafluoride.

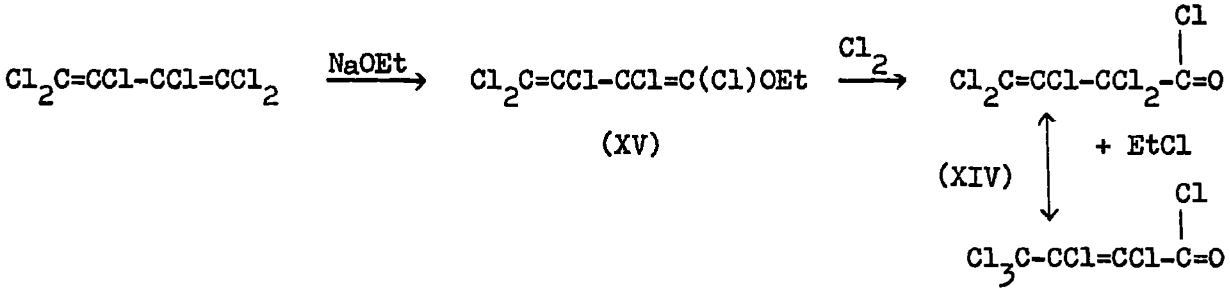
These results, and those of Blake and Schaar, indicate that the reaction between dichloromaleic anhydride and sulphur tetrafluoride is complicated, and optimum conditions are difficult to determine. The composition of the fluorinating agent is very difficult to regulate because of the ease of hydrolysis of sulphur tetrafluoride, and may be one of the main factors in causing uncertainty in the yields.

Due to these factors an alternative synthesis was sought for 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV). One plausible route was replacement of the allylic chlorines, in perchloro-2,5-dihydrofuran (XIII), by fluorine.



(XIII)

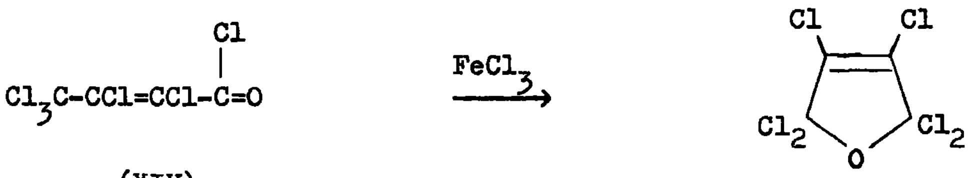
Several syntheses of (XIII) were reported in the literature, the chlorination of furan,[26] the chlorination of 2,3-dichlorotetrahydrofuran[27], and the catalytic cyclisation of perchlorocrotonyl chloride.[19] The direct chlorination of furan at -40°C as reported in the patent literature[26] was attempted several times; a great deal of polymerisation occurred, the only identifiable product being trichlorofuran. Due to the difficulties encountered, it was decided to attempt the cyclisation of perchlorocrotonyl chloride (XIV). The published synthesis starting from hexachlorobut-1,3-diene[28] involves reaction with sodium ethoxide to give 1-ethoxypentachlorobut-1,3-diene (XV), which on chlorination with elemental chlorine and distillation under reduced pressure, gives perchlorocrotonyl chloride (XIV).



$$\mathrm{Cl_2C{=}CCl{-}CCl{=}CCl_2} \xrightarrow{\mathrm{NaOEt}} \underset{\text{(XV)}}{\mathrm{Cl_2C{=}CCl{-}CCl{=}C(Cl)OEt}} \xrightarrow{\mathrm{Cl_2}} \mathrm{Cl_2C{=}CCl{-}CCl_2{-}C(Cl){=}O} + \mathrm{EtCl}$$

$$\text{(XIV)}\quad \mathrm{Cl_2C{=}CCl{-}CCl_2{-}C(Cl){=}O} \longleftrightarrow \mathrm{Cl_3C{-}CCl{=}CCl{-}C(Cl){=}O}$$

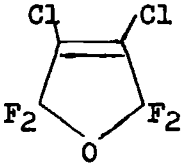
Initially, the cyclisation of (XIV), using ferric chloride, to perchloro-2,5-dihydrofuran (XIII) proved difficult, but after extensive drying of the ferric chloride with thionyl chloride, the yield for the



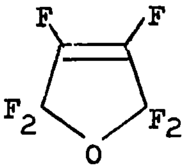
(XIV) (XIII)

cyclisation was greatly enhanced. The work up procedure was slightly modified from that of the original authors,[28] in that on completion of the ethoxylation stage excess water was added and the organic phase containing the required product separated. This was found to be quicker and more convenient than filtering off the sodium chloride. It was also unnecessary to isolate the acid chloride (XIV), the ferric chloride catalyst being added when all the ethyl chloride had evolved as shown by the disappearance of the C-H absorbtion at 2923 cm.$^{-1}$ and appearance of carbonyl absorbtion at 1810 cm.$^{-1}$ in the infra-red spectra. The previous authors report the synthesis of perchloro-2,5-dihydrofuran from hexachlorobut-1,3-diene in 62% overall yield, but the best yields obtained in this work were 48%.

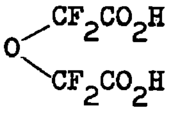
The fluorination of perchloro-2,5-dihydrofuran (XIII) to give 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) was acheived in 77% yields using antimony trifluoride - antimony pentachloride mixtures, and fluorination with potassium fluoride in N-methylpyrrolidone gave



(IV)



(XVI)



(V)

perfluoro-2,5-dihydrofuran (XVI) in 49% yield. The fluorination of (XIII) is discussed fully in Chapter III.

The oxidation of (IV) to perfluoro-oxydiacetic acid (V) was accomplished quite readily using permanhanate in acetone[29] in yields of up to 82%, whilst aqueous permanganate oxidation of (XVI) in a sealed autoclave gave (V) in 66% yield, the acid being identified by correct elemental analysis, infra-red spectra and ^{19}F n.m.r. showing a single resonance at -5•8 p.p.m. from trifluoroacetic acid, as well as characterisation of derivatives.

Using the above route, perfluoro-oxydiacetic has been repeatedly prepared in yields greater than 60% from perchloro-2,5-dihydrofuran.

Experimental.

Dichloromaleic anhydride was obtained from Aldrich Chemical Co. Inc., and was used without further purification; infrared spectroscopic examination showed no detectable amounts of dichloromaleic acid. Sulphur tetrafluoride was obtained in cylinders from Peninsular ChemResearch Inc., or prepared as follows:[20]

Sodium fluoride (3kg.) was placed in a flange head flask (20 l.) fitted with a 5-necked head, to which was attached a vibro stirrer, thermometer well, nitrogen inlet, inlet for sulphur dichloride with pressure equalising system, and an outlet to which was attached two vertical condensers in series cooled by water at 0°C. The outlet from the top water cooled condenser was connected to a drikold/acetone condenser which led to the cooled product flask, the whole of the apparatus being continually flushed by dry nitrogen. Acetonitrile (7 l.), twice distilled from phosphorus pentoxide and refluxed over a molecular sieve (24 hr.), was distilled into the reaction vessel, which was then heated by means of an isomantle to maintain a solvent temperature of 68-70°C. Sulphur dichloride (1700 ml.) was then added over 2½ hr., with constant stirring, after an induction period of one hour product began to condense in the product flask, and the mixture then refluxed for 1 further hour after complete addition of sulphur dichloride to complete the reaction. Repeated flask to flask distillation of the product under reduced pressure separated the product from any distilled sulphur dichloride, the product then being transferred to a stainless steel pressure container for storage. (Wt. of product, 800g.). Estimation of purity by infrared and mass spectrometries followed by molecular weight determinations showed the product to be 67% SF_4, 33% SOF_2.

An alternative synthesis was suggested by Tullock[30] using an autoclave but was found to be not as practicable as the previous synthesis since large quantities of sulphur tetrafluoride were required.

Autoclave preparation.

Sodium fluoride (150g.) and sulphur (64g.) were placed in a stainless steel autoclave (800 ml.) which contained a short length of steel bar to aid mixing. The autoclave was then sealed and cooled in liquid air, chlorine gas (150g.) then being transferred into the cooled autoclave under reduced pressure, and the valve closed. The autoclave was heated and rotated for 5 hr./50°C, 1½ hr./150°C and 16 hr./235°C. After cooling, the volatile contents of the autoclave were transferred to a second pressure vessel containing sulphur (33g.), and allowed to stand overnight. Retransfer of the contents of the vessel afforded a gaseous mixture (69g.), shown by infrared spectroscopy to contain both SF_4 and SOF_2.

Fluorinations using sulphur tetrafluoride were carried out in stainless steel autoclaves, which were first dried by heating under reduced pressure. The dichloromaleic anhydride was added to the autoclave which was then sealed, cooled, and sulphur tetrafluoride added under reduced pressure. The vessels were either rocked or rotated, mixing being assisted by inclusion of a short steel bar. In some reactions a 0-400 Ats. pressure gauge, previously checked in the range 0-100 Ats., was attached to the autoclave; at no stage was a pressure in excess of 40 Ats. observed, even though the calculated pressures for all experiments were far in excess of this figure. On completion of the reaction the autoclave was cooled to room temperature and the gaseous material vented through two glass traps cooled in liquid air. Water was added to the traps whilst cold, and the contents were allowed to warm to room temperature. The lower organic layer was separated, dried ($MgSO_4$), and added to the major part of the organic product obtained from the autoclave by vacuum transfer. Product proportions are given in Table 1 page 14, the products being separated by preparative gas chromatography (Dinonylphthalate/Celite: N_2 carrier; 47°) to give, in order of emergence from the column:-

(i) Trans-2,3-dichlorohexafluorobut-2-ene. Found M (mass spectrometry) 231·9243; required for $C_4F_6{}^{35}Cl_2$; M, 231·9281; fragment ions [$^{m}/e$, assignment, (% base)] 232, $C_4F_6{}^{35}Cl_2$ (44); 213, $C_4F_5{}^{35}Cl_2$ (28);

197, $C_4F_6{}^{35}Cl$ (23); 163, $C_3F_3{}^{35}Cl_2$ (100); 147, $C_3F_4{}^{35}Cl$ (31); 109, $C_3F_2{}^{35}Cl$ (26); 93, C_3F_3 (31); 81, C_2F_3 (17); 69, CF_3 (72). $\nu_{max.}$ (gas), 1250, 1210, 1190, 940 and 665 cm.$^{-1}$

(ii) Cis-2,3-dichlorohexafluorobut-2-ene. Found M (mass spectrometry) 231·9248; required for $C_4F_6{}^{35}Cl_2$; M, 231·9281; fragment ions, 232, $C_4F_6{}^{35}Cl_2$ (58); 213, $C_4F_5{}^{35}Cl_2$ (27); 197, $C_4F_6{}^{35}Cl$ (21); 163, $C_3F_3{}^{35}Cl_2$ (100); 147, $C_3F_4{}^{35}Cl$ (30); 109, $C_3F_2{}^{35}Cl$ (28); 93, C_3F_3 (21); 81, C_2F_3 (22); 69, CF_3 (59). $\nu_{max.}$ (gas), 1610 ($>C{=}C<$), 1275, 1210 and 930 cm.$^{-1}$

(iii) 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran b.p. 76° (Lit.[4,21] 74°). Found: C, 23·0; F, 35·9; Cl, 33·8; required for $C_4OCl_2F_4$: C, 22·8; F, 36·0; Cl, 33·6. M (mass spectrometry) 209·9383; required for $C_4O^{35}Cl_2F_4$; 209·9262, fragment ions, 210, $C_4O^{35}Cl_2F_4$ (41); 175, $C_4O^{35}ClF_4$ (28); 163, $C_3{}^{35}Cl_2F_3$ (100); 147, $C_3{}^{35}ClF_4$ (40); 144, $C_3O^{35}ClF_3$ (10); 109, $C_3{}^{35}ClF_2$ (84); 94, $C_2{}^{35}Cl_2$ (7); 82, $C^{35}Cl_2$ (14); 81, C_2F_3 (21); 69, CF_3 (23); 47, $C^{35}Cl$ (7). $\nu_{max.}$ (gas) 1668 ($>C{=}C<$), 1360, 1290, 1168, 1050, 985 and 860 cm.$^{-1}$ U.V. (cyclohexane) $\lambda_{max.}$ 210 mμ ($\epsilon_{max.}$ 7·5 x 10^3). ^{19}F n.m.r. showed a singlet at -91·3 p.p.m. from hexafluorobenzene as external reference.

(iv) 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone b.p. 122° (Lit.[21] 124°). Found: C, 25·3; F, 19·8; Cl, 37·1; required for $C_4O_2Cl_2F_2$: C, 25·4; F, 20·1; Cl, 37·5. M (mass spectrometry) 187·9210, required for $C_4O_2{}^{35}Cl_2F_2$: 187·9243, fragment ions, 188, $C_4O_2{}^{35}Cl_2F_2$ (81); 169, $C_4O_2{}^{35}Cl_2F$ (6); 160, $C_3O^{35}Cl_2F_2$ (6); 153, $C_4O^{35}Cl_2F$ (11); 144, $C_3{}^{35}Cl_2F_2$ (22); 141, $C_3O^{35}Cl_2F$ (11); 125, $C_3{}^{35}Cl_2F$ (10); 122, $C_3O^{35}Cl_2$ (17); 113, $C_2{}^{35}Cl_2F$ (18); 109, $C_3{}^{35}ClF_2$ (100); 94, $C_2{}^{35}Cl_2$ (28); 87, $C_3O^{35}Cl$ (6); 74, C_3F_2 (18); 44, CO_2 (30); 43, C_2F (34); 31, CF (17). $\nu_{max.}$ 1856 ($>$C=O), 1640 ($>$C=C$<$), 1307, and 925 $cm.^{-1}$ in agreement with literature.[21] U.V. (cyclohexane) $\lambda_{max.}$ 235 mμ ($\epsilon_{max.}$ 8·9 x 10^2); ^{19}F n.m.r. showed a singlet at -80·5 p.p.m. from hexafluorobenzene as external reference (Lit.[21] +7·3 p.p.m. from CF_3CO_2H).

Other minor products were detected by analytical gas chromatography but were not isolated.

Chlorination of furan.

Furan (13 ml.) and methylene chloride (215 ml.) were placed in a 3-necked flask (500 ml.) fitted with stirrer, thermometer, and a gas inlet. The flask and contents were cooled to -40°C, and chlorine gas (215g.) was passed through during 100 min. The flask was then allowed to slowly attain room temperature, a constant flow of nitrogen being passed through the solution. The methylene chloride was removed by distillation and the residue distilled under reduced pressure, the only identifiable product being 2,3,5-trichlorofuran (7g., 22%). Found: C, 28·2; H, 0·65; Cl, 59·5; required for C_4HOCl_3: C, 28·2; H, 0·59;

Cl, 61·8. ^{1}H n.m.r. shows single peak at 3·84τ. Mass spectrum shows parent peak $^m/e$ 170, $C_4HO^{35}Cl_3$ with isotope pattern confirming $3^{35}Cl$, and breakdown pattern consistent with this formulation.

Repeated chlorinations using iron filings, and then aluminium chloride, as catalyst produced no other identifiable product.

Preparation of perchloro-2,5-dihydrofuran from hexachlorobut-1,3-diene.

Stage 1. 1-Ethoxypentachlorobut-1,3-diene.

Sodium (28·1g., 1·22 mole) was added in small amounts to dried ethanol (500 ml.) contained in a 3-necked flask (1 l.) fitted with a mechanical stirrer, dropping funnel, and a double surface water cooled reflux condenser. Hexachlorobut-1,3-diene (208g., 0·78 mole) was then added with vigorous stirring over several minutes, causing an exothermic reaction. When the addition was complete, the mixture was refluxed for 2 hr., followed by the addition of distilled water (1 l.). The lower organic phase was separated and the aqueous solution extracted with ether (5 x 200 ml.), the organic phases combined, dried ($MgSO_4$), and the ether removed by distillation. The residue was fractionated (12" x ½" fractionating column packed with glass helices) under reduced pressure to yield: hexachlorobut-1,3-diene (77·7g.) and 1-ethoxypentachlorobut-1,3-diene (72·7g., 55% based on diene consumed) b.p. 140°/15 mm. Found: C, 26·8; H, 2·1; Cl, 66·1; required for $C_6H_5OCl_5$: C, 26·8; H, 1·9; Cl, 65·6. $\nu_{max.}$ 1645 ($>C=C<$), 1592 ($>C=C<$), 1228 and

850 cm.$^{-1}$ Mass spectrometry fragment ions, 268, $C_6H_5O^{35}Cl_5$ (95); 240, $C_4HO^{35}Cl_5$ (50); 233, $C_6H_5O^{35}Cl_4$ (6); 223, $C_4{}^{35}Cl_5$ (8); 205, $C_4HO^{35}Cl_4$ (99); 204, $C_4O^{35}Cl_4$ (73); 188, $C_4{}^{35}Cl_4$ (13); 177, $C_3H^{35}Cl_4$ (58); 176, $C_3{}^{35}Cl_4$ (100); 170, $C_4HO^{35}Cl_3$ (14); 169, $C_4O^{35}Cl_3$ (9); 157, $C_3O^{35}Cl_3$ (18); 153, $C_4{}^{35}Cl_3$ (96); 141, $C_3{}^{35}Cl_3$ (96); 134, $C_4O^{35}Cl_2$ (9); 123, $C_3HO^{35}Cl_2$ (92); 107, $C_3H^{35}Cl_2$ (13); 106, $C_3{}^{35}Cl_2$ (49); 94, $C_2{}^{35}Cl_2$ (7); 87, $C_3O^{35}Cl$ (7); 83, $CH^{35}Cl_2$ (8); 82, $C^{35}Cl_2$ (7); 71, $C_3{}^{35}Cl$ (34); 63, $CO^{35}Cl$ (7); 47, $C^{35}Cl$ (13).

Stage 2. Perchlorocrotonyl chloride.

1-Ethoxypentachlorobut-1,3-diene (21·5g., 0·08 mole) was placed in a 2-necked flask (100 ml.) fitted with a gas inlet, thermometer, a water cooled reflux condenser and a magnetic stirrer. Whilst vigorously stirring the solution, dry chlorine gas was passed for 9 hr., causing an initial exothermic reaction. On completion of the reaction the flask was slowly heated to 130°, gas being evolved. The residue was distilled under reduced pressure to give perchlorocrotonyl chloride (18·4g., 84%) b.p. 114°/13 mm. shown by analytical g.l.c. col. 'O' at 220° to be one component. Found: C, 17·5; Cl, 76·4; required for C_4OCl_6: C, 17·4; Cl, 76·9. Mass spectrometry fragment ions: 274, $C_4O^{35}Cl_6$ (6); 258, $C_4{}^{35}Cl_6$ (4); 239, $C_4O^{35}Cl_5$ (14); 223, $C_4{}^{35}Cl_5$ (5); 211, $C_3{}^{35}Cl_5$ (100); 204, $C_4O^{35}Cl_4$ (7); 192, $C_3O^{35}Cl_4$ (2); 176, $C_3{}^{35}Cl_4$ (12); 157, $C_3O^{35}Cl_3$ (3); 141, $C_3{}^{35}Cl_3$ (36); 129, $C_2{}^{35}Cl_3$ (2); 122, $C_3O^{35}Cl_2$ (2); 117,

$C^{35}Cl_3$ (21); 106, $C_3{}^{35}Cl_2$ (17); 94, $C_2{}^{35}Cl_2$ (4); 87, $C_3O^{35}Cl$ (3); 82, $C^{35}Cl_2$ (4); 71, $C_3{}^{35}Cl$ (15); 63, $CO^{35}Cl$ (9); 47, $C^{35}Cl$ (6). $\nu_{max.}$ 1810 ($>$C=O), 1625 ($>$C=C$<$), 1565 ($>$C=C$<$), 1125, 1010, 965, 812 and 762 $cm.^{-1}$

Stage 3. Perchloro-2,5-dihydrofuran.

Perchlorocrotonyl chloride (40g., 0·146 mole) was placed in a 2-necked round-bottomed flask (100 ml.) fitted with thermometer, reflux condenser and magnetic stirrer, and the flask slowly warmed to internal temperature of 150°C. Ferric chloride (0·07g.) was added and the mixture stirred, the reaction being followed by infra-red spectroscopy, the complete disappearance of band at 1125 $cm.^{-1}$ and the appearance of band at 1210 $cm.^{-1}$, probably associated with the change in environment of the vinylic C-Cl bond, marking completion of reaction. The reaction was complete after 7 hr., and the product was distilled. Perchloro-2,5-dihydrofuran was obtained from the material boiling below 220° by cooling and filtration; (yield 18·0g., 45%). Found: C, 17·4; Cl, 77·3; required for C_4OCl_6: C, 17·4; Cl, 76·9. Mass spectrometry fragment ions: 274, $C_4O^{35}Cl_6$ (3); 258, $C_4{}^{35}Cl_6$ (4); 239, $C_4O^{35}Cl_5$ (86); 223, $C_4{}^{35}Cl_5$ (6); 211, $C_3{}^{35}Cl_5$ (100); 204, $C_4O^{35}Cl_4$ (23); 176, $C_3{}^{35}Cl_4$ (21); 157, $C_3O^{35}Cl_3$ (4); 141, $C_3{}^{35}Cl_3$ (55); 129, $C_2{}^{35}Cl_3$ (2); 122, $C_3O^{35}Cl_2$ (1); 117, $C^{35}Cl_3$ (16); 106, $C_3{}^{35}Cl_2$ (26); 94, $C_2{}^{35}Cl_2$ (5); 87, $C_3O^{35}Cl$ (3); 82, $C^{35}Cl_2$ (3); 71, $C_3{}^{35}Cl$ (19); 63, $CO^{35}Cl$ (6); 47, $C^{35}Cl$ (8). $\nu_{max.}$ 1646 ($>$C=C$<$), 1210, 1020, 985 and 810 $cm.^{-1}$ The filtrate was examined by analytical g.l.c. col. 'O' at 200° and shown to consist of unreacted perchlorocrotonyl chloride and perchloro-2,5-dihydrofuran. This unrecovered perchloro-2,5-dihydrofuran could be utilised since fluorination of this mixture gave 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran using the procedure described below.

Fluorination of perchloro-2,5-dihydrofuran.

Perchloro-2,5-dihydrofuran (20g., 0·073 mole) and antimony trifluoride (30g., 0·158 mole) were placed in a round-bottomed flask (100 ml.) fitted with distillation head. Antimony pentachloride (7 ml., 0·045 mole) was added, the flask and contents heated to 110° when the required 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (11·7g., 75%) was collected, identified by its infrared spectrum.

Perfluoro-oxydiacetic acid.

Potassium permanganate (5·5g., 0·035 mole) and dry acetone (500 ml.) were placed in a 3-necked flask (1 l.) fitted with a stirrer, a double surface reflux condenser and a dropping funnel. 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (7·0g., 0·033 mole) was added to the stirred solution, the contents of the flask refluxed 1 hr., distilled water added (300 ml.), the solution decolourised with sulphur dioxide and the acetone removed under reduced pressure. The solution was continuously extracted with ether (48 hr.), ether extracts dried ($MgSO_4$), the ether removed by distillation to leave a crude solid which on sublimation (100^{o}/0·01 mm.) afforded perfluoro-oxydiacetic acid (5·64g., 82%). Found: C, 23·5; H, 1·02; F, 37·3; E. Wt. 103; required for $C_4H_2F_4O_5$: C, 23·3; H, 0·97; F, 36·9; E. Wt. 103. ^{19}F n.m.r. of aqueous solution showed singlet at -5·8 p.p.m. from CF_3CO_2H as external reference.

Perfluoro-oxydiacetic acid (1·23g., 0·006 mole) in dry ether (10 ml.) was treated with aniline (2·5 ml.), and crystallisation of the crude precipitate from 1:1 chloroform/carbon tetrachloride yielded dianilinium perfluoro-oxydiacetate (2·1g., 89%), m.p. 175° (Lit.[15] 189-190°). Found: C, 48·6; H, 3·9; F, 19·5; required for $C_{16}H_{16}F_4N_2O_5$: C, 49·0; H, 4·1; F, 19·4.

CHAPTER II.

REACTIONS OF PERFLUORO-OXYDIACETIC ACID AND ITS DERIVATIVES.

Introduction.

Once a satisfactory route to perfluoro-oxydiacetic acid (V) had been devised (see Chapter I), the primary aim was its decarboxylation in the presence of iodine to give the 1,3-diiodotetrafluoro-2-oxapropane (VI),

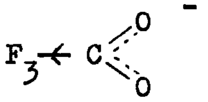
$$O(CF_2CO_2H)_2 \longrightarrow O(CF_2I)_2$$

(V) (VI)

Other properties of the acid and its derivatives were also investigated.

Generally, perfluoroalkane carboxylic acids are much stronger acids than the analogous 'hydrocarbon' acids, due to the ability of the strong electron-attracting power of the perfluoroalkyl group to stabilise the anion:

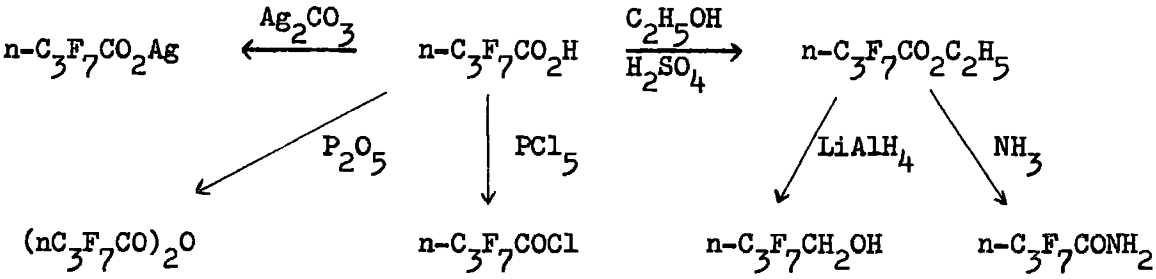
$CF_3CO_2H \rightleftharpoons$



$+ \; H^+$ Ref. 31

CF_3CO_2H K_a 1·8 CH_3CO_2H K_a $1{\cdot}8 \times 10^{-5}$

Many of the reactions of perfluoroalkane carboxylic acids and their derivatives follow the same course as the 'hydrocarbon' acids, a typical selection of such reactions is shown in the following diagram.



However, certain reactions of perfluoroalkanecarboxylic acids are unique to these fluorinated acids and their derivatives: for example, perfluorocarboxylic acid amides R_fCONH_2 do not undergo the Hoffmann degradation with alkali hypohalite to give the primary amines R_fNH_2, the corresponding fluorocarbon bromide being formed instead:[32]

$$nC_3F_7CONH_2 \xrightarrow{Ag_2O/Br_2} n\text{-}C_3F_7Br\ (70\%) + NCO^-$$

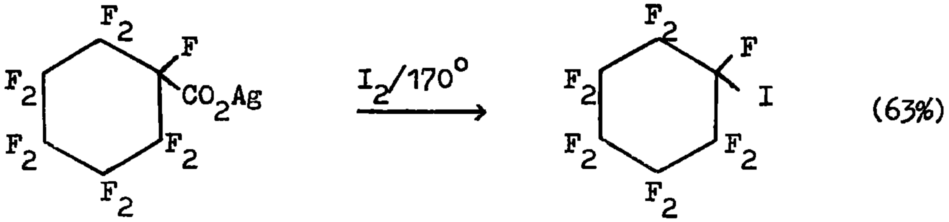
A general reaction which has found extensive use in the fluorocarbon field is the Hunsdiecker reaction, which involves the decarboxylation of the silver salt of a carboxylic acid in the presence of iodine. This reaction has been used mainly for the preparation of perfluoroalkyl iodides, the first example being the preparation of trifluoromethyl iodide:[33,34]

$$CF_3CO_2Ag + I_2 \xrightarrow{100^\circ} \underset{>90\%}{CF_3I} + CO_2 + AgI$$

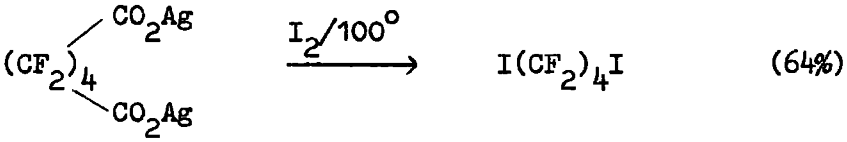
This reaction has been extended to the preparation of perfluoroalkyl chlorides and bromides[35] in addition to iodides:

$$n\text{-}C_5F_{11}CO_2Ag \begin{array}{l} \xrightarrow{Cl_2/100^\circ} n\text{-}C_5F_{11}Cl \qquad (71\%) \\ \xrightarrow{Br_2/80\text{-}90^\circ} n\text{-}C_5F_{11}Br \qquad (82\%) \end{array}$$

as well as to perfluoroalicyclic carboxylic acids[36]

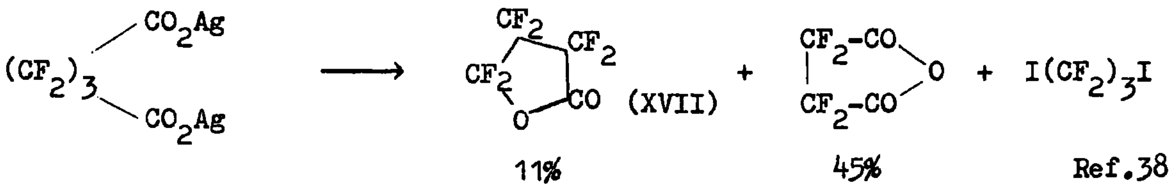


and to dicarboxylic acids[37]



$$(CF_2)_4(CO_2Ag)_2 \xrightarrow{I_2/100^\circ} I(CF_2)_4I \qquad (64\%)$$

The reaction of silver perfluoroglutarate with iodine produces a mixture containing two cyclic products, perfluorobutyrolactone (XVII) and perfluorosuccinic anhydride; together with 1,3-diiodohexafluoropropane and other minor products:



However, with chlorine and bromine the 1,3-dihalogenohexafluoropropanes are formed in high yield.[35]

The decarboxylation of the silver salt of perfluoro-oxydipropionic acid in the presence of iodine is reported to give the 1,5-diiodo-3-oxaperfluoropentane.[10,39]

$$O(CF_2CF_2CO_2Ag)_2 \xrightarrow{I_2} O(CF_2CF_2I)_2$$

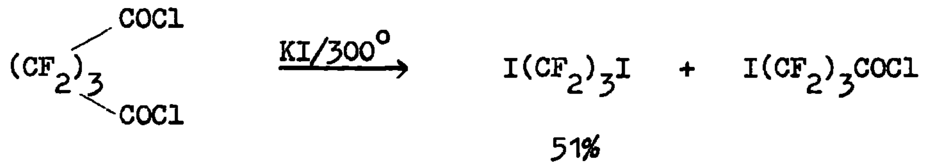
The reaction of perfluorocarboxylic acids, and their anhydrides, with bromine alone has been reported in the patent literature[40] to produce the corresponding perfluoroalkyl bromides.

$$R_fCO_2H \xrightarrow{Br_2} R_fBr + CO_2 + HBr$$

$$(R_fCO)_2O \xrightarrow{Br_2} R_fBr + R_fCOBr + CO_2$$

The preparation of 1,3-diiodotetrafluoro-2-oxapropane (VI) could be envisaged from perfluoro-oxydiacetic acid via a Hunsdiecker reaction, or by reaction of perfluoro-oxydiacetyl chloride with potassium iodide, since the analogous reaction with perfluoroglutaryl chloride gives

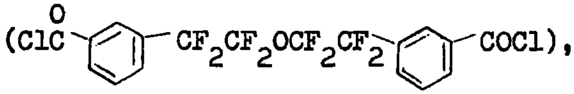
1,3-diiodohexafluoropropane.[41] The attempted synthesis of (VI) is part

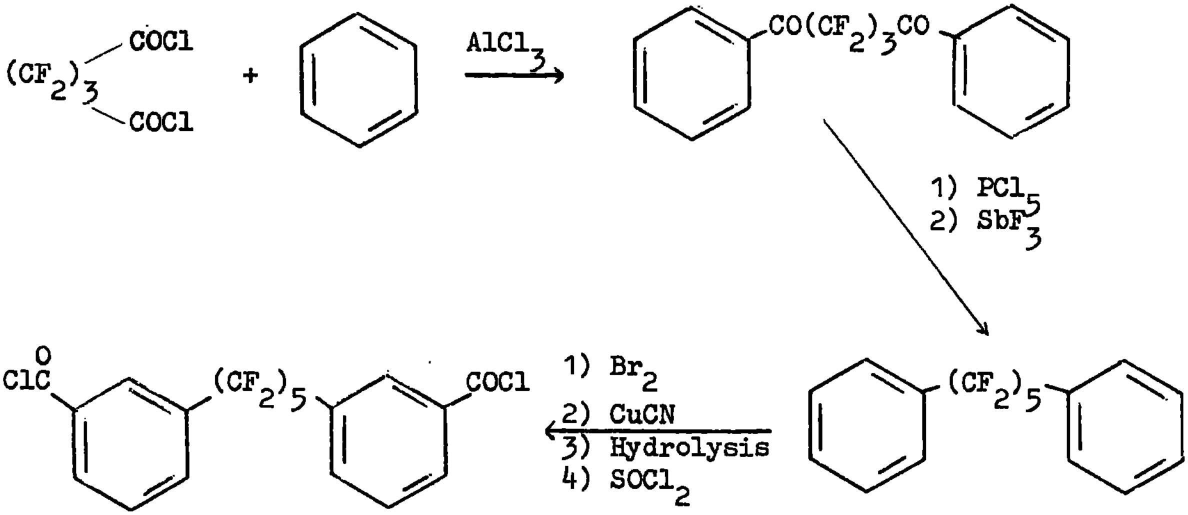


$$(CF_2)_3(COCl)_2 \xrightarrow{KI/300^\circ} \underset{51\%}{I(CF_2)_3I} + I(CF_2)_3COCl$$

of the work described in this chapter. Whilst this, and other reactions of perfluoro-oxydiacetic acid, was being investigated, two publications appeared in the literature[42,43] describing several of the reactions, and compounds, described herein, agreeing with the results of this work in that a reasonable synthesis of 1,3-diiodotetrafluoro-2-oxapropane (VI) from perfluoro-oxydiacetic acid could not be found.

Due to the difficulties found in the preparation of diiodoperfluoroethers of type (II) i.e. $I(CF_2)_xO(CF_2)_yI$, the synthesis of polymers of type I, via a copper coupling reaction with aromatic diiodides, could not be completed. However, the effect of the $-CF_2-O-CF_2-$ link on the physical properties of polymers could still be investigated utilising perfluoro-oxydiacetic acid and its derivatives. The diol, 2,2,4,4-tetrafluoro-3-oxa-pentane-1,5-diol, $O(CF_2CH_2OH)_2$, could be used in the synthesis of polyesters, which could be compared with analogous polymers prepared from hexafluoropentane-1,5-diol. Other derivatives of perfluoro-oxydiacetic acid could be used to provide additional possible polymer precursors. For example, the preparation of the diacid chlorides

 may be envisaged via a route analogous to that established for the synthesis of 1,5-di(3-chlorocarbonylphenyl)decafluoropentane (XXXVI) from perfluoroglutaryl chloride:



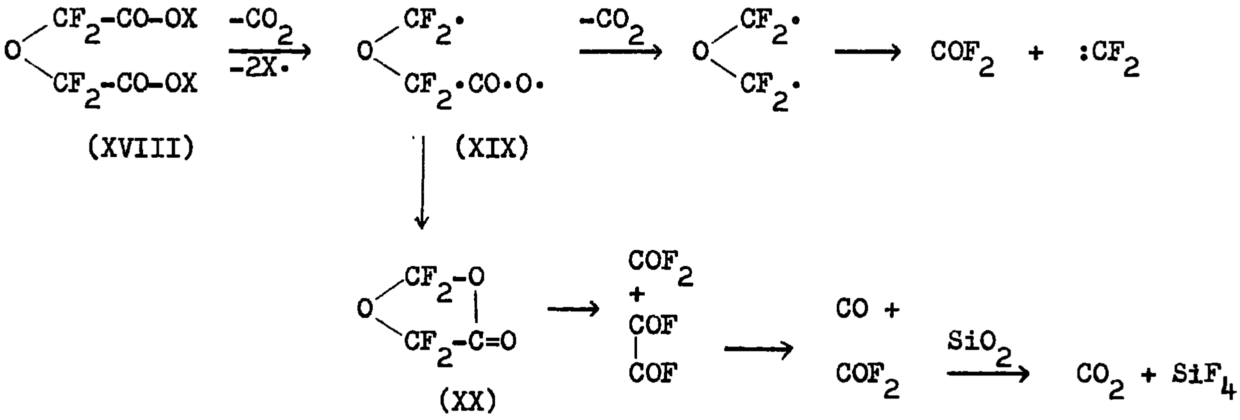
(XXXVI)

(see ref. 46)

The preparation of 2,2,4,4-tetrafluoro-3-oxa-pentane-1,5-diol, $O(CF_2CH_2OH)_2$, and some reactions of perfluoro-oxydiacetic acid and its derivatives are described in this chapter.

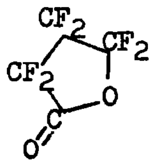
Discussion.

By analogy with previously reported Hunsdiecker reactions, decarboxylation of perfluoro-oxydiacetic acid derivatives ought to give 1,3-diiodotetrafluoro-2-oxapropane (VI). However, treatment of silver perfluoro-oxydiacetate with iodine in a closed system did not produce (VI), the identified products were silicon tetrafluoride, carbon monoxide, carbon dioxide and carbonyl fluoride; a further volatile product was isolated but was not successfully characterised. This volatile material did not react with water, but showed C-F vibrations (1075 $cm.^{-1}$) and possibly a C-O-C vibration (1200-1000 $cm.^{-1}$) in the infra-red spectrum, the mass spectrum showing peaks at $^{m}/e$ 127, 100, 85 and 81 possibly due to I, C_2F_4, CF_3O and C_2F_3 respectively. Treatment of silver perfluoro-oxydiacetate with iodine in an open system at 100°C produced no volatile material and gave a high recovery of starting material. A report of this reaction has since been published by workers at Manchester,[42] who found carbon monoxide, carbon dioxide, silicon tetrafluoride and carbonyl fluoride as the only products at temperatures greater than 100°, but at lower temperatures perfluoro-oxydiacetic anhydride was an additional product. No perfluoro-oxydiacetic anhydride was found from the reaction in this work; this is reasonable since all reactions were carried out at temperatures of 100° or higher. The mechanism for the reaction put forward by the Manchester group[42] postulates formation of the acid dihypohalite (XVIII) which decomposes to give an intermediate (XIX) which can breakdown in either of two ways; to give carbon dioxide, carbonyl fluoride and difluorocarbene, or by formation of perfluoro-β-oxa-γ-butyrolactone (XX) which breaks down to carbonyl fluoride and oxalyl fluoride.



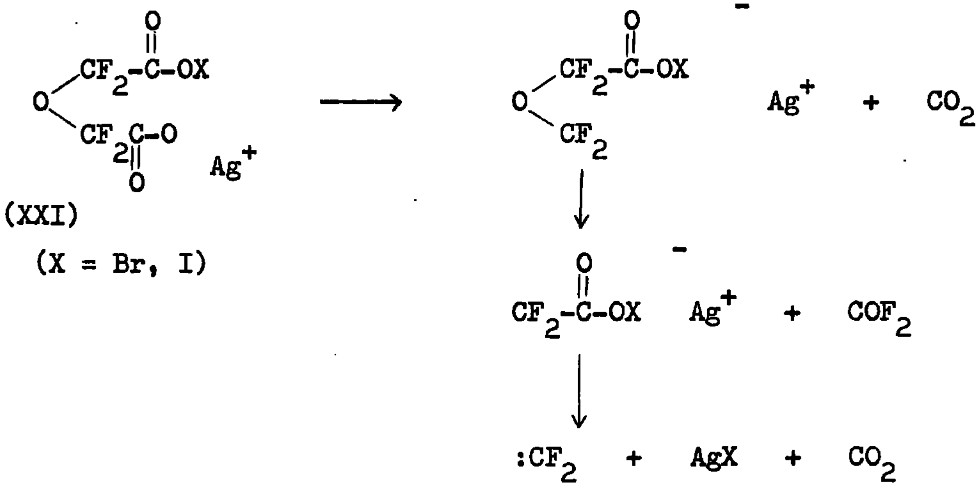
$$2F_2C: \xrightarrow{SiO_2} SiF_4 + 2CO$$

The only evidence to support the formation of (XX) is from the analogous reaction with silver perfluoroglutarate[38] for which perfluoro-γ-butyrolactone (XVII) was found.



(XVII)

No experimental evidence was found to support the formation of (XX), and a mechanism can be written to explain the formation of the products found without the inclusion of a cyclic intermediate. This alternative mechanism postulates the decomposition of the monohypohalite (XXI) to give difluorocarbene, by successive loss of carbon dioxide, carbonyl fluoride and again loss of carbon dioxide, as follows:

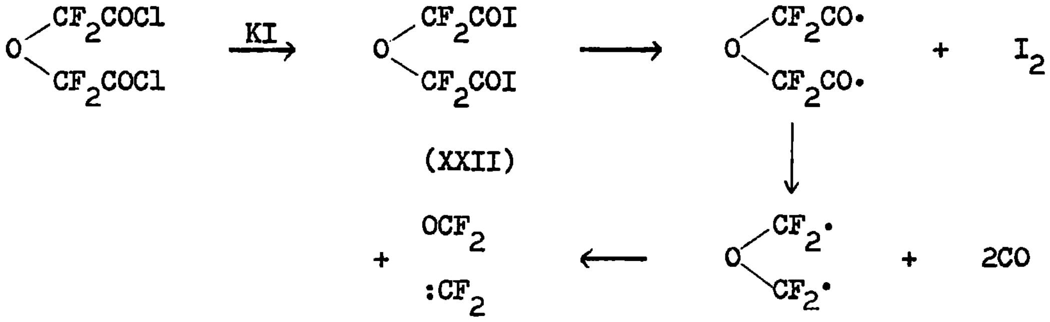


(XXI)

(X = Br, I)

$$2{:}CF_2 + SiO_2 \longrightarrow SiF_4 + 2CO$$

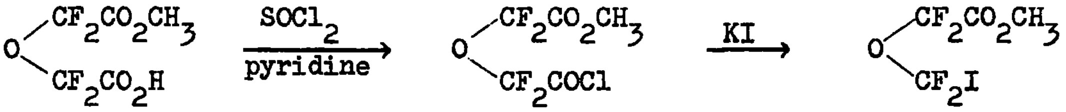
Since perfluoroglutaryl chloride gives 1,3-diiodohexafluoropropane in reasonable yield when passed over heated potassium iodide,[41] the analogous reaction with perfluoro-oxydiacetyl chloride was attempted, the acid chloride being prepared by reaction of the acid with thionyl chloride. Perfluoro-oxydiacetyl chloride was heated with potassium iodide in a sealed tube at 200°, and passed as a vapour through a column packed with potassium iodide at 300°. The same products were isolated as from the reaction of the silver salt with iodine, although the carbon dioxide content of the product was much reduced. Iodine was also liberated from the iodide. Formation of the acid iodide (XXII) followed by its thermal decomposition could account for the formation of these products including the liberation of iodine:



(XXII)

$$2{:}CF_2 + SiO_2 \longrightarrow SiF_4 + 2CO$$

However, the decarboxylation of a compound containing a $-CF_2-O-CF_2-$ group adjacent to the carboxylic acid derivative group to produce an iodide, has been suggested in the patent literature.[44] This involves the synthesis of methyl 4-iodo-3-oxa-2,2,4,4-tetrafluorobutyrate, $ICF_2OCF_2CO_2CH_3$, from the corresponding acid chloride by reaction with potassium iodide; the flow sequence given in the patent is as follows:

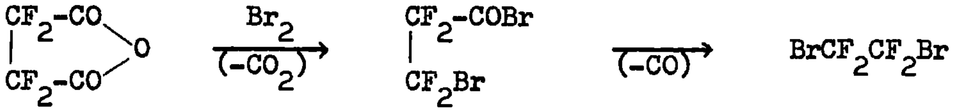


No evidence is given to say whether this reaction scheme was successful or even whether it had been attempted.

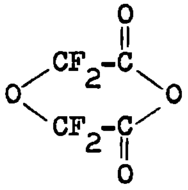
Reports in the patent literature[40] also state that the thermal decomposition of perfluorocarboxylic acids, and their intra- and inter-molecular anhydrides, in the presence of one mole of bromine at elevated temperatures gives the fluorocarbon bromide;

$$R_fCO_2H \longrightarrow R_fBr + CO_2 + HBr$$

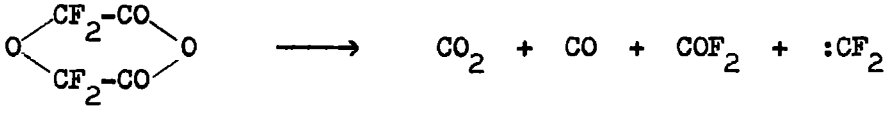
This also applies to cyclic anhydrides, for example



An analogous treatment of perfluoro-oxydiacetic anhydride with iodine may be expected to give 1,3-diiodotetrafluoro-2-oxapropane. The dehydration of perfluoro-oxydiacetic acid was achieved using phosphorus pentoxide to give perfluoro-oxydiacetic anhydride



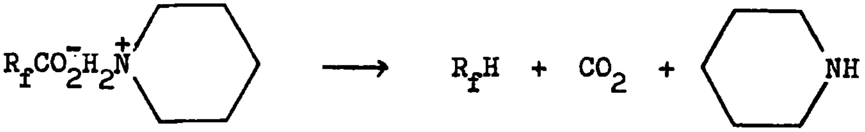
(subsequently reported in Ref.44). Reaction of this with molecular iodine in an autoclave at 385° resulted in the formation of carbon monoxide, carbon dioxide and carbonyl fluoride as the only characterised products with some carbonisation and pitting of the autoclave. This result was subsequently confirmed by the work of Banks et al.[42] A similar breakdown route to that postulated in the reactions of the disilver salt and the diacyl chloride can be suggested:



$$:CF_2 \longrightarrow \text{carbon + attack on autoclave.}$$

From the data available it would seem that the system $HO_2CCF_2OCF_2CO_2H$, and derivatives, is unstable with respect to thermal decomposition to give difluorocarbene and carbonyl fluoride. The inclusion of an extra difluoromethylene group appears to stabilise the system so that decarboxylation of perfluoro-oxydipropionic acid in the presence of iodine gives 1,5-diiodo-3-oxaperfluoropentane $(ICF_2CF_2)_2O$.[10,39]

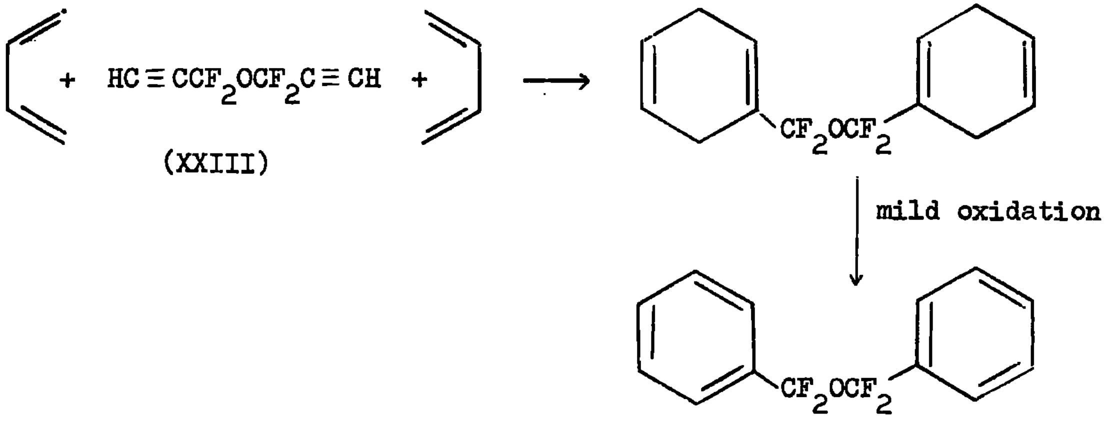
To investigate the stability of the $-CF_2-O-CF_2-$ link adjacent to a carboxylic acid group, dipiperidinium perfluoro-oxydiacetate was prepared. The piperidinium salts of perfluorocarboxylic acids usually decarboxylate on heating to the fluorohydrocarbon:



Treatment of perfluoro-oxydiacetic acid with piperidine produced a white solid which was identified as dipiperidinium perfluoro-oxydiacetate, $O(CF_2CO_2^-H_2\overset{+}{N}$$)_2$; ^{19}F n.m.r. showed a single peak at -89·3 p.p.m. from hexafluorobenzene whilst the ^1H n.m.r. spectrum showed peaks at 0·81τ ($>\overset{+}{N}H_2$), 7·00τ and 8·46τ in relative areas 1:2:3. Correct elemental analysis was also obtained. Heating of this salt to 200° produced a gaseous mixture which was separated by distillation to give carbon dioxide and 1,1,3,3-tetrafluoro-2-oxapropane, HCF_2OCF_2H. This was characterised by its infra-red spectrum, the ^{19}F n.m.r. spectrum showed a doublet ($J \sim 71$ Hz) at -79·2 p.p.m. from hexafluorobenzene; the ^1H n.m.r. showed a triplet ($J \sim 71$ Hz) at 3·45τ; and the expected mass spectrometric fragmentation pattern was obtained.

From this result, it would appear that the stability of the $-CF_2-O-CF_2-$ link is not the factor which determines the failure to obtain the desired halodecarboxylation products in the reactions reported. Presumably the explanation of this failure must lie in a detailed understanding of the mechanisms of the reactions involved. Unfortunately, no physico-chemical study of these reactions has been reported. Since the silver salts of perfluoroglutaric and perfluoro-oxydipropionic acids undergo halodecarboxylation, and perfluoro-oxydiacetic acid does not, it can be postulated that the determining factor is the stability of the intermediates involved and the ease with which these intermediates either react with halogen or decompose. Thus in the decarboxylation of perfluoro-oxydiacetic acid derivatives the intermediate appears to be sufficiently long lived to pick up a hydrogen atom, but undergoes decomposition to difluorocarbene and carbonyl fluoride before it can react with a halogen atom. Alternatively, the detailed mechanism of decarboxylation of the piperidinium and silver salts may be different. The former may involve a cyclic intermediate whereas the latter may proceed via an intermediate having either a difluoromethylene radical, or anion, which undergoes rapid decomposition in the perfluoro-oxydiacetic acid case, but not in the other examples.

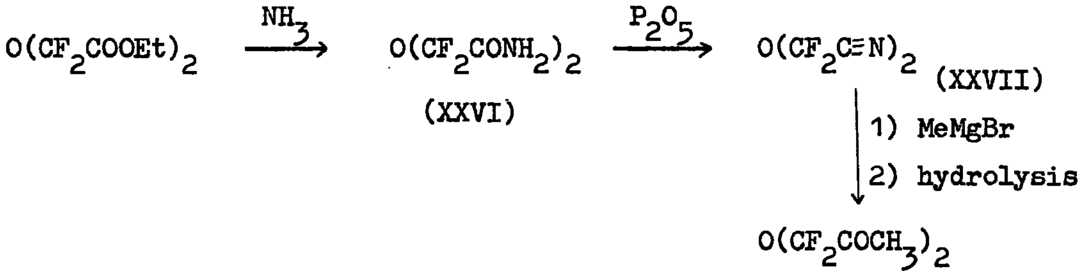
Since no success was achieved in the attempted synthesis of 1,3-diiodotetrafluoro-2-oxapropane (VI), the synthesis of a model compound $C_6H_5-CF_2OCF_2-C_6H_5$ was envisaged which could be incorporated into polymers. The preparation of this compound was postulated via a Diels-Alder reaction of buta-1,3-diene with 3,3,5,5-tetrafluoro-4-oxahept-1,6-diyne (XXIII).



The preparation of (XXIII) was envisaged by dehydrochlorination of 2,2,6,6-tetrachloro-3,3,5,5-tetrafluoro-4-oxa-n-heptane, $CH_3CCl_2CF_2OCF_2CCl_2CH_3$, this being prepared by chlorination of 3,3,5,5-tetrafluoro-4-oxa-n-hepta-2,6-dione, $CH_3COCF_2OCF_2COCH_3$ (XXIV). The whole reaction scheme can be written as follows:

$$CH_3COCF_2OCF_2COCH_3 \longrightarrow CH_3CCl_2CF_2OCF_2CCl_2CH_3 \longrightarrow HC{\equiv}C\text{-}CF_2OCF_2\text{-}C{\equiv}CH$$

The preparation of (XXIV) was attempted by reaction of perfluoro-oxydiacetyl chloride, $O(CF_2COCl)_2$ (XXV), with dimethyl cadmium, but only starting material was recovered from the reaction. The reaction of (XXV) with triphenylphosphine dichloromethylene, $Ph_3P{=}CCl_2$, in a Wittig type reaction was also attempted in order to produce $O(CF_2CCl{=}CCl_2)_2$, but again only starting material was recovered after work-up. A further possibility for the preparation of (XXIII) was via the scheme:



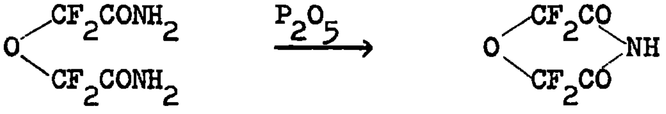
$$\begin{tikzcd} O(CF_2COOEt)_2 \arrow[r, "NH_3"] & \underset{(XXVI)}{O(CF_2CONH_2)_2} \arrow[r, "P_2O_5"] & \underset{(XXVII)}{O(CF_2C{\equiv}N)_2} \arrow[d, "\text{1) MeMgBr}", "\text{2) hydrolysis}"'] \\ & & O(CF_2COCH_3)_2 \end{tikzcd}$$

Perfluoro-oxydiacetamide (XXVI) was prepared by reaction of diethyl perfluoro-oxydiacetate with ammonia gas, when the diamide

$$O(CF_2CO_2C_2H_5)_2 \xrightarrow{NH_3} O(CF_2CONH_2)_2$$

precipitated. The structure of (XXVI) was confirmed by the presence of one fluorine environment as shown by a single peak in the ^{19}F n.m.r. spectrum at -86·1 p.p.m. from hexafluorobenzene, and the ^{1}H n.m.r. spectrum showed a single peak at 2·27τ. Elemental analysis and the infra-red spectrum were consistent with this assignment.

On attempting to dehydrate the diamide (XXVI) to give the dinitrile (XXVII) by heating with phosphorus pentoxide, one molecule of ammonia was eliminated to give 1-aza-4-oxa-3,3,5,5-tetrafluorocyclohexa-2,6-dione (XXVIII).

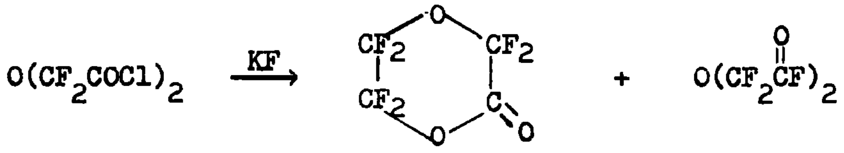


(XXVI) (XXVIII)

(XXVIII) was characterised by elemental analysis; ^{19}F n.m.r. which showed one fluorine environment at -89·3 p.p.m. from hexafluorobenzene, and infra-red spectroscopy which showed a carbonyl absorbtion at 1738 $cm.^{-1}$, a broad ether band at 1110-1250 $cm.^{-1}$ and N-H stretching modes at 3365 and 3185 $cm.^{-1}$. The formation of (XXVIII) again demonstrates the stability and ease of formation of the six-membered rings from perfluoro-oxydiacetic acid derivatives.

Several derivatives of perfluoro-oxydiacetic acid have been reported in the literature,[45] both Throckmorton[43] and Banks et al.[42]

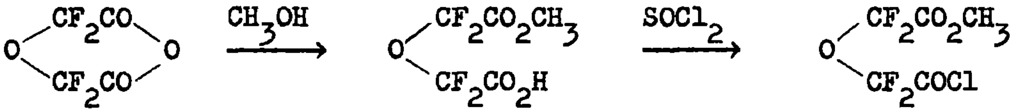
reporting the reaction of perfluoro-oxydiacetyl chloride with potassium fluoride to give a mixture of perfluoro-oxydiacetyl fluoride and perfluoro-β-oxa-δ-valerolactone (XXIX).



(XXIX)

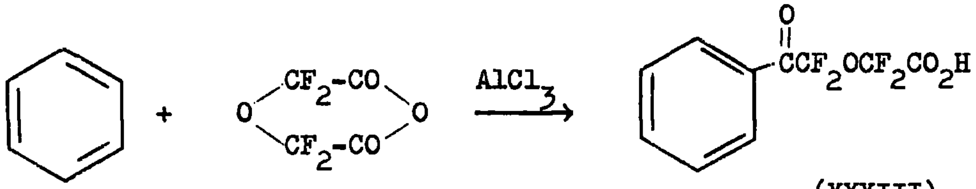
Reaction of (XXIX) with methanol gave the dimethyl perfluoro-oxydiacetate which on treatment with ammonia gave perfluoro-oxydiacetamide. In this work the dimethyl ester, and the diethyl ester, were prepared by direct esterification of the acid.

Several reactions of perfluoro-oxydiacetic anhydride were investigated in addition to the reaction with iodine mentioned earlier. The monomethyl ester (XXX), which was formed by reaction of the anhydride with methanol gave the monoacyl chloride (XXXI) on treatment with thionyl chloride.



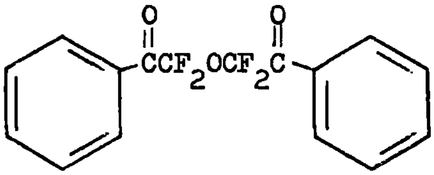
(XXXII) (XXX) (XXXI)

It was also found that the anhydride (XXXII) would undergo a Friedel-Crafts reaction with benzene, in the presence of aluminium chloride, to give 5-phenyl-3-oxa-tetrafluoropentanoic acid 5-one (XXXIII).

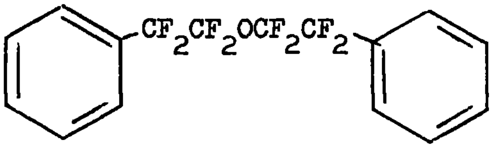


(XXXIII)

A Friedel-Crafts reaction was also attempted with perfluorooxydiacetyl chloride and benzene in an attempt to produce 1,5-diphenyl-3-oxa-2,2,4,4-tetrafluoropentan-1,5-dione (XXXIV).

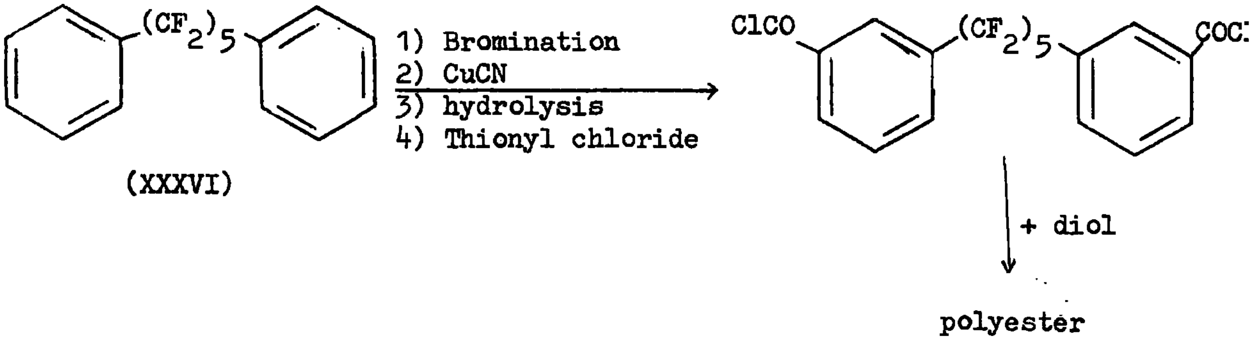


(XXXIV)



(XXXV)

It was hoped that fluorination of (XXXIV) would give 1,5-diphenyl-3-oxa-octafluoropentane (XXXV), which could be incorporated into polyesters in an analogous manner to 1,5-diphenyldecafluoropentane (XXXVI)[46]



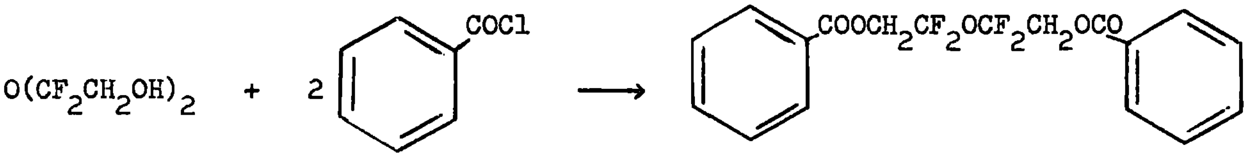
(XXXVI)

However, up to the present time, formation of (XXXV) has not been achieved, extensive decomposition occurring at the acylation stage. The reaction between perfluoroglutaryl chloride and benzene to give 1,5-diphenylhexafluoropentan-1,5-dione is extremely temperature sensitive, too high a temperature causing decomposition and too low a temperature no reaction. The reaction between perfluoro-oxydiacetyl chloride and benzene may similarly be extremely temperature sensitive, the optimum reaction conditions having not yet been found.

Due to the difficulties found in the preparation of 1,3-diiodotetrafluoro-2-oxapropane (VI), 2,2,4,4-tetrafluoro-3-oxa-pentane-1,5-diol, $O(CF_2CH_2OH)_2$ (XXXVII), was synthesised by reduction of diethyl perfluoro-oxydiacetate with lithium aluminium hydride. The product was

$$O(CF_2CO_2C_2H_5)_2 \longrightarrow \underset{\text{(XXXVII)}}{O(CF_2CH_2OH)_2}$$

characterised by a single fluorine resonance, with fine structure, at +80·9 p.p.m. from fluorotrichloromethane, the ^1H n.m.r. spectrum showed a broad peak at 5·30τ (-OH) and a peak at 6·20τ ($-CH_2-$) with fine structure, and correct elemental analysis was obtained. The dibenzoyl derivative of (XXXVII) was prepared by reaction with benzoyl chloride, this being fully characterised also.



(XXXVII)

The diol (XXXVII) could now be used for the preparation of polyesters by reaction with diacyl chlorides, and the properties of these polymers compared to the analogous polymers from hexafluoropentane-1,5-diol. This work is described in this thesis in Chapters IV and V.

Experimental.

Disilver perfluoro-oxydiacetate.

A mixture of perfluoro-oxydiacetic acid (0·28g., 0·00136 mole) and silver oxide (0·36g., 0·00155 mole) in water (0·7 ml.) was heated in a round-bottomed flask (25 ml.) for 75 mins., filtered, and the product recrystallised from water to give disilver perfluoro-oxydiacetate (0·39g., 69%), M.p. 163° (decomp.). Found: C, 11·7; F, 17·7; required for $C_4F_4O_5Ag_2$: C, 11·45; F, 18·1.

Reaction of disilver perfluoro-oxydiacetate.

(i) with iodine.

a) Disilver perfluoro-oxydiacetate (4·3g., 10·3 m.moles), and iodine (7·0g., 27·5 m.moles) were ground together, placed in a flask (25 ml.) and covered with a layer of iodine (3·0g., 11·8 m.mole). The flask was connected to two traps, one cooled in liquid air, and heated in an oil bath to 100°C. No volatile product was observed in the traps. The flask and its contents were ether extracted (200 ml.), the ether extract washed with 5% thiosulphate solution, dried ($MgSO_4$), and the ether distilled to leave perfluoro-oxydiacetic acid (1·16g., 56%), identified as its dianilinium salt.

b) Disilver perfluoro-oxydiacetate (3·40g., 8·10 m.moles) and iodine (6·10g., 24·0 m.moles) were placed in a glass tube (120 ml.) which was sealed under reduced pressure, and heated at 200°C/12 hr. The tube was cooled in liquid air, opened, and the volatile material transferred (0·17g.), and shown by infra-red spectroscopy to contain SiF_4, CO, CO_2 and an unknown product. The mixture was passed through 10% NaOH solution, then washed with water. The residual gas was shown by g.l.c. col. 'L' at 0°C to be one component, infra-red spectrum shows absorbtions at 1075 and 1200–1000 $cm.^{-1}$, the mass spectrum showed peaks at $^m/e$ 127, 100, 85 and 81 possibly due to I, C_2F_4, CF_3O and C_2F_3 respectively, but could not be identified. Ether extraction of the tube and contents yielded no product.

(ii) with bromine.

a) Disilver perfluoro-oxydiacetate (3·40g., 8·10 m.moles) and bromine (2 ml., 36·3 m.moles) were placed in a stainless steel autoclave (35 ml.) which was heated with shaking at 110°C/17 hr. The autoclave was cooled in liquid air, opened, and allowed to warm to room temperature, the volatile product being transferred to a receiver (0·20g.). This product was shown by infra-red spectroscopy to consist of COF_2, CO_2, SiF_4 and the unknown compound above. The residue in the autoclave was added to water, acidified, extracted with ether and the ether removed to give perfluoro-oxydiacetic acid (0·48g., 29%).

b) Disilver perfluoro-oxydiacetate (2·44g., 5·80 m.moles) and bromine (1·6 ml., 20 m.moles) were placed in a flask (25 ml.) connected to two traps, the second cooled in liquid air. The flask was heated in an oil bath, and the distillate to 110°C collected. Additional bromine (1·0 ml., 12·5 m.moles) was then added, and the heating continued for 30 min. The product in the first trap dissolved in 2N KOH solution, and yielded no product when acidified and ether extracted. The product in the liquid air trap was transferred to a storage bulb (0·08g.) and shown by infra-red spectroscopy to be identical to the uncharacterised material isolated above. The flask and contents were extracted with ether to yield perfluoro-oxydiacetic acid (0·54g., 45%).

Perfluoro-oxydiacetyl chloride.

Perfluoro-oxydiacetic acid (4·63g., 0·0225 mole) and thionyl chloride (10 ml.) were placed in a round-bottomed flask (50 ml.) fitted with a water-cooled reflux condenser, and the mixture heated under reflux for 3 hr. Fractionation (6" x 1" vacuum-jacketed column) of the product gave perfluoro-oxydiacetyl chloride (4·16g., 76%), b.p. 95° (Lit.[44] 96°). Found: C, 19·97; Cl, 28·8; F, 31·8; required for $C_4Cl_2F_4O_3$: C, 19·77; Cl, 29·19; F, 31·3. ^{19}F n.m.r. shows singlet at -87·3 p.p.m. from hexafluorobenzene. $\nu_{max.}$ (gas) 1815 ($>C{=}O$), 1210, 1138 and 1035 $cm.^{-1}$ (Lit.[43] liquid film 1810 $cm.^{-1}$, ^{19}F n.m.r. singlet at +76·8 p.p.m. from $CFCl_3$). Mass spectrometry fragment ions: $^{m}/e$ 122, C_3ClFO_2 (2); 116, C_2F_2O (100); 113, $C_2F_3O_2$ (1); 94, $C_2F_2O_2$ (1); 87, C_3O_2F (2); 81, C_2F_3 (7); 78, C_2F_2O (12); 75, C_2FO_2 (24); 69, CF_3 (10);

31, CF (41); 28, CO (31).

Reaction of perfluoro-oxydiacetyl chloride with potassium iodide.

(i) Perfluoro-oxydiacetyl chloride (7·67g., 31 m.moles) was passed down a heated glass column (29 x 1·5 cm.), containing potassium iodide (20g., 121 m.moles), which was connected to a 2-necked flask (25 ml.) fitted with a water cooled condenser connected to a trap cooled in liquid air. The potassium iodide had been previously dried at 255°C/48 hr. with a continuous flow of dry nitrogen. The temperature of the column was kept at 300°C during the addition, and when completed, dry nitrogen was passed down the column. The contents of the flask were examined by g.l.c. and shown to be perfluoro-oxydiacetyl chloride. The contents of the flask were again passed down the column, and g.l.c. showed only the acid chloride. This process was again repeated, the quantity of material condensed greatly diminished each time. The contents of the flask were treated with excess saturated sodium bicarbonate, acidified with conc. hydrochloric acid, ether extracted, the ether extracts combined, dried ($MgSO_4$) and the ether removed by distillation to give perfluoro-oxydiacetic acid (0·89g., 14%). The carbon monoxide in the trap cooled in liquid air was removed at -180°, the residual volatile material being SiF_4, COF_2 and the uncharacterised material.

(ii) Perfluoro-oxydiacetyl chloride (2·93g., 12·0 m.moles) was transferred into a glass tube (35 ml.) containing potassium iodide (10·0g., 60·4 m.moles), the tube sealed and heated at 200°C/12 hr. The tube was cooled in liquid air, opened and the volatile contents transferred to a gas storage bulb (0·15g.), the products shown to be SiF_4, CO, COF_2 and the unknown product. The residue in the tube was extracted with ether (3 x 50 ml.), the ether extracts washed with dilute thiosulphate solution, dried and the ether removed to give perfluoro-oxydiacetic acid (0·52g., 22%).

Perfluoro-oxydiacetic anhydride.

An intimate mixture of perfluoro-oxydiacetic acid (1·95g., 9·45 m.moles) and phosphorus pentoxide (4·12g., 29·1 m.moles) was placed in a round-bottomed flask (25 ml.) which was attached to a conventional distillation apparatus, the whole apparatus being kept under dry nitrogen. The flask was rapidly heated with a bunsen burner, and the material distilling below 95°C collected. The product was separated from traces of phosphorus pentoxide by transfer under reduced pressure to give perfluoro-oxydiacetic anhydride (1·37g., 76%), b.p. 66° (Lit.[43] b.p. 64°). Found: C, 25·8; F, 40·0; required for $C_4F_4O_4$: C, 25·55; F, 40·4. ^{19}F n.m.r. shows a singlet at -91·6 p.p.m. from hexafluorobenzene (Lit.[43] +74·5 p.p.m. from $CFCl_3$). $\nu_{max.}$ 1845 (>C=O), 1215, 1140, 1108 and 1037 cm.$^{-1}$ (Lit.[43] 1840 cm.$^{-1}$). Mass spec. shows $^{m}/e$ 172, $C_4F_4O_3$ (2); 116, C_2F_4O (35); 85, CF_3O (4); 78, C_2F_2O (4); 75, C_2FO_2 (16); 69, CF_3 (5); 66, CF_2O (6); 50, CF_2 (100); 47, CFO (51); 44, CO_2 (62); 31, CF (12·5); 28, CO (49).

Reaction of perfluoro-oxydiacetic anhydride with iodine.

Dry iodine (3·5g., 0·0138 mole) was placed in a stainless steel autoclave (10 ml.), perfluoro-oxydiacetic anhydride (1·34g., 7·15 m.moles) transferred into the cooled autoclave under reduced pressure. The autoclave was sealed and heated to 385° for 4 hr. After cooling, the volatile contents of the autoclave were transferred to a storage bulb (wt. of product 0·06g.) and shown by infra-red spectroscopy to contain CO_2, CO and COF_2. Ether extraction of the autoclave afforded no residue.

Dipiperidinium perfluoro-oxydiacetate.

To a solution of perfluoro-oxydiacetic acid (0·20g., 9·7 m.moles) in dry ether (10 ml.), piperidine (2 ml.) was added dropwise. The crude precipitate was crystallised from $CHCl_3$/80-100 petrol (1:1) to give dipiperidinium perfluoro-oxydiacetate (0·27g., 74%), decomp. 180°C. Found: C, 44·9; H, 6·2; F, 20·6; N, 7·2; required for $C_{16}H_{24}F_4O_5N_2$: C, 44·7; H, 6·4; F, 20·2; N, 7·45. ^{19}F n.m.r. in $CHCl_3$ shows single peak at -89·3 p.p.m. from h.f.b. as external reference, ^{1}H n.m.r. shows peaks at 0·18τ ($-NH_2$), 7·00τ and 8·46τ in relative areas 1:2:3. $\nu_{max.}$

2960, 1680 (>C=O), 1232, 1188 and 1076ish cm.$^{-1}$

1,1,3,3-tetrafluoro-2-oxapropane.

A mixture of perfluoro-oxydiacetic acid (2·5g., 12·3 m.moles) and piperidine (1·22 ml., 16·9 m.moles) was heated in a flask connected to two traps cooled in liquid air. A crude fractionation of the products gave carbon dioxide and 1,1,3,3-tetrafluoro-2-oxapropane (0·37g., 26%). ^{19}F n.m.r. shows a doublet at -79·2 p.p.m. from h.f.b. as external reference (J ~ 71 c.p.s.) and ^{1}H n.m.r. shows a triplet at 3·45τ (J ~ 71 c.p.s.). $\nu_{max.}$ 3000 (≥C-H), 1370, 1210-1070, 1010 and 790 cm.$^{-1}$

Reaction of perfluoro-oxydiacetyl chloride with dimethyl cadmium.

To a suspension of magnesium turnings (0·26g.) in dry ether (150 ml.), methyl iodide (1·48g., 10·5 m.moles) in dry ether (20 ml.) was added, and the mixture refluxed 15 mins. To this was added dried cadmium bromide (3·40g., 12·5 m.moles), the mixture refluxed 30 min., dry benzene (50 ml.) added, followed by the removal of the ether by distillation. Perfluoro-oxydiacetyl chloride (1·71g., 7·1 m.moles) in dry benzene (20 ml.) was added over 5 min., and the mixture stirred overnight. Contents of the flask were added to iced water (100 ml.), the organic phase separated, and the aqueous phase extracted with ether (2 x 50 ml.), the organic phases combined, dried (MgSO$_4$), and the solvents removed to afford a residue which on sublimation (100°/0·01 mm.) gave perfluoro-oxydiacetic acid (0·21g., 15%), identified as its dianilinium salt.

Reaction of perfluoro-oxydiacetyl chloride with triphenyl phosphine dichloromethylene.

To a solution of triphenyl phosphine (2·50g., 9·6 m.moles) in carbon tetrachloride (20 ml.), perfluoro-oxydiacetyl chloride (1·11g., 4·6 m.moles) in carbon tetrachloride (10 ml.) was added. The mixture was stirred 63 hr., petroleum ether added (30 ml.), the mixture filtered and the organic solvents removed by distillation to give perfluoro-oxydiacetic acid (0·50g., 53%).

Diethyl perfluoro-oxydiacetate.

Perfluoro-oxydiacetic acid (2·00g., 9·8 m.moles), benzene (15 ml.), and absolute ethanol (6 ml.) were refluxed in a Dean and Stark apparatus for 48 hr. Removal of the organic solvents by distillation afforded a crude liquid residue which on distillation under reduced pressure gave diethyl perfluoro-oxydiacetate (1·63g., 64%), b.p. 96°/ 7 mm. Found: C, 36·64; H, 3·99; F, 29·30; required for $C_8H_{10}O_5F_4$: C, 36·65; H, 4·12; F, 28·98. ^{19}F n.m.r. showed a singlet at -88·0 p.p.m. from hexafluorobenzene as external reference, ^{1}H n.m.r. showed a triplet at 8·58τ and a quadruplet at 5·56τ. $\nu_{max.}$ 2920 (>C-H), 1782 (>C=O), 1235-1085 $cm.^{-1}$ (Lit.[45] b.p. 52-4°/2 mm. $\nu_{max.}$ 1786 (>C=O) $cm.^{-1}$)

Mass spec. fragment ions: 217, $C_6H_5F_4O_4$ (2); 190, $C_5H_6F_4O_3$ (8); 189, $C_5H_5F_4O_3$ (12); 162, $C_3H_2O_3F_4$ (3); 161, $C_3HF_4O_3$ (3); 152, $C_5H_6F_2O_3$ (6); 142, $C_4H_5F_3O_2$ (3); 139, $C_4H_5F_2O_3$ (1); 125, $C_4H_7F_2O_2$ (11); 124, $C_4H_6F_2O_2$ (73); 123, $C_4H_5F_2O_2$ (21); 121, $C_4H_3F_2O_2$ (2); 116, C_2F_4O (3); 115, $C_2H_2F_3O_2$ (4); 96, $C_2H_2F_2O_2$ (100); 95, $C_2HF_2O_2$ (10); 78, C_2F_2O (11); 73, $C_3H_5O_2$ (3); 66, CF_2O (1); 59, $C_2H_3O_2$ (6); 52, CH_2F_2 (2); 51, CHF_2 (9); 50, CF_2 (5); 45, CHO_2 (14); 44, CO_2 (12); 31, CF (11).

Dimethyl perfluoro-oxydiacetate.

Perfluoro-oxydiacetic acid (3·32g., 16·1 m.moles), methanol (3 ml.), benzene (20 ml.) and conc. sulphuric acid (1 ml.) were placed in a round-bottomed flask (100 ml.) and heated under reflux for 14 hr. The contents of the flask were added to water (100 ml.), the aqueous solution ether extracted, the ether extracts dried ($MgSO_4$), and the ether distilled to afford a crude liquid residue which on transfer under reduced pressure gave dimethyl perfluoro-oxydiacetate (2·12g., 57%). Found: C, 31·1; H, 2·78; F, 33·0; required for $C_6H_6F_4O_5$: C, 30·78; H, 2·58; F, 32·46. ^{19}F n.m.r. showed a singlet at -89·4 p.p.m. from h.f.b. as external reference and ^{1}H n.m.r. showed a single peak at 5·87τ. $\nu_{max.}$ 1780 ($>$C=O), and 1138 cm.$^{-1}$ (Lit.[43] ^{19}F n.m.r. +77·7 p.p.m. from $CFCl_3$, $\nu_{max.}$ 1787 cm.$^{-1}$). Mass spec. fragment ions: 219, $C_5H_3F_4O_5$ (1);

203, $C_5H_3F_4O_4$ (1); 175, $C_4H_3F_4O_3$ (27); 156, $C_4H_3F_3O_3$ (3); 124, $C_4H_6F_2O_2$ (100); 109, $C_3H_3F_2O_2$ (57); 94, $C_2F_2O_2$ (13); 81, C_2F_3 (68); 78, C_2F_2O (16); 65, $C_2H_3F_2$ (72); 51, CHF_2 (11); 50, CF_2 (20); 45, CHO_2 (40); 44, CO_2 (9).

Perfluoro-oxydiacetamide.

Diethyl perfluoro-oxydiacetate (0·62g., 2·4 m.moles) in dry ether (20 ml.) in 2-necked flask (35 ml.), was treated with ammonia gas for 20 min., the ether removed by distillation and the residue sublimed (92°/0·001 mm.) to afford perfluoro-oxydiacetamide (0·46g., 95%). A small portion was recrystallised from water, m.p. 143-4° (with decomp.). Found: C, 23·3; H, 1·76; F, 37·37; N, 14·0; required for $C_4H_4F_4N_2O_3$: C, 23·54; H, 1·97; F, 37·24; N, 13·74. ^{19}F n.m.r. showed a singlet at -86·1 p.p.m. from h.f.b. and ^1H n.m.r. showed a broad peak at 2·27τ with a solution in acetone. $\nu_{max.}$ 3365, 3185 ($-NH_2$), 1723 ($>C=O$), 1188 and 1097 cm.$^{-1}$ (Lit.[43] ^{19}F n.m.r. singlet at +78·0 p.p.m. from $CFCl_3$, $\nu_{max.}$ 3390, 3195 and 1725 cm.$^{-1}$). Mass spec. fragment ions: 184, $C_4H_3F_3N_2O_3$ (9); 183, $C_4H_2F_3N_2O_3$ (9); 168, $C_4HF_3NO_3$ (7); 167, $C_4F_3NO_3$ (8); 155, $C_4H_2F_3O_3$ (10); 137, $C_4F_3O_2$ (8); 119, C_4F_3N (9); 117, $C_4F_2N_2H_3$ (10); 109, C_3F_3O (13); 93, C_3F_3 (8); 69, CF_3 (100).

1-aza-4-oxa-3,3,5,5-tetrafluorocyclohexa-2,6-dione.

An intimate mixture of perfluoro-oxydiacetamide (1·57g., 8·4 m.moles) and phosphorus pentoxide (4·0g., 28·0 m.moles) was placed in a round-bottomed flask (10 ml.) fitted with a conventional distillation apparatus. Upon rapidly heating the flask, a solid was found in the condenser which on sublimation (60°/0·005 mm.) gave the hygroscopic 1-aza-4-oxa-3,3,5,5-tetrafluorocyclohexa-2,6-dione (0·87g., 60%) m.p. 54°C. Found: C, 25·4; H, 0·78; F, 41·0; required for $C_4HF_4O_3N$: C, 25·68; H, 0·53; F, 40·62. ^{19}F n.m.r. showed a singlet at -89·3 p.p.m. from h.f.b. with solution in acetone. $\nu_{max.}$ 1738 ($\gt$C=O) and 1178ish cm.$^{-1}$ Mass spec. fragment ions: 187, $C_4HF_4NO_3$ (21); 168, $C_4HF_3NO_3$ (7); 167, $C_4F_3NO_3$ (7); 159, $C_3HF_4NO_2$ (34); 121, $C_3HF_2NO_2$ (16); 116, C_2F_2O (32); 93, C_2HF_2NO (89); 78, C_2F_2O (93); 74, C_3F_2 (25); 70, CHF_3 (18); 69, CF_3 (20); 65, CHF_2N (33); 51, CHF_2 (13); 50, CF_2 (100); 47, CFO (55); 31, CF (17).

Monomethyl perfluoro-oxydiacetate.

To perfluoro-oxydiacetic anhydride (2·17g., 11·5 m.moles) in a round-bottomed flask (5 ml.), dry methanol (0·500 ml.) was added and the mixture stirred for 30 min. Distillation under reduced pressure gave monomethyl perfluoro-oxydiacetate (2·35g., 92%), b.p. 52°/0·05 mm. Found: C, 30·5; H, 2·68; F, 32·8; E. Wt. 111; required for $C_5H_4F_4O_5$: C, 30·78; H, 2·58; F, 32·46; E. Wt. 110. ^{19}F n.m.r. showed a multiplet at +79·9 p.p.m. from $CFCl_3$ as external reference and ^1H n.m.r. showed peaks at -0·43τ (-OH) and 6·05τ ($-OCH_3$) in relative areas 1:3. $\nu_{max.}$ 1777 ($\gt$C=O) and 1155ish cm.$^{-1}$ Mass spec. fragment ions:

179, $C_3H_3F_4O_4$ (11); 125, $C_3F_3O_2$ (38); 109, C_3F_3O (46); 95, $C_2HF_2O_2$ (5); 82, C_2HF_3 (17); 66, CF_2O (19); 60, $C_2H_4O_2$ (100); 50, CF_2 (8); 44, CO_2 (19).

Monomethyl perfluoro-oxydiacetyl chloride.

Monomethyl perfluoro-oxydiacetate (1·71g., 7·8 m.moles) and thionyl chloride (0·85 ml.) were placed in a round-bottomed flask (5 ml.) fitted with a reflux condenser, and heated under reflux for 37 hr. Excess thionyl chloride was removed by transfer under reduced pressure to leave monomethyl perfluoro-oxydiacetyl chloride (1·56g., 84%). Found: C, 24·9; H, 1·10; F, 32·5; Cl, 15·3; required for $C_5H_3ClF_4O_5$: C, 25·16; H, 1·26; F, 31·89; Cl, 14·86. ^{19}F n.m.r. showed a multiplet at +79·9 p.p.m. from $CFCl_3$ as external reference, ^1H n.m.r. showed singlet at 6·40τ. $\nu_{max.}$ 1788 (>C=O), 1250-1093 and 922 $cm.^{-1}$

5-Phenyl-3-oxa-perfluoropentanoic acid-5-one.

To a suspension of freshly sublimed aluminium chloride (5·3g., 0·040 mole) in sodium dried benzene (100 ml.) contained in a 2-necked flask (250 ml.) fitted with a reflux condenser, dropping funnel and containing a magnetic stirrer, perfluoro-oxydiacetic anhydride (2·34g., 0·0125 mole) in dry benzene (10 ml.) was added with vigorous stirring. After 15 min., a mixture of conc. hydrochloric acid (11 ml.) and water (50 ml.) was added and the mixture stirred for 30 min. The organic phase was separated, washed with aqueous sodium carbonate solution (5 x 20 ml.), the aqueous extract acidified (conc. HCl) and extracted with ether (3 x 50 ml.), the ether extracts dried ($MgSO_4$) and the ether removed to leave a residue which on transfer under reduced pressure ($100^{o}/0{\cdot}01$ mm.) afforded 5-phenyl-3-oxa-perfluoropentanoic acid-5-one (1·14g., 33%). Found: C, 44·8; H, 2·05; F, 28·8; required for $C_{10}H_6F_4O_4$: C, 45·1; H, 2·27; F, 28·55. ^{19}F n.m.r. showed two sets of triplets at -89·4 and -92·9 p.p.m. from h.f.b. as external reference (J 10·4 c.p.s.) in relative areas 1:1, and ^{1}H n.m.r. showed peaks at -1·16, 2·12 and 2·74τ in relative areas 1:2:3. $\nu_{max.}$ 3175 (-OH), 1785 (>C=O), 1725 (>C=O), 1603 (>C=C<), 1170 and 1087 $cm.^{-1}$ Mass spec. fragment ions: 237, $C_{12}H_7F_2O_3$ (3); 213, $C_{10}H_7F_2O_3$ (4); 195, $C_{10}H_5F_2O_2$ (5); 168, $C_9H_6F_2O$ (4); 155, $C_8H_5F_2O$ (19); 116, C_2F_4O (1); 105, C_7H_5O (25); 100, C_2F_4 (5); 96, $C_2H_2F_2O_2$ (17); 81, C_2F_3 (100); 77, C_6H_5 (26).

2,2,4,4-Tetrafluoro-3-oxa-pentane-1,5-diol.

Sodium dried ether (60 ml.) was added to lithium aluminium hydride (3·0g., 0·079 mole) in a 3-necked flask (250 ml.) fitted with a reflux condenser, mechanical stirrer, dropping funnel and a gas inlet and outlet, the whole of the apparatus being kept under dry nitrogen. Diethyl perfluoro-oxydiacetate (4·40g., 0·0165 mole) in dry ether (10 ml.) was added over 30 min., with vigorous stirring, causing a slight exothermic reaction. After stirring one hr., ether (10 ml.) was added, followed by the dropwise addition of water (10 ml.), ether (60 ml.) being added to replace that evaporated. Dilute sulphuric acid (2N., 120 ml.) was then added, the ether layer decanted, the aqueous phase ether extracted (5 x 10 ml.), the ether extracts combined and the ether removed by distillation. To the crude residue, dry benzene (50 ml.) was added and the mixture refluxed in a Dean and Stark apparatus for 2 hr. The bulk of the benzene (~40 ml.) was removed by distillation, and crystallisation from the residual liquor afforded 2,2,4,4-tetrafluoro-3-oxa-pentane-1,5-diol (2·49g., 83%), recrystallised from dry benzene m.p. 66°C. Found: C, 27·00; H, 3·40; F, 42·3; required for $C_4H_6F_4O_3$: C, 26·98; H, 3·40; F, 42·67. ^{19}F n.m.r. showed single peak with fine structure at +80·9 p.p.m. from $CFCl_3$ as external reference, ^1H n.m.r. showed broad peak at 5·30τ (-OH) and peak at 6·20τ ($-CH_2-$) in relative areas 1:2, for solution in acetone. $\nu_{max.}$ 3280 (-OH), 1295 and 1110 $cm.^{-1}$ Mass spec. fragment ions: 178, $C_4H_6F_4O_3$ (1); 160, $C_4H_4F_4O_2$ (2); 149, $C_3H_5F_4O_2$ (10); 141, $C_4H_4F_3O_2$ (8); 129, $C_3H_4F_3O_2$ (91); 113, $C_3H_4F_3O$ (21); 94, $C_2F_2O_2$ (100); 69, CF_3 (61).

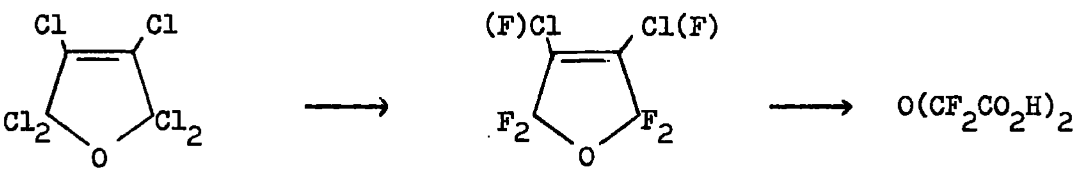
2,2,4,4-Tetrafluoro-3-oxa-pentane-1,5-diol (0·1873g., 1·05 m.moles), benzoyl chloride (0·5 ml.) and sodium hydroxide solution (10%, 7 ml.) were placed in a separating funnel (25 ml.) and shaken vigorously for 10 min. Sodium carbonate solution (10%, 5 ml.) was added and the resultant precipitate sublimed (79°/0·002 mm.) to give 2,2,4,4-tetrafluoro-3-oxa-pentane-1,5-dibenzoate (0·308g., 82%), m.p. 65°. Found: C, 55·7; H, 3·57; F, 20·0; required for $C_{16}H_{14}F_4O_5$: C, 55·98; H, 3·65; F, 19·67.

CHAPTER III.

THE FLUORINATION OF PERCHLORO-2,5-DIHYDROFURAN, AND REACTIONS OF SOME CHLOROFLUORO-2,5-DIHYDROFURANS WITH NUCLEOPHILES.

Introduction.

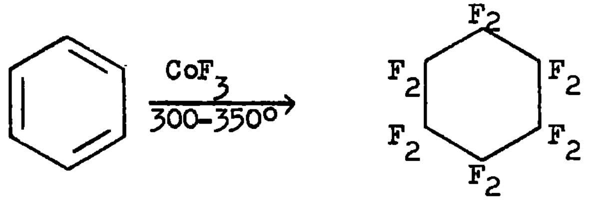
The work to be described in this chapter arose from the investigation of one step in the synthesis of perfluoro-oxydiacetic acid from perchlorobut-1,3-diene, described in Chapter I. It was necessary to find an effective method of converting perchloro-2,5-dihydrofuran (XIII) to a derivative in which the allylic dichloromethylene groups were replaced by difluoromethylene groups while retaining both the ether link and the C3-C4 double bond. Further objectives were that the chosen reaction should proceed in high yield, preferably using conventional apparatus and readily available reagents, since this was to be one stage in a multistep synthesis of a starting material for other work.



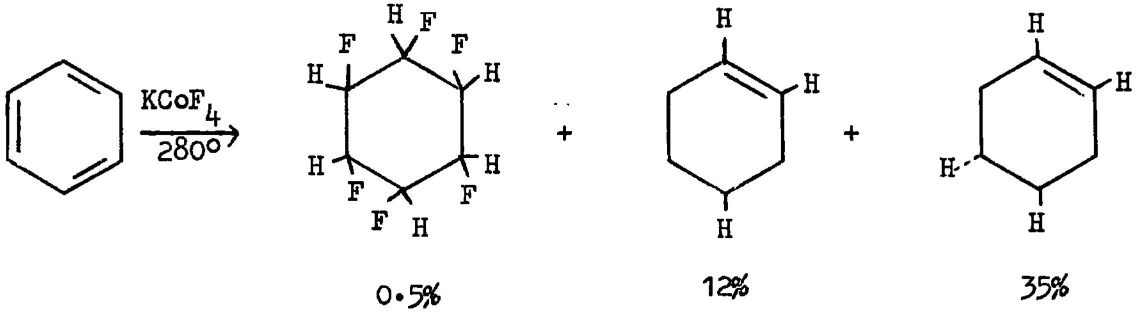
(XIII)

Fluorination of organic compounds.

Fluorinated organic compounds have been prepared in many ways, and reviewers[47] have suggested that the methods which have been developed may be classified under the two main headings according to the overall result of the fluorination. In this classification, methods such as direct elemental fluorination, fluorination with halogen fluorides or high valence metallic fluorides, and electrochemical fluorination are grouped under the heading 'exhaustive' fluorination. The application of these methods generally, but not exclusively, results in the replacement of hydrogen and functional groups by fluorine, and saturation of double bonds and aromatic rings. The other group of reactions is classified as 'selective' fluorination and results in the specific replacement of substituents in the original compound without affecting the rest of the molecule; examples of this class of reaction are the conversion of carbonyl to difluoromethylene with sulphur tetrafluoride (see Chapter I), the Balz-Schiemann reaction for conversion of aromatic amino derivatives to fluoro derivatives via their diazonium salts, and the selective replacement of a halogen atom (Cl, Br, I) in the organic compound by a fluorine atom from the fluorinating reagent. This classification is not rigidly applicable and a particular reagent may fall into either group depending on the conditions under which it is used; for example, high valence metallic fluorides give saturated perfluoro compounds at high temperatures, but when the reaction temperature is kept relatively low, products retaining both hydrogen and unsaturation may be obtained from the fluorination of benzene.



predominantly (Ref. 48)



(Ref. 49)

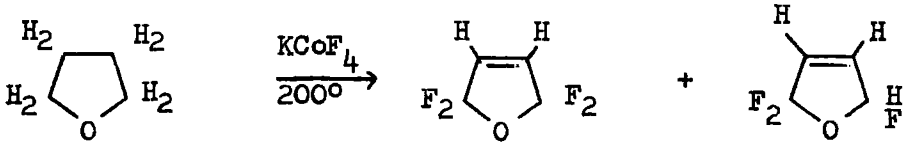
+ other partially fluorinated cyclohexanes

Elemental fluorination of organic compounds is a highly exothermic process, the bond energies of C-F, H-F, C-H, C-C and F-F bonds are respectively, 107-116, 134·6, 98·7, 82-88 and 36·6 Kcal./mole and consequently in the reaction,

$$\geqslant C{-}H \quad + \quad F_2 \quad \longrightarrow \quad \geqslant C{-}F \quad + \quad HF$$

there will be 106-115·3 Kcal./mole released. Unless this energy can be rapidly dissipated extensive fragmentation of the carbon skeleton of the molecule undergoing fluorination results. Much work has gone into the problem of heat dispersal and a variety of types of reactor have been constructed for direct fluorination. Generally, these workers have used an inert gas or liquid diluent for one, or both, substrate and fluorine. Margrave and Lagow[50] have recently improved the yields and ease of applicability of direct fluorination by using very low pressures of fluorine gas, an efficient heat sink and long reaction times; they argued that although the overall heat of reaction was high, kinetic evidence showed that the heat associated with individual steps in the process was not exceptionally great. A reasonable approach to solving the heat dispersal problem was to slow down the rate of reaction as much as possible in order to allow the heat dissipation to proceed at a reasonable rate. This proved successful and high yields of perfluorinated materials were obtained in reactions carried out at room temperature, low initial fluorine concentration and over long duration (12-36 hrs.). In all its modifications direct fluorination results in saturation of the carbon skeleton, also, although in some cases functional groups may be retained, direct fluorination of compounds containing heteroatoms has generally resulted in a complex mixture of products and much fragmentation; on both counts direct fluorination is unsuitable for the immediate aims of this work.

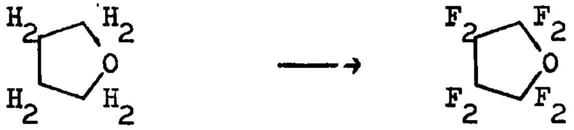
Fluorinations with halogen fluorides or high valence metallic fluorides suffer from the same general restrictions as direct elemental fluorination. Although the reactions are more readily controlled and less fragmentation occurs, the products are usually saturated, and fluorination of compounds containing heteroatoms is usually accompanied by elimination of the heteroatom. There are exceptions to these generalisations; thus for example, the fluorination of tetrahydrofuran over cobaltic fluoride[51] under carefully controlled conditions gives polyfluorotetrahydrofurans as the major products. Further, the development of new high valence metal fluorides as fluorinating reagents by the Birmingham group promise an enhanced degree of control over fluorination reactions. In particular, the fluorination of tetrahydrofuran over potassium tetrafluorocobaltate[16] gives 2,2,5,5-tetrafluoro- and 2,2,5-trifluoro-2,5-dihydro-furan as the major products.



Although the overall yield of 2,2,5,5-tetrafluoro-2,5-dihydrofuran reported is only 3·5% it is to be expected that optimising conditions could increase the yield to the point where this reaction could form the starting point of a preferred route to perfluoro-oxydiacetic acid (Chapter I).

Electrochemical fluorination normally produces completely fluorinated products although it is often possible to obtain products in which functional groups and heteroatoms are retained. Thus, for example, ethers and carboxylic acids may be fluorinated by this technique in

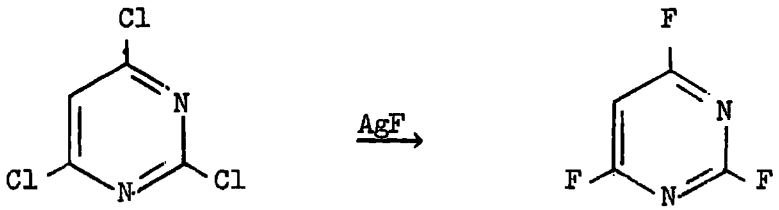
$$CH_3CH_2CH_2CO_2H \longrightarrow CF_3CF_2CF_2COF \qquad \text{(Ref. 52)}$$



(41%) (Ref. 53)

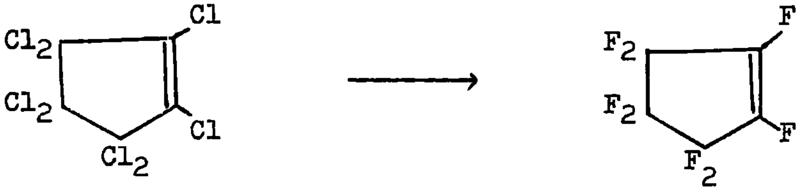
quite respectable yields. However the products are invariably saturated and the method was therefore unsuitable for the immediate needs of this project.

The reaction of halocarbons with fluorinating agents is considerably less exothermic than the corresponding reaction of hydrocarbons, due principally to the fact that no hydrogen fluoride is produced. One of the earliest methods of fluorination reported was the exchange of a halogen atom for fluorine. An extensive literature on this type of fluorination has accumulated since Moissan[54] first reported the synthesis of alkyl fluorides from alkyl iodides and silver monofluoride. The inefficiency of silver monofluoride as a selective fluorinating reagent is due to the formation of complexes between silver fluoride and silver halide produced during the reaction, and has led to it being superceded by cheaper and more effective reagents. However it is still used in specific syntheses, for example:[55]

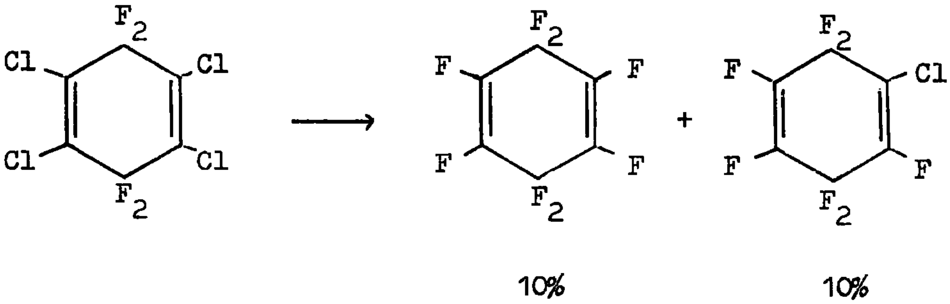


(76%)

Both silver fluoride, and mercurous fluoride, which has similar fluorinating ability to silver fluoride, have been replaced in many cases by potassium fluoride which is cheap and readily available. This reagent will readily exchange reactive halogens in aliphatic compounds, as in the preparation of acyl fluorides from acyl chlorides,[56] in unsaturated halogenated aliphatic compounds,[57] and also accomplishes the fluorination of perchlorocyclo-alkenes and -dienes.

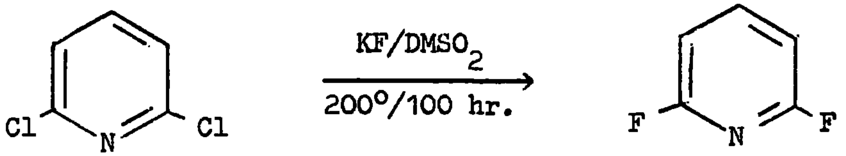


(72%) (Ref.58)



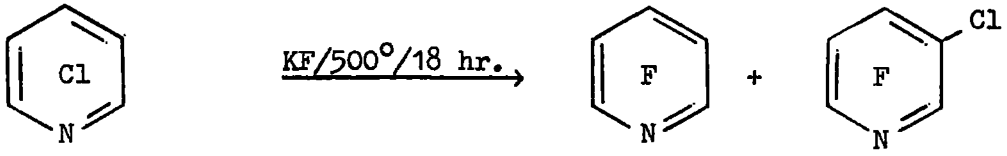
(Ref.58)

The use of potassium fluoride as a halogen exchange reagent has been extended to the aromatic field, used either in a solvent as in the fluorination of 2,6-dichloropyridine[59] or without a solvent; to



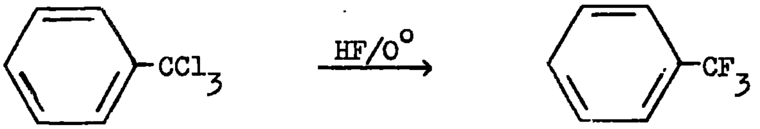
52%

prepare pentafluoropyridine[60,61]



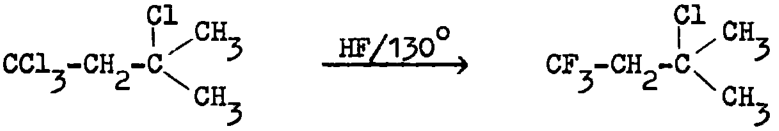
83% 7% (Ref. 61)

Other alkali metal fluorides can be used, and the efficiency of alkali metal fluorides in halogen exchange reactions decreases CsF > RbF > KF > NaF > LiF, potassium fluoride usually being used because of its ready availability. Perhaps the most common 'selective' fluorinating reagent, particularly on an industrial scale, is hydrogen fluoride. The ease of displacement of a halogen atom by hydrogen fluoride depends on the strength of the carbon-halogen bonds and the number of halogen atoms to be replaced. A smooth replacement is that of halogens attached to a carbon adjacent to a double bond or an aromatic ring, as in the fluorination of benzotrichloride:[62]



(75-95%)

In an unactivated molecule replacement of halogen is more difficult, for example:[63]



$$CCl_3-CH_2-C(Cl)(CH_3)_2 \xrightarrow{HF/130^\circ} CF_3-CH_2-C(Cl)(CH_3)_2 \quad (40\%)$$

For difficult fluorinations, the inclusion of a catalyst, usually an antimony halide, may enable the fluorination to be carried out at reduced temperatures, but for the conversion of 1,1,1,2-tetrachloroethane to 1-chloro-2,2,2-trifluoroethane, the very active reagent $SbF_3Cl_2 \cdot 2HF$ was used at elevated temperature and considerable pressure:[64]

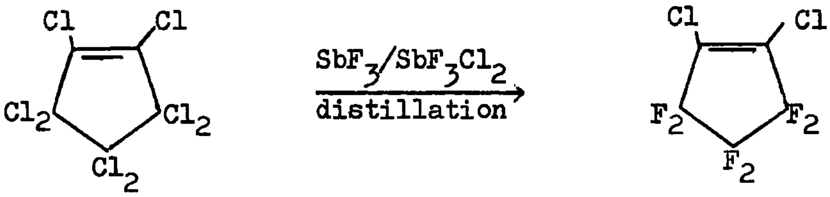
$$CH_2Cl-CCl_3 \xrightarrow[133^\circ/46\ \text{Ats.}]{SbF_3Cl_2 \cdot 2HF} CH_2Cl-CF_3 \qquad (95\%)$$

Antimony fluoride was first used for fluorinations by Swarts who made a variety of aliphatic fluorides[65] using this reagent. Further development has shown that antimony fluorides or mixed fluorides/chlorides can effect similar fluorinations to hydrogen fluoride, particularly in the ability to react with $-CX_2-$ and $-CX_3$ groupings (X = halogen) and replace the halogens successively by fluorine:

$$Cl_2C{=}CCl-CCl_3 \xrightarrow{SbF_3/150^\circ} \underset{13\%}{Cl_2C{=}CCl-CCl_2F} + \underset{28\%}{Cl_2C{=}CClCClF_2} + \underset{43\%}{Cl_2C{=}CCl-CF_3}$$

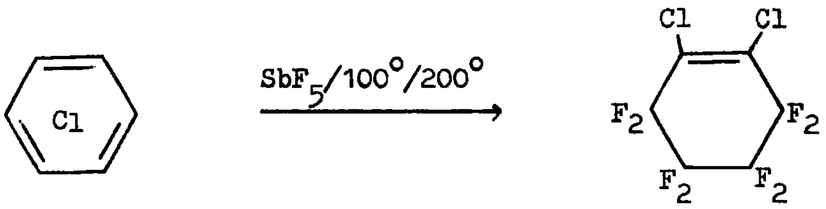
(Ref. 66)

The efficiency of antimony trifluoride as a fluorinating agent can be increased by transforming the antimony partly, or totally, from the trivalent to the pentavalent state by the addition of halogen, or antimony pentachloride. A mixture of antimony trifluoride and antimony pentachloride will substitute fluorine for halogens in many types of aliphatic or alicyclic halides:[67]



(72%)

The increased fluorinating power of pentavalent antimony fluoride is shown by the extensive fluorination of hexachlorobenzene in which replacement of chlorine and addition of fluorine occurs:[68]



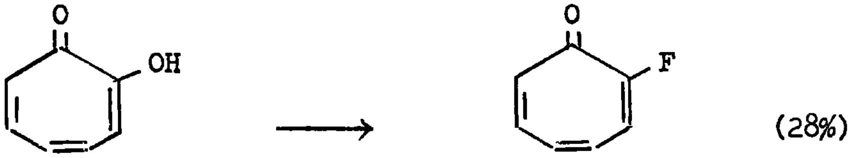
(44%)

The replacement of a lone halogen atom on carbon provided it is not adjacent to fluorine or other halogens can be achieved by mercuric fluoride, a replacement which is difficult by most of the previous 'selective' fluorinating reagents:[69]

$$C_2H_5Br \xrightarrow{HgF_2/0^\circ C} C_2H_5F \qquad (100\%)$$

Various other metallic and non-metallic fluorides have been used as possible exchange fluorinating agents, such as thallous fluoride to make fluoroformates,[70] and caesium fluoride for the preparation of fluoroaromatic compounds, but very little advantage seems to be gained from using these much more expensive reagents.

The introduction of fluorine into a molecule at a particular position can be achieved by replacement of some other functional group, a useful reagent being sulphur tetrafluoride, which reacts with alcohols to form alkyl fluorides, and converts acidic hydroxyl groups to fluorides:[4]



This reagent, as reported fully in Chapter I, converts carbonyl and carboxylic groups to difluoromethylene and trifluoromethyl groups respectively.

Replacement of acidic hydrogens by fluorine in β-dicarbonyl compounds can be achieved using perchloryl fluoride:[71]

$$CH_3COCH_2CO_2Et \xrightarrow{NaOEt} CH_3COCNa_2CO_2Et \xrightarrow{FClO_3} CH_3COCF_2CO_2Et \quad (59\%)$$

and the addition of hydrogen fluoride to an unsaturated molecule produces a 'selectively' fluorinated compound:[72]

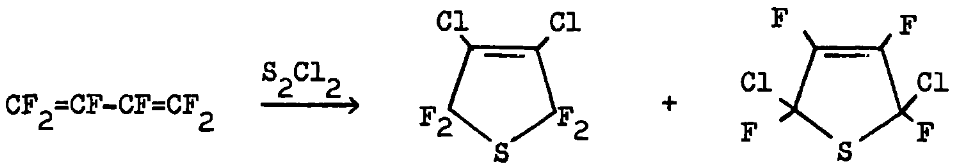
$$CH_2{=}C{=}CH_2 \xrightarrow{HF} CH_3CF_2CH_3 \qquad (50\%)$$

Apart from halogen exchange, an important method for the introduction of fluorine into an aromatic nucleus is the exchange of diazonium groups for fluorine via diazotisation in hydrogen fluoride. Monofluorinated benzenes[73] and pyridines[74,75] have been prepared in this way. A modification of this procedure is the Balz-Schiemann reaction which involves the isolation of a diazonium fluoroborate which decomposes at a definite temperature to afford an aromatic fluorine compound:[76,77]

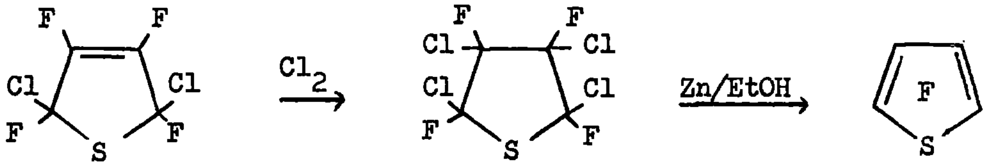
$$ArN_2^+BF_4^- \longrightarrow ArF + BF_3 + N_2$$

By stepwise repetition of nitration etc., several fluorine atoms can be introduced into the aromatic nucleus, as exemplified in the preparation of 1,2,4,5-[78] and 1,2,3,5-[79] tetrafluorobenzenes.

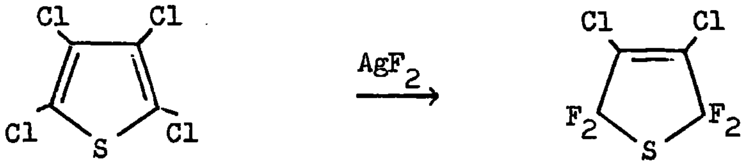
All the methods referred to under the general heading of 'specific' fluorinating agents have fairly wide applicability in the synthesis of organic fluorine compounds, but several preparative procedures have been developed which relate to the preparation of particular polyfluorinated compounds. This is especially noticeable for polyfluorinated heterocyclics, as in the preparation of polyfluorinated 2,5-dihydrothiophenes from perfluorobut-1,3-diene:[80]



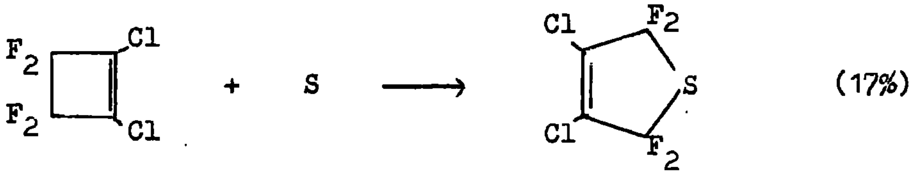
Further chlorination of 2,5-dichloro-2,3,4,5-tetrafluoro-2,5-dihydrothiophen followed by dehalogenation gives perfluorothiophen.



Additional specific syntheses for polyfluoro-2,5-dihydrothiophenes, involve the fluorination of tetrachlorothiophen with silver difluoride:[81]

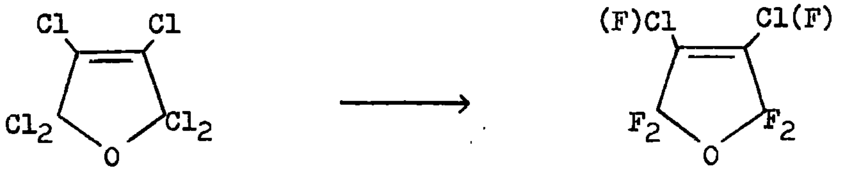


and the reaction of sulphur with 1,2-dichlorotetrafluorocyclobut-1-ene:[82]



The preparation of polyfluoro-2,5-dihydrofuran from the reaction of dichloromaleic anhydride with sulphur tetrafluoride is covered fully in Chapter I.

In the light of this review of the methods available for the synthesis of organic fluorine compounds and considering the conditions set out at the beginning of the chapter, it seemed that the conversion of perchloro-2,5-dihydrofuran to a compound of the required type would probably best be achieved using one of the 'specific' fluorinating agents. The reactions of perchloro-2,5-dihydrofuran with various 'specific' fluorinating reagents is reported in the following section.

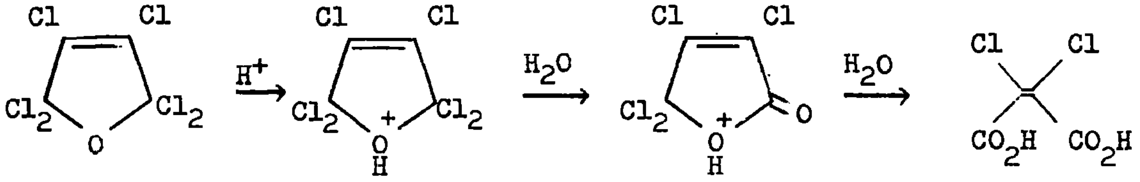


Discussion.

The fluorination of perchloro-2,5-dihydrofuran.

(i) with hydrogen fluoride.

Due to the relative ease of replacement of halogens attached to a carbon alpha to a double bond, it was decided to attempt the fluorination using anhydrous hydrogen fluoride, the reaction to be carried out in a nickel-lined autoclave. Initial attempts resulted in extensive decomposition due to an excessively high reaction temperature of 200°, and upon lowering the temperature below 80°C, the product of the reaction was identified as dichloromaleic acid, characterised by analysis, infra-red and mass spectrometry. The formation of this can be explained by acidic hydrolysis of unreacted perchloro-2,5-dihydrofuran in the work-up of the reaction mixture.

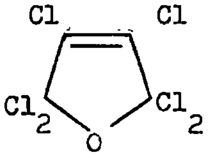
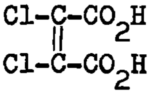
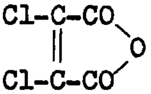
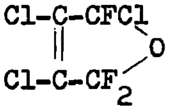
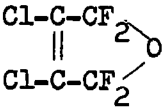
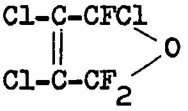
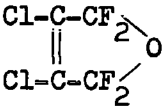
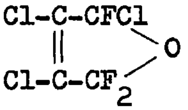
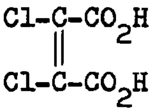


The ease of hydrolysis of perchloro-2,5-dihydrofuran was shown by treatment with conc. sulphuric acid at 90° for 3 hr. to afford dichloromaleic acid in 95% yield.

When the attempted fluorination was carried out at 90° (see Table 2)

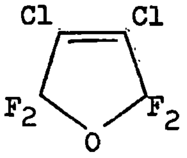
Table 2.

Reaction of perchloro-2,5-dihydrofuran with anhydrous hydrogen fluoride.

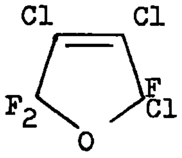
m.moles 	m.moles A.HF	Temp. °C	Time hr.	Products
47·5	500	200	21	Decomposition
47·5	450	130	21	Decomposition
47·5	600	60	21	
47·5	250	75	15	 + 
47·5*	650	90	15	 + 
47·5	600	90	19	 +  + 

* With SbF_3

the major product was 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) produced in 26% yield, together with an unknown product later identified as 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (XXXVIII)



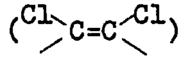
(IV)

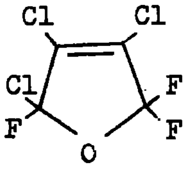


(XXXVIII)

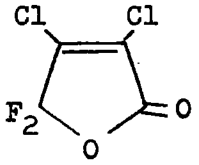
and dichloromaleic acid. The inclusion of an antimony halide as a catalyst in the fluorination produced no increase in the yield of products, the lowness of which is probably due to comparatively high material losses during work-up where a small amount of organic material had to be separated from a highly diluted aqueous layer, and possible loss of materials due to hydrolysis. Because of these difficulties, alternative fluorinating agents were sought.

(ii) <u>antimony trifluoride</u>.

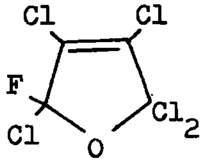
This fluorination was carried out in glass apparatus, the product being distilled from the reaction vessel as it formed. Examination of the product by gas-liquid chromatography showed the presence of three major components, one having the same retention time as 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran. Separation of these products by preparative scale gas chromatography afforded: 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran, identified by its infra-red spectrum, an unknown material and a third product. Elemental analysis and mass spectrometry data on the unknown gave a molecular formula $C_4OCl_3F_3$, infra-red spectrometry showed an absorbtion at 1660 cm.$^{-1}$ ($\mathrm{Cl}\!>\!C{=}C\!<\!\mathrm{Cl}$) and ^{19}F n.m.r. spectrometry showed a typical ABx spectrum with δ_A + 67•2, δ_B + 72•6 and δ_x + 53•6 p.p.m. with respect to external fluorotrichloromethane and J_{AB} 151 Hz, $J_{Ax(Bx)}$ 7•5 Hz and $J_{Bx(Ax)}$ 4•6 Hz. The limitations imposed by the molecular formula and the presence of a -CCl=CCl- double bond led to the deduction of the structure (XXXVIII), 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran, for this compound.



(XXXVIII)



(VIII)



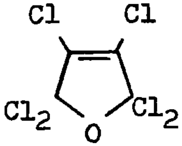
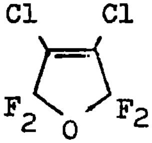
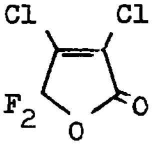
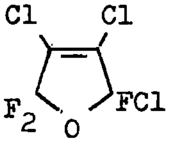
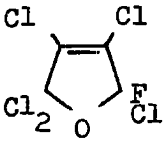
(XXXIX)

Hydrolysis of (XXXVIII) gave dichloromaleic acid in 53% yield. The third product from the reaction was identified by infra-red spectroscopy as 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (VIII).

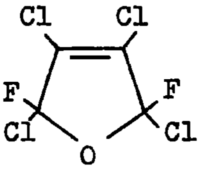
Upon reducing the ratio of fluorinating agent to perchloro-2,5-dihydrofuran (Table 3), other products appeared at the expense of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran. These were separated by preparative gas chromatography and identified by elemental

Table 3.

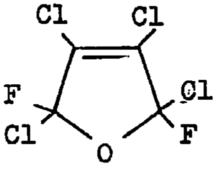
Reaction of perchloro-2,5-dihydrofuran with antimony halides.

m.moles	m.moles	m.moles	Product %				
	SbF$_3$	SbCl$_5$					difluoro compounds
72·8	168	41	77	-	-	-	-
72·8	168	-	29	11	20	-	-
72·8	140	-	-	6	16	-	29
72·8	111	-	3	7	20	9	25

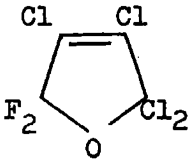
analysis and spectral data as: 2-fluoro-2,3,4,5,5-pentachloro-2,5-dihydrofuran (XXXIX), which showed a single fluorine resonance at +65·3 p.p.m. from fluorotrichloromethane; and a mixture of isomers of difluoro-tetrachloro-2,5-dihydrofurans. These isomers could not be separated by gas-liquid chromatography, and ^{19}F n.m.r. on the isomer mixture showed resonances at +61·0, +63·1, +71·6 and +77·6 p.p.m. from fluorotrichloromethane. The two resonances at lowest fields, which were the most intense, were provisionally assigned to the cis- and trans-2,5-difluoro-2,3,4,5-tetrachloro-2,5-dihydrofurans, (XXXX) and (XXXXI), likewise the resonance at +71·6 p.p.m. was provisionally assigned to



(XXXX)



(XXXXI)



(XXXXII)

2,2-difluoro-3,4,5,5-tetrachloro-2,5-dihydrofuran (XXXXII), whilst the highest field resonance, at +77·6 p.p.m., whose relative intensity was very low, possibly arose from some ring opened product of unknown structure. The synthesis of 2,2-difluoro-3,4,5,5-tetrachloro-2,5-dihydrofuran (XXXXII) was attempted by reaction of 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (VIII) with phosphorus pentachloride, to confirm the assignment of the ^{19}F n.m.r. data. However, no reaction occurred after 300 hr. at constant reflux.

(iii) antimony dichlorotrifluoride.

Antimony dichlorotrifluoride was prepared by the action of chlorine on antimony trifluoride at 340°C. The fluorination of perchloro-2,5-dihydrofuran using antimony dichlorotrifluoride yielded the desired 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran in 26% yield. However, extensive decomposition always occurred when using this reagent.

(iv) antimony trifluoride/antimony pentachloride.

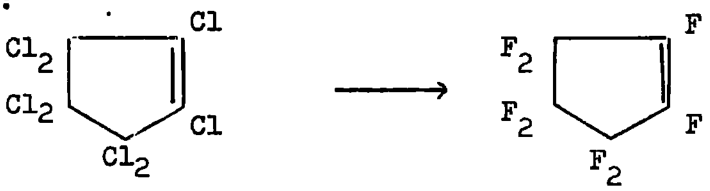
Due to the incomplete allylic replacement of the chlorines in perchloro-2,5-dihydrofuran using antimony trifluoride, and the extensive decomposition with antimony dichlorotrifluoride, the fluorination was attempted using antimony trifluoride-pentachloride mixture.

The fluorination of perchloro-2,5-dihydrofuran using these reagents was initially carried out in an autoclave, when 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) was obtained in 42% yield. However, upon effecting the fluorination in glass apparatus, and distilling out the product as it formed, the yield of (IV) increased to 77%, this being the only volatile material formed. The antimony trifluoride to antimony pentachloride ratio was found not to be critical within fairly wide limits.

In all cases of halogen exchange using these reagents, no products in which vinylic replacement of chlorine by fluorine had occurred were found.

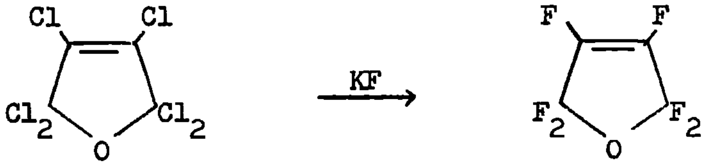
(v) <u>potassium fluoride</u>.

Since potassium fluoride had effected complete halogen exchange in perchlorocycloalkenes, as in the fluorination of perchlorocyclopentene:

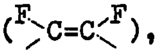
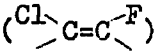
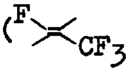


72% (Ref. 58)

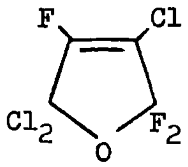
the fluorination of perchloro-2,5-dihydrofuran using this reagent may be expected to produce perfluoro-2,5-dihydrofuran (XVI).



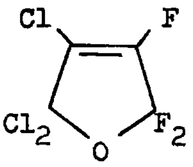
(XVI)

On the basis of Maynard's results,[58] in which it was found that most effective halogen exchange using potassium fluoride occurred with N-methylpyrrolidone as solvent, the fluorination was carried out by addition of perchloro-2,5-dihydrofuran to a suspension of potassium fluoride in N-methylpyrrolidone at 195°C. The volatile material which distilled from the reaction vessel was collected and shown by gas-liquid chromatography to consist of two major products which were separated by distillation. High resolution mass spectrometry and elemental analysis showed that these compounds had the molecular formulae C_4F_6O and $C_4Cl_3F_3O$. The compound with molecular formula C_4F_6O was assigned as perfluoro-2,5-dihydrofuran (XVI) on the basis of a carbon-carbon double bond stretching frequency in the infra-red spectrum at 1802 $cm.^{-1}$ (), and the ^{19}F n.m.r. which showed two bands in the ratio 2 to 1 at +78•1 and +155•7 p.p.m. from fluorotrichloromethane. The high field resonance, assigned to vinylic fluorine, was found to be a triplet (J ~ 7 Hz) and the low field resonance, assigned to the allylic difluoromethylene fluorines, to be a doublet (J ~ 7 Hz), both resonances showing further unresolved fine structure. The structure of the other product was assigned on the basis of an infra-red absorbtion at 1735 $cm.^{-1}$ () and ^{19}F n.m.r. resonances at +66•3 and +126•7 p.p.m. from fluorotrichloromethane in relative intensities 2 to 1. The high field resonance, assigned to vinylic fluorine, was found to be a triplet (J, 6•5 Hz) and the low field resonance, assigned to the allylic difluoromethylene group, to be a doublet (J, 6•5 Hz) which is consistent with a 2,4-coupling rather than a 2,3-coupling since the corresponding values for the coupling constants in <u>trans</u>-1,1,1,3-tetrafluoroprop-2-ene and 1,1,1,2-tetrafluoroprop-2-ene derivatives ( and ) are 8 Hz. and 20 Hz. respectively.

On this basis the structure was assigned as 2,2,4-trichloro-3,5,5-trifluoro-2,5-dihydrofuran (XXXXIII) rather than the only alternative 2,2,3-trichloro-4,5,5-trifluoro-2,5-dihydrofuran (XXXXIIIb).



(XXXXIII)

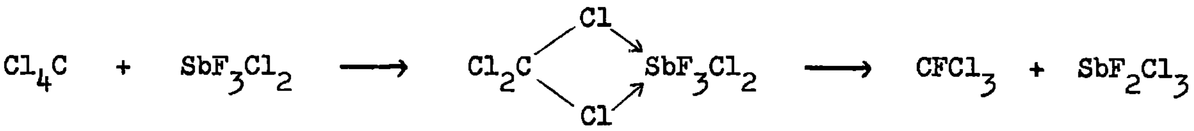


(XXXXIIIb)

Several minor products were also formed in this fluorination but could not be isolated pure, and variations in the molar ratios of reactants did not increase the yields of these products.

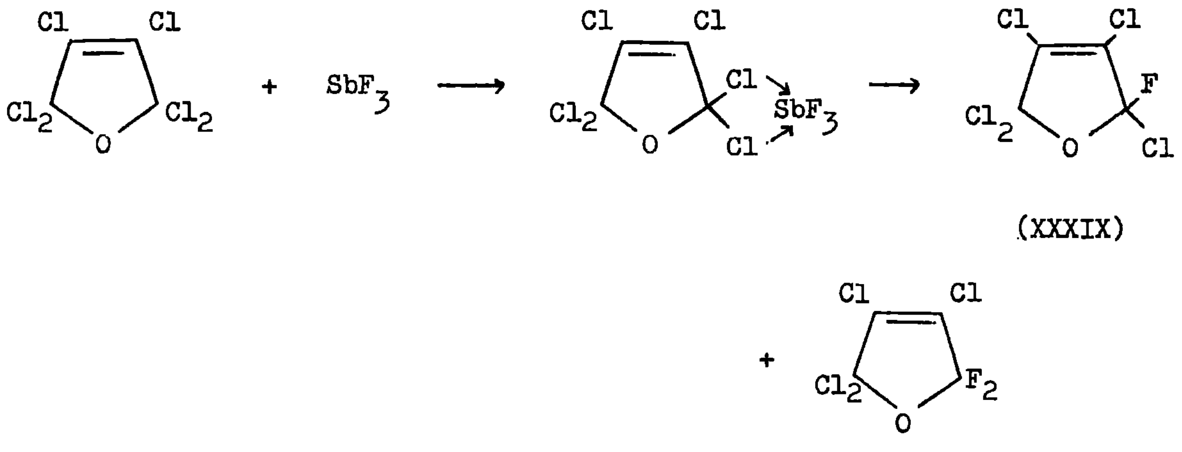
To account for the various products obtained with different fluorinating agents, different reaction mechanisms would appear to be in operation.

The fluorination with hydrogen fluoride may be expected to proceed via an SN2 mechanism involving nucleophilic displacement of a chloride ion by fluoride ion, whereas for halogen exchange with antimony halides intermediate co-ordination compounds have been postulated by Booth and Swinehart:[83]



$$Cl_4C + SbF_3Cl_2 \longrightarrow Cl_2C\begin{matrix} Cl \\ \\ Cl \end{matrix}SbF_3Cl_2 \longrightarrow CFCl_3 + SbF_2Cl_3$$

An analogous mechanism can be written for the reaction of antimony trifluoride with perchloro-2,5-dihydrofuran.



(XXXIX)

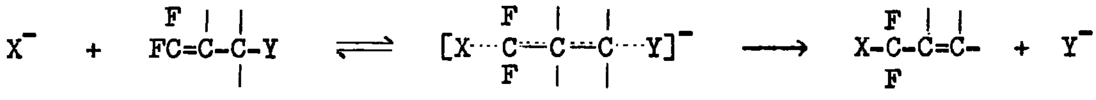
(XXXXII)

A repetition of this mechanism on the unreacted allylic chlorine atoms would give 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) and the isomeric 2,5-difluoro-2,3,4,5-tetrachloro-2,5-dihydrofurans (XXXX) and (XXXXI).

Several aliphatic halogen exchange reactions using potassium fluoride have produced rearranged products, as shown by Fried and Miller:[84]

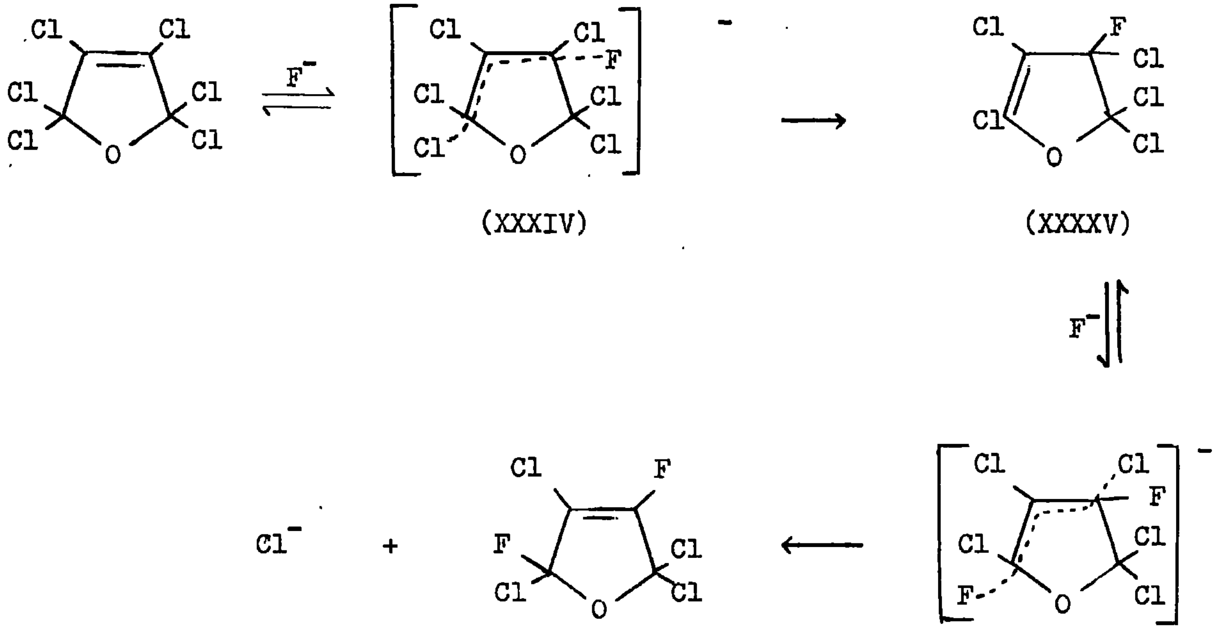
$$F_2C{=}CFCCl_2F \quad + \quad F^- \longrightarrow CF_3CF{=}CClF \quad + \quad Cl^-$$

To account for this, and similar observations, a SN2' mechanism was put forward which involves a 1,2 shift of the double bond and displacement of an allylic halogen:



$$X^- + F\overset{F}{C}{=}\overset{|}{C}{-}\underset{|}{\overset{|}{C}}{-}Y \rightleftharpoons [X\cdots\underset{F}{\overset{F}{C}}{=}\underset{|}{\overset{|}{C}}{=}\underset{|}{\overset{|}{C}}\cdots Y]^- \longrightarrow X{-}\underset{F}{\overset{F}{C}}{-}\overset{|}{C}{=}\overset{|}{C}{-} + Y^-$$

The formation of 2,2,4-trichloro-3,5,5-trifluoro-2,5-dihydrofuran (XXXXIII) and perfluoro-2,5-dihydrofuran (XVI) from the reaction of perchloro-2,5-dihydrofuran with potassium fluoride could be accounted for on the basis of either a total SN2' mechanism or a SN2' followed by a SN2 mechanism.

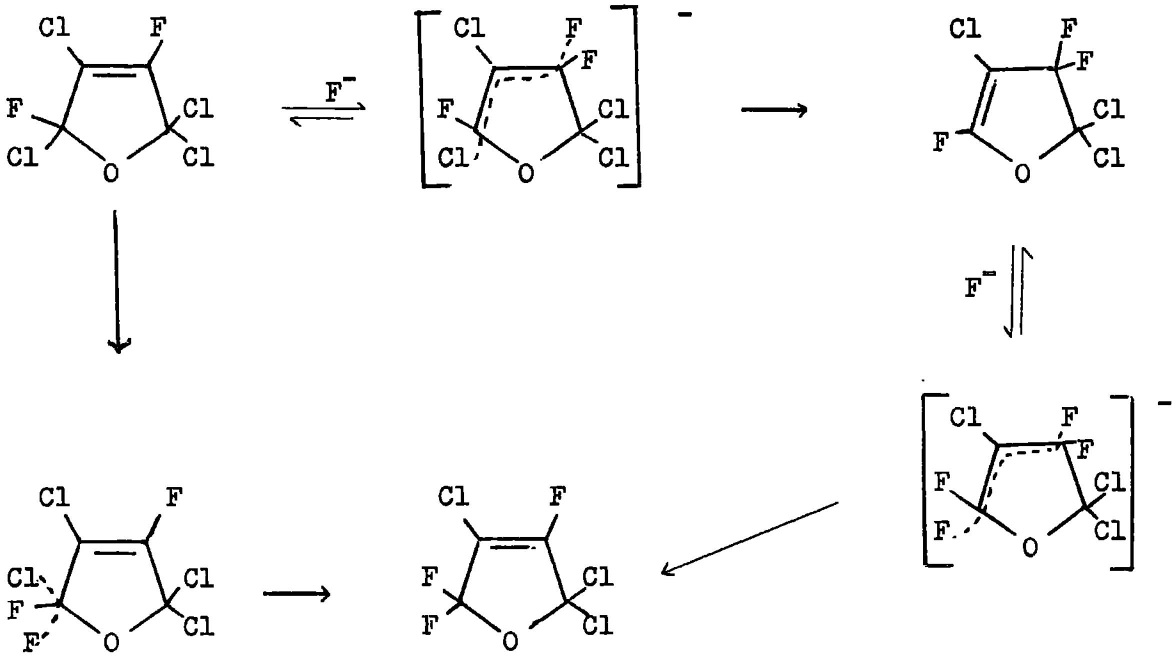

(XXXIV)

(XXXXV)

(XXXXVII)

(XXXXVI)

To produce 2,2,4-trichloro-3,5,5-trifluoro-2,5-dihydrofuran (XXXXIII), the intermediate (XXXXVII) could then react with fluoride ion via a SN2 or SN2' mechanism:

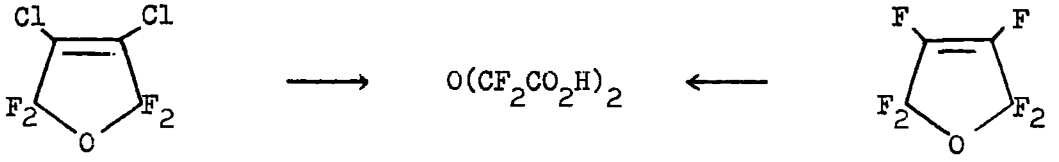


(XXXXIII)

A repeat of these mechanisms on (XXXXIII) would produce perfluoro-2,5-dihydrofuran (XVI). No intermediates of structures similar to (XXXXV) or (XXXXVII) were isolated although some uncharacterised minor components were shown to be present in the reaction product by gas chromatography.

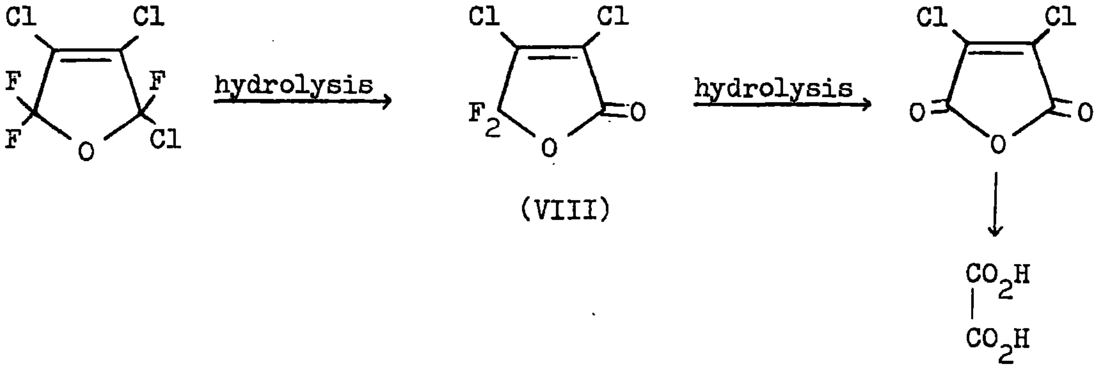
The difference in mechanism between hydrogen fluoride and potassium fluoride is possibly due to the stabilisation of the intermediates (XXXXIV) and (XXXXVI) by the polar solvent N-methyl pyrrolidone.

The basic structure of the chlorofluoro-2,5-dihydrofurans, and perfluoro-2,5-dihydrofuran, isolated was shown by hydrolysis, in the presence of alkali or acid, to give either dichloromaleic acid, or its anhydride. Oxidation of both 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV), and perfluoro-2,5-dihydrofuran (XVI) gave perfluoro-oxydiacetic acid (V).



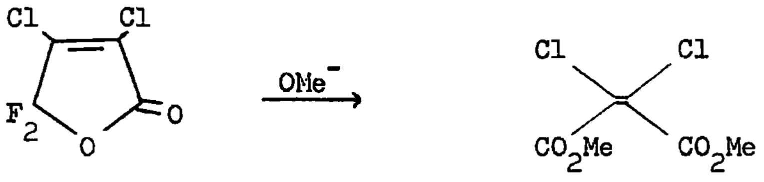
(IV) (V) (XVI)

However, oxidation of 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (XXXVIII) and the isomer mixture of difluorotetrachloro-2,5-dihydrofurans produced oxalic acid in low yield. This, presumably, is due to the relative ease of hydrolysis of a chlorofluoro- or dichloro-methylene group which would give dichloromaleic acid, or its anhydride, which when oxidised would produce oxalic acid; for example:



(VIII)

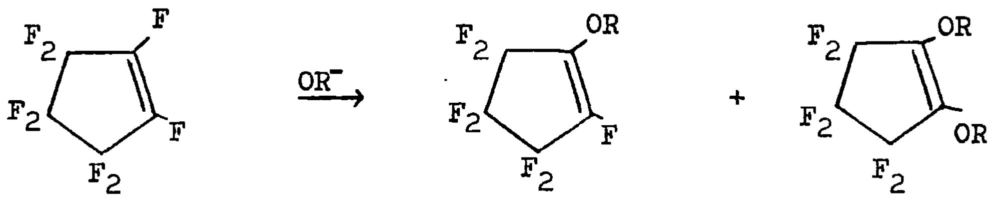
The ease of hydrolysis of lactone (VIII) was shown by reaction with dilute alkali to give dichloromaleic anhydride, and reaction with methoxide ion gave dimethyl-dichloro-maleate:



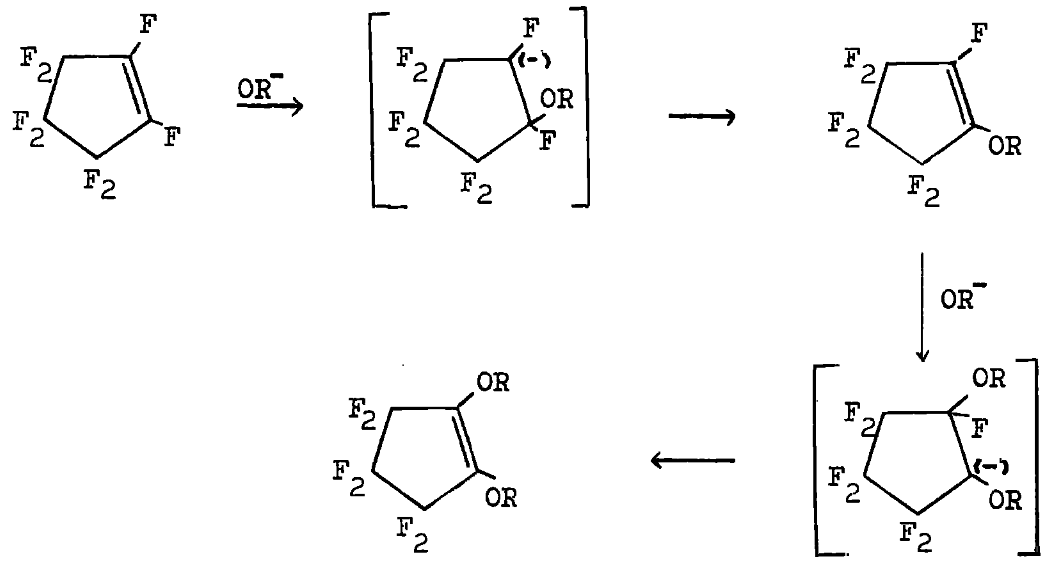
Reactions of some chlorofluoro-2,5-dihydrofurans with nucleophiles.

The reaction of alkoxides with acyclic[85] and cyclic[86] fluoro-olefins has been extensively studied, acyclic olefins usually giving addition products although subsequent elimination can occur to give olefinic ethers,[85] and cyclic olefins usually give unsaturated ethers. Four different mechanisms have been suggested to explain the various products, viz., direct vinylic substitution, addition to the double bond followed by elimination, allylic SN2 and allylic SN2'.[87]

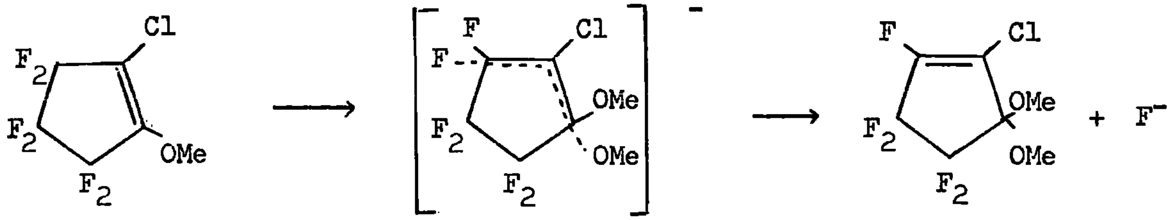
The reaction of perfluorocyclopentene with alkoxide results in 1- and 1,2-substitution:[88]



These products are explained on the basis of two consecutive addition and elimination reactions:



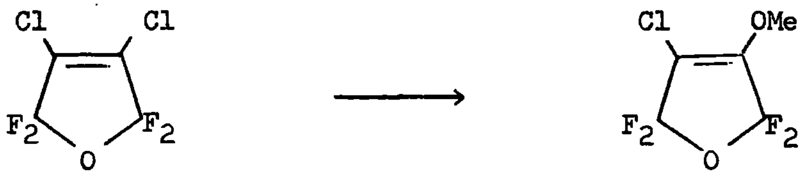
However, in the reaction of 1,2-dichlorohexafluorocyclopentene with alkoxide, addition elimination occurs to give the 1-chloro-2-alkoxy derivative which further reacts to produce 2-chloro-3,3-dialkoxypentafluorocyclopent-1-ene:[89]



Due to the availability of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran, and other chlorofluoro-2,5-dihydrofurans, in this work, it was decided to investigate the reactions of these compounds with alkoxides, to observe the effects, if any, of replacement of the

4-difluoromethylene group by oxygen in nucleophilic displacements of cyclopentene derivatives.

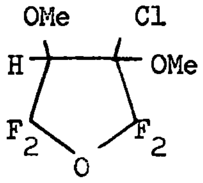
Treatment of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (IV) with one mole of methoxide gave the expected 4-chloro-3-methoxy-2,2,5,5-tetrafluoro-2,5-dihydrofuran (XXXXVIII).



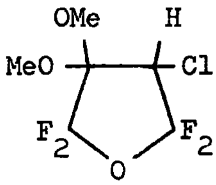
(IV) (XXXXVIII)

This was characterised by correct elemental analysis, with an infra-red absorbtion at 1707 $\mathrm{cm.}^{-1}$ $(^{\mathrm{Cl}}\diagdown\mathrm{C{=}C}\diagup^{\mathrm{OMe}})$, and the ^{19}F n.m.r. spectrum showed a typical A_2X_2 system of two sets of triplets centred at +78·3 and +78·9 p.p.m. from fluorotrichloromethane in relative intensity ratios of one to one, and a coupling constant of 5·5 Hz., whilst the ^{1}H n.m.r. spectrum showed a single peak at 6·18τ.

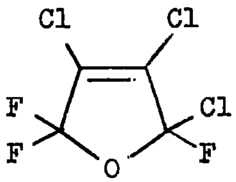
Reaction of (IV) with excess methoxide in methanol produced (XXXXVIII) in addition to a saturated compound whose elemental analysis gave the molecular formula $C_6H_7ClF_4O_2$. The ^{19}F n.m.r. spectrum of this compound showed two peaks at +70·5 and +78·3 p.p.m. from fluorotrichloromethane in relative areas of one to one, whilst the ^{1}H n.m.r. spectrum showed three peaks at 5·78, 6·40 and 6·60 in relative areas of one to three to three. From the data it would seem that addition of methanol to the C3-C4 double bond in 4-chloro-3-methoxy-2,2,5,5-tetrafluoro-2,5-dihydrofuran (XXXXVIII) has occurred. The evidence available is insufficient to distinguish between the two possible addition products 3-chloro-3,4-dimethoxy-2,2,5,5-tetrafluorotetrahydrofuran (XXXXIXa) and 3-chloro-4,4-dimethoxy-2,2,5,5-tetrafluorotetrahydrofuran (XXXXIXb).



(XXXXIXa)

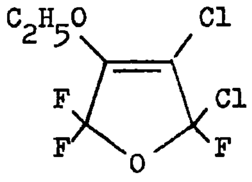


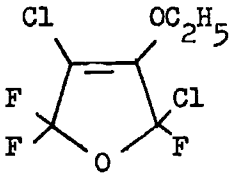
(XXXXIXb)



(XXXVIII)

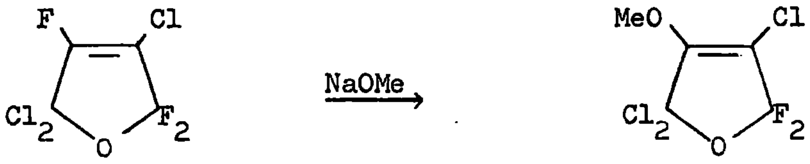
Reaction of 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (XXXVIII) with ethoxide gave the expected ethoxy-dichlorotrifluoro-2,5-dihydrofuran. Infra-red spectroscopy showed an absorbtion at 1700 cm.$^{-1}$ $\left({}^{Cl\diagdown}_{\diagup}C{=}C{}^{\diagup OC_2H_5}_{\diagdown}\right)$, the ^{1}H n.m.r. showed a quartet at $4{\cdot}24\tau$ and a triplet at $8{\cdot}58\tau$ in relative areas of two to three, whilst the ^{19}F n.m.r. showed a typical ABX spectrum with δ_A +71·4, δ_B +76·8 and δ_x +52·0 p.p.m. with respect to external fluorotrichloromethane, and J_{AB} 151 Hz., $J_{Ax(Bx)}$ 10·2 Hz., and $J_{Bx(Ax)}$ 5·4 Hz., in relative intensity ratios of one to one to one. Again, two structures can be postulated, 2,3-dichloro-4-ethoxy-2,5,5-trifluoro-2,5-dihydrofuran (La) and 2,4-dichloro-3-ethoxy-2,5,5-trifluoro-2,5-dihydrofuran (Lb):


(La)


(Lb)

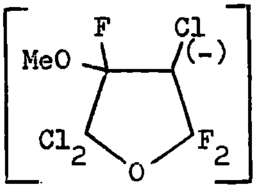
Insufficient data has been obtained to distinguish between these isomers.

Treatment of 2,2,4-trichloro-3,5,5-trifluoro-2,5-dihydrofuran (XXXXIII) with sodium methoxide gave only one product 2,2,4-trichloro-5,5-difluoro-3-methoxy-2,5-dihydrofuran (LI):

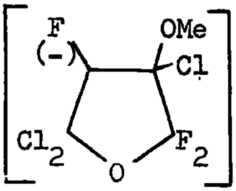

(XXXXIII) (LI)

This product was assigned on spectroscopic evidence since the vinylic fluorine resonance for (XXXXIII) at -36·2 p.p.m. from hexafluorobenzene disappeared completely to leave the single allylic fluorine resonance at -96·7 p.p.m., whilst the ^1H n.m.r. showed a single resonance at $5{\cdot}48\tau$. Mass spectrometry data showed the parent peak at $^m/e$ 238 with an isotope pattern consistent with three Cl atoms, and the infra-red spectrum showed the expected olefinic absorbtion at 1700 cm.$^{-1}$

The replacement of the vinylic fluorine in preference to the vinylic chlorine, assuming an addition-elimination mechanism, can be explained on the basis of the relative stabilities of the anionic intermediates. These would involve the negative charge on either the C-Cl or the C-F carbon viz:



(LIIa)



(LIIb)

It has been found that the order of stability of these carbanions is $\overset{(-)}{>C}\text{-Cl} > \overset{(-)}{>C}\text{-F}$,[90] hence replacement of fluorine occurs in preference to chlorine.

In this limited investigation, it has been found that only vinylic displacement occurs, and no allylic SN2' products of the type found in the dichloro hexafluorocyclopentene reactions,[89] were observed.

Experimental.

Reaction of perchloro-2,5-dihydrofuran with hydrogen fluoride.

(i) Perchloro-2,5-dihydrofuran (13g., 47·5 m.moles) and anhydrous hydrogen fluoride (13 ml., 650 m.moles) were placed in a cooled nickel-lined autoclave (200 ml.), the autoclave sealed and heated at 90°/15 hr. After cooling to -78°C, excess ice/water was added and the autoclave allowed to warm to room temperature. The contents were phase separated, the lower organic layer cooled in ice and treated with potassium carbonate (5g.). The crude product was transferred from phosphorus pentoxide under reduced pressure to afford 3,4-dichloro-2,2,5,5-tetra-fluoro-2,5-dihydrofuran (2·4g., 23%), identified by its infra-red spectrum.

(ii) Perchloro-2,5-dihydrofuran (13g., 47·5 m.moles) and anhydrous hydrogen fluoride (9 ml., 450 m.moles) were placed in a cooled nickel-lined autoclave (80 ml.), and the autoclave heated at 60°C/21 hr. The autoclave was cooled to room temperature, vented through iced water, opened, and the contents added to crushed ice. The aqueous solution was extracted with ether (5 x 50 ml.), the extracts dried ($MgSO_4$), and distilled to leave a solid residue which on sublimation (72°/0·002 mm.) gave dichloromaleic acid (2·42g., 28%), identified by its infra-red spectrum.

(iii) Perchloro-2,5-dihydrofuran (13g., 47·5 m.moles) and anhydrous hydrogen fluoride (12 ml., 600 m.moles) were placed in a cooled nickel-lined autoclave (200 ml.) and the autoclave heated at 75°C/15 hr. After cooling to -78°C, the autoclave was opened and ether extracted (5 x 100 ml.), sodium fluoride (10g.) was added to the ethereal extract, the extracts filtered, potassium carbonate (2g.) was then added, again filtered, and removal of the ether afforded a solid-liquid mixture. Transfer under reduced pressure separated the liquid from the solid, which was shown by infra-red spectroscopy to be dichloromaleic anhydride (0·19g., 3%). The liquid which transferred under reduced pressure was later identified by its infra-red spectrum as 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (0·56g., 5%).

Reaction of perchloro-2,5-dihydrofuran with antimony trifluoride.

(i) An intimate mixture of perchloro-2,5-dihydrofuran (20g., 73 m.moles) and antimony trifluoride (30g., 168 m.moles) were placed in a round-bottomed flask (50 ml.) fitted with a conventional distillation apparatus. The flask was heated with a bunsen burner and the distillate to b.p. 140°C collected. The product was found to consist of three components which were separated by preparative gas chromatography (Dinonylphthalate/Celite: N_2 carrier 200 ml./min., col. temperature 115°) to give, in order of emergence from the column:

a) 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (4·3g., 28%) identified by infra-red spectroscopy,

b) 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (3·2g., 20%).

Found: C, 21·4; F, 25·1; Cl, 46·3; required for $C_4Cl_3F_3O$: C, 21·1; F, 25·1; Cl, 46·8. Mass spec. fragment ions: 226, $C_4Cl_3F_3O$ (15); 207, $C_4Cl_3F_2O$ (2); 191, $C_4Cl_3F_2$ (100); 179, $C_3Cl_3F_2$ (10); 172, $C_4Cl_2F_2O$ (1); 163, $C_3Cl_2F_3$ (44); 144, $C_3Cl_2F_2$ (4); 125, C_3Cl_2F (8); 113, C_2Cl_2F (8); 109, C_3ClF_2 (16); 106, C_3ClFO (1); 96, C_3ClF (2); 93, C_3F_3 (3); 90, C_3ClF (6); 85, $CClF_2$ (11); 78, C_2F_2O (2); 74, C_3F_2 (5); 71, C_3Cl (2); 69, CF_3 (27); 63, CClO (1); 59, C_2FO (2); 55, C_3F (5); 50, CF_2 (1); 47, CCl (6); 35, Cl (3); 31, CF (5). $\nu_{max.}$ 1660 ($>C=C<$), 1325, 1237, 1140, 1030, 942 and 800 cm.$^{-1}$ U.V. (cyclohexane) $\lambda_{max.}$ 222 mμ; $\epsilon_{max.}$ 1·7 x 10^3. ^{19}F n.m.r. showed a group of four peaks centred at +53·6 p.p.m. and two groups of four peaks centred at +67·2 and +72·6 p.p.m. from $CFCl_3$ as external reference, in relative group intensity ratios 1:1:1 with J_{AB}, 151 Hz., J_{Ax}, 7·5 Hz., and J_{Bx}, 4·6 Hz.

c) 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (1·25g., 9%) identified by its infra-red spectrum,

(ii) An intimate mixture of perchloro-2,5-dihydrofuran (20g., 73 m.moles) and antimony trifluoride (20g., 112 m.moles) was treated as above, the distillate to 200°C being collected. The distillate (12g.)

was separated into its constituent parts by preparative gas chromatography (Dinonylphthalate/Celite: N_2 carrier gas, col. temp. 120°C) to give in order of emergence from the column:

a) 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (0·3g., 2%),

b) 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (2·4g., 15%),

c) 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (0·64g., 5%),

d) <u>difluorotetrachloro-2,5-dihydrofurans</u> (3·35g., 19%), a mixture of isomers which could not be separated by gas-liquid chromatography.

Found: C, 19·8; F, 15·5; Cl, 57·8; required for $C_4Cl_4F_2O$: C, 19·7; F, 15·6; Cl, 58·2. Mass spec. fragment ions: 242, $C_4Cl_4F_2O$ (10); 207, $C_4Cl_3F_2O$ (100); 195, C_3Cl_4F (6); 188, C_4Cl_3FO (1); 179, $C_3Cl_3F_2$ (46); 172, $C_4Cl_2F_2O$ (4); 160, C_3Cl_3F (2); 151, $C_2Cl_2F_3$ (1); 144, $C_3Cl_2F_2$ (4); 141, C_3Cl_3 (2); 137, C_4Cl_2F (1); 125, C_3Cl_2F (24); 109, C_3ClF_2 (20); 106, C_3Cl_2 (3); 101, CCl_2F (5); 94, C_2Cl_2 (4); 90, C_3ClF (17); 85, $CClF_2$ (48); 82, CCl_2 (2); 80, C_3ClF (3); 78, C_2F_2O (4); 71, C_3Cl (6); 66, CF_2O (2); 63, CClO (3); 59, C_2Cl (3); 55, C_3F (13); 47, CCl (8); 35, Cl (5); 31, CF (14). $\nu_{max.}$ 1662 ($>C=C<$), 1238, 1111, 1020, 902 and 746ish $cm.^{-1}$ U.V. (cyclohexane) $\lambda_{max.}$ 217 mμ; $\epsilon_{max.}$ 9×10^3. ^{19}F n.m.r. shows peaks at +61·0, +63·1, +71·6 and +77·6 p.p.m. from $CFCl_3$ as external reference.

e) <u>2-fluoro-2,3,4,5,5-pentachloro-2,5-dihydrofuran</u> (1·21g., 6·5%). Found: C, 18·7; F, 7·6; Cl, 68·6; required for C_4Cl_5FO: C, 18·45; F, 7·3; Cl, 68·1. Mass spec. fragment ions: 258, C_4Cl_5FO (6); 239, C_4Cl_5O (7); 223, C_4Cl_4FO (100); 211, C_3Cl_5 (14); 207, C_4Cl_4F (14); 195, C_3Cl_4F (82); 188, C_4Cl_3FO (14); 179, $C_3Cl_3F_2$ (11); 169, C_4Cl_3O (8); 160, C_3Cl_3F (29); 153, C_4Cl_3 (5); 141, C_3Cl_3 (38); 125, C_3Cl_2F (78); 117, CCl_3 (4); 113, C_2Cl_2F (6); 106, C_3Cl_2 (32); 101, CCl_2F (60); 94, C_2Cl_2 (17); 90, C_3ClF (33); 87, C_3ClO (12); 82, CCl_2 (8); 78, C_2ClF (3); 71, C_3Cl (30); 63, CClO (12); 59, C_2Cl (9); 55, C_3F (17); 47, CCl (21); 43, C_2F (12); 35, Cl (15); 31, CF (14). $\nu_{max.}$ 1642 ($>C=C<$), 1252, 1106, 1007, 815 and 702 $cm.^{-1}$ U.V. (cyclohexane) $\lambda_{max.}$ 218·5 mμ; $\epsilon_{max.}$ 1×10^4. ^{19}F n.m.r. shows single peak at +65·33 p.p.m. from $CFCl_3$ as external reference.

<u>Reaction of perchloro-2,5-dihydrofuran with antimony dichlorotrifluoride.</u>

Antimony trifluoride (100g., 0·63 mole) was placed in a nickel beaker (200 ml.) and heated in a sand bath to 330-350°C. Gaseous chlorine (35g., 0·5 mole) was passed through the melt over 4 hr. Perchloro-2,5-dihydrofuran (5g., ·0183 mole), antimony trifluoride (2g., 0·0126 mole) and antimony dichlorotrifluoride (7g.), prepared as above, were placed in a round-bottomed flask (25 ml.) fitted with a conventional distillation apparatus. The flask was heated and the distillate boiling below 160°C collected. Transfer of the distillate under reduced pressure gave 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (1·0g., 26%) identified by its infra-red spectrum.

Reaction of perchloro-2,5-dihydrofuran with antimony trifluoride/antimony pentachloride.

A mixture of perchloro-2,5-dihydrofuran (20g., 0·073 mole) and antimony trifluoride (30g., 0·168 mole) was placed in a round-bottomed flask (100 ml.) fitted with a conventional distillation apparatus. Antimony pentachloride (6 ml.) was added, the flask and contents heated to 110°C when the required 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (13·4g., 78%) distilled. This was identified by its infra-red spectrum.

Reaction of perchloro-2,5-dihydrofuran with potassium fluoride.

A mixture of potassium fluoride (60g., 1·05 mole) and dried N-methyl pyrrolidone (100 ml.) was placed in a 3-necked round-bottomed flask (250 ml.) fitted with thermometer, mechanical stirrer, gas inlet, dropping funnel, and a claisen head fitted to product flask, in series with two traps cooled in liquid air. The flask and contents were heated on an isomantle with stirring, to 195°C, with a gentle flow of nitrogen, and perchloro-2,5-dihydrofuran (20g., 0·073 mole) in N-methyl pyrrolidone (20 ml.) was added over 90 min. The contents of the flask were then heated and stirred for a further 120 min. at 195-205°C. The contents of the liquid air traps were purified by flask to flask distillation to yield perfluoro-2,5-dihydrofuran (6•1g., 49%). Found: M (mass spectrometry) 177•9852; required for C_4F_6O: M, 177•9853; fragment ions: 178, C_4F_6O (31); 159, C_4F_5O (19); 131, C_3F_5 (100); 128, C_3F_4O (4); 112, C_3F_4 (23); 109, C_3F_4O (7); 100, C_2F_4 (8); 93, C_3F_3 (41); 81, C_2F_3 (8); 74, C_3F_2 (6); 69, CF_3 (45); 66, CF_2O (3); 55, C_3F (3); 50, CF_2 (5); 47, CFO (6); 43, C_2F (9). $\nu_{max.}$ 1802 ($>$C=C$<$), 1400, 1172, 1098 and 956 cm.$^{-1}$ ^{19}F n.m.r. showed doublet at -84•8 and a triplet at -7•2 p.p.m. from C_6F_6 in relative areas 2:1 with J, 6•8 c.p.s.

The contents of the product vessel were transferred under reduced pressure to give 2,2,4-trichloro-3,5,5-trifluoro-2,5-dihydrofuran (0•77g., 5%). Found: C, 21•4; F, 24•6; Cl, 46•0; required for $C_4Cl_3F_3O$: C, 21•1; F, 25•05; Cl, 46•8. Mass spec. fragment ions: 226, $C_4Cl_3F_3O$ (4); 210, $C_4Cl_3F_3$ (2); 198, $C_3Cl_3F_3$ (1); 191, $C_4Cl_3F_2$ (63); 179, $C_3Cl_3F_2$ (6); 175, $C_4Cl_2F_2$ (5); 172, C_4Cl_3F (4); 163, $C_3Cl_2F_3$ (100); 156, $C_4Cl_2F_2$ (1); 147, C_3F_4Cl (4); 141, C_3Cl_2FO (2); 128, C_3ClF_3 (7); 125, C_3ClF_2O (5); 113, C_2ClF_2O (1); 109, C_3ClF_2 (5); 106, C_3ClFO (1); 93, C_3F_3 (16); 90, C_3F_2O (3); 85, CF_2Cl (7); 78, C_2F_2O (5); 74, C_3F_2 (3); 69, CF_3 (20); 63, CClO (6); 59, C_2Cl (1); 55, C_3F (3); 47, CCl (3); 35, Cl (2); 31, CF (4). $\nu_{max.}$ 1738 ($>$C=C$<$), 1326, 1150, 1045, 990 and 820 cm.$^{-1}$ U.V. (cyclohexane) $\lambda_{max.}$ 209 mμ; $\epsilon_{max.}$ 6 x 10^2. ^{19}F n.m.r. shows doublet at -96•6 and triplet at -36•2 p.p.m. from C_6F_6 in relative areas 2:1 with J, 6·5 Hz.

Hydrolysis of perchloro-2,5-dihydrofuran.

Perchloro-2,5-dihydrofuran (2·75g., 0·01 mole) and conc. sulphuric acid (10 ml.) were placed in a round-bottomed flask (25 ml.) containing a magnetic stirrer and fitted with a water-cooled reflux condenser, and heated at 90°C/3 hr. The contents of the flask were added to distilled water (50 ml.) and the aqueous solution continuously extracted with ether (20 hr.). The ether extracts were dried ($MgSO_4$), and distilled to afford a residue which on sublimation (80°C/·01 mm.) afforded dichloromaleic acid (1·75g., 95%) identified by its infrared spectrum.

Hydrolysis of 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran.

2,3,4-Trichloro-2,5,5-trifluoro-2,5-dihydrofuran (0·62g., 2·76 m.moles) and conc. sulphuric acid (10 ml.) were placed in a round-bottomed flask (20 ml.) containing a magnetic stirrer and fitted with a water-cooled reflux condenser, and heated at 100°C/2 hr. The contents of the flask were added to distilled water (20 ml.) and the solution continuously ether extracted (17 hr.). Removal of the ether gave dichloromaleic acid (0·24g., 53%).

Reaction of 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone with phosphorus pentachloride.

4-Hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (1·0g., 5·3 m.moles) and phosphorus pentachloride (2·0g., 9·7 m.moles) were placed in a round-bottomed flask (10 ml.) containing a magnetic stirrer and fitted with a water-cooled reflux condenser. The contents of the flask were heated under total reflux 300 hr. but infra-red spectroscopy showed no change in the intensities of the carbonyl, olefinic and halogen stretching frequencies.

Hydrolysis of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran.

(i) with alkali.

3,4-Dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (1·67g., 8·9 m.moles) and potassium hydroxide pellets (3·5g., 62 m.moles) were placed in a round-bottomed flask (25 ml.) fitted with a water-cooled reflux condenser and heated at 70°C/40 hr. Concentrated hydrochloric acid (10 ml.) was added and continuous ether extraction, followed by removal of the ether yielded dichloromaleic acid (0·50g., 38%).

(ii) with acid.

3,4-Dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (2·67g., 12·75 m.moles) and conc. sulphuric acid (10 ml.) were heated together at 60°/48 hr. Work-up as above gave dichloromaleic acid (1·42g., 57%).

Hydrolysis of other fluoro- and chlorofluoro-2,5-dihydrofurans.

(i) 2,2,4-Trichloro-3,5,5-trifluoro-2,5-dihydrofuran.

2,2,4-Trichloro-3,5,5-trifluoro-2,5-dihydrofuran (0·50g., 2·2 m.moles) and conc. sulphuric acid (3 ml.) were heated together at 65°C/90 min. Work-up as above gave chlorofluoromaleic acid (0·18g., 49%) identified by mass and infra-red spectrometric analysis.

(ii) Difluoro-tetrachloro-2,5-dihydrofurans.

The isomer mixture of difluoro-tetrachloro-2,5-dihydrofurans (0·84g., 3·5 m.moles) and conc. sulphuric acid (4 ml.) were heated at 100°C/4 hr. Work-up as above gave dichloromaleic acid (0·60g., 95%).

(iii) Perfluoro-2,5-dihydrofuran.

To a cooled autoclave (35 ml.) containing conc. sulphuric acid (10 ml.), perfluoro-2,5-dihydrofuran (1·40g., 7·9 m.moles) was added and the autoclave sealed and heated with shaking at 80°C/12 hrs. and 120°C/46 hrs. The autoclave was cooled, water (100 ml.) was added to the autoclave and work-up as above gave difluoromaleic acid (0·18g., 42%) identified by spectral data and elemental analysis.

(iv) 4-Hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone.

4-Hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (0·82g., 4·3 m.moles) and sodium hydroxide solution ($^{N}/10$., 10 ml.) were placed in a round-bottomed flask (25 ml.) fitted with a water-cooled reflux condenser and heated under reflux for 90 min. Acidification with conc. hydrochloric acid (5 ml.) followed by usual work-up gave dichloromaleic acid (0·60g., 86%).

Oxidation of fluoro- and chlorofluoro-2,5-dihydrofurans.

(i) Perfluoro-2,5-dihydrofuran.

Potassium permanganate (7•1g., 45 m.moles), potassium hydroxide (5•1g.) and water (20 ml.) were placed in an autoclave (35 ml.) and perfluoro-2,5-dihydrofuran (3•7g., 20•8 m.moles) was transferred into the autoclave under reduced pressure. The autoclave was sealed and shaken at room temperature for 41 hr. The autoclave was then opened, the contents added to water (200 ml.), acidified, decolourised with sulphur dioxide, and the solution continuously extracted with ether (48 hr.). The ether extract was dried ($MgSO_4$), filtered and distilled to afford a crude solid which on sublimation (100°/•001 mm.) yielded perfluoro-oxydiacetic acid (2•71g., 66%), identified by its dianilinium salt.

(ii) 2,3,4-Trichloro-2,5,5-trifluoro-2,5-dihydrofuran.

To a solution of potassium permanganate (2•1g., 0•0133 mole) in acetone (200 ml.) contained in a 3-necked flask (500 ml.) fitted with a mechanical stirrer, dropping funnel and reflux condenser, 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (1•26g., 0•0056 mole) was added. The mixture was stirred for 4 hrs., water (200 ml.) was added, the solution decolourised with sulphur dioxide and then continuously extracted with ether 48 hr. The ether extracts were dried ($MgSO_4$), and the ether removed to leave oxalic acid (0•14g., 28%) identified by its infra-red spectrum and its dianilinium salt.

(iii) Difluoro-tetrachloro-2,5-dihydrofurans.

The isomer mixture of difluoro-tetrachloro-2,5-dihydrofurans (1•12g., 0•00464 mole) was oxidised by permanganate (4•1g., 0•026 mole) in acetone (200 ml.) in a similar manner to above, to give oxalic acid (0•03g., 7%) identified by its infra-red spectrum.

Reaction of 4-hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone with methoxide ion.

4-Hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone (2•57g., 13•7 m.moles) in a round-bottomed flask (10 ml.) was treated with sodium methoxide (13•7 m.moles) in methanol (2•6 ml.) and the mixture heated at 120°/2 hr. Transfer under reduced pressure removed excess methanol, and transfer of the residue with heating under reduced pressure gave dimethyl dichloromaleate (1•12g., 39%). Found: C, 34•02; H, 3•04; required for $C_6H_6Cl_2O_4$: C, 33•83; H, 2•84. ^{1}H n.m.r. showed a single peak at 6•12τ and mass spec. showed parent ion $^m/e$ 212 with isotope pattern consistent with the presence of two Cl's. $\nu_{max.}$ 2960 (⩾C-H), 1750 (>C=O) and 1600 (>C=C<) cm.$^{-1}$

Reaction of 3,4-dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran with sodium methoxide in methanol.

3,4-Dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran (3•11g., 14•8 m.moles) was placed in a round-bottomed flask (25 ml.) fitted with a reflux condenser and a magnetic stirrer. Sodium methoxide (1•43g., 26•6 m.mole) in methanol (5 ml.) was added dropwise, the mixture then heated under reflux for 2 hr. Distillation under reduced pressure with a liquid air trap in series with the product vessel, afforded, from the liquid air trap a mixture of methanol and an unknown material. Water (5 ml.) was added to the contents of the liquid air trap, and the lower layer separated and transferred under reduced pressure to give 4-chloro-3-methoxy-2,2,5,5-tetrafluoro-2,5-dihydrofuran (2•04g., 67%). Found: C, 29•3; H, 1•46; F, 37•1; Cl, 17•1; required for $C_5H_3ClF_4O_2$: C, 29•08; H, 1•46; F, 36•80; Cl, 17•16. Mass spec. fragment ions: 206, $C_5H_3ClF_4O_2$ (31); 171, $C_5H_3F_4O_2$ (10); 159, $C_4H_3ClF_3O$ (85); 149, $C_5F_3O_2$ (21); 137, C_4ClF_2O (20); 125, C_3ClF_2O (62); 105, $C_4H_3F_2O$ (100); 84, C_4HFO (57); 77, $C_3H_3F_2$ (61); 57, C_3H_2F (97); 47, CCl (22). $\nu_{max.}$ 1708 ($\rangle$C=O), 1312, 1145 and 1105 $cm.^{-1}$ ^{19}F n.m.r. showed two sets of triplets at +78•32 and +78•91 p.p.m. from $CFCl_3$ as external reference in relative group intensity ratios 1:1 with J, 5•5 c.p.s.

The distillate was shown by analytical g.l.c. (col. 'A', 140°) to be one major and one minor component. These were separated by preparative scale g.l.c. (Dinonylphthalate/Celite: N_2 carrier gas, col. temp. 120°) to give chloro-dimethoxy-2,2,5,5-tetrafluorotetrahydrofuran (0•14g., 6%). Found: C, 30•7; H, 2•96; M (mass spectrometry), 238•0019; required for $C_6H_7ClF_4O_3$: C, 30•2; H, 2•96; M, 238•0020. $\nu_{max.}$ 1190, 1150 and 1098 cm^{-1}. ^{19}F n.m.r. showed two peaks in relative areas 1:1 at +70•5 and +78•3 p.p.m. from $CFCl_3$. ^1H n.m.r. showed three peaks with relative intensities 1:3:3 at 5•78, 6•40 and 6•60τ respectively.

Insufficient material of the other component was obtained to enable it to be characterised.

Reaction of 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran with potassium ethoxide in ethanol.

To 2,3,4-trichloro-2,5,5-trifluoro-2,5-dihydrofuran (3•54g., 0•095 mole) in a round-bottomed flask (25 ml.) containing a magnetic stirrer, a solution of potassium hydroxide (0•49g., 0•088 mole) in ethanol (7 ml.) was added with vigorous stirring. The mixture was stirred overnight, added to iced water (50 ml.) and the aqueous solution extracted with methylene chloride (3 x 50 ml.), the extracts washed with water, dried ($MgSO_4$) and the organic solvent removed by distillation. The residue was transferred under reduced pressure to give dichloroethoxy-2,5,5-trifluoro-2,5-dihydrofuran (1•32g., 60%), shown by analytical g.l.c. (col. 'O'/200°) to be one component. Found: C, 29•9; H, 2•2; F, 24•4; Cl, 30•2; required for $C_6H_5Cl_2F_3O_2$: C, 30•4; H, 2•1; F, 24•05; Cl, 29•9. $\nu_{max.}$ 1705 ($>C=C<$), 1302, 1142 and 1106

$cm.^{-1}$ ^{19}F n.m.r. showed multiplets at +52•0 and +73•1 p.p.m. from $CFCl_3$ with relative intensities of 1:2. U.V. (cyclohexane) $\lambda_{max.}$ 216 mμ, $\epsilon_{max.}$ 7 x 10^3.

Reaction of 2,2,4-trichloro-3,5,5-trifluoro-2,5-dihydrofuran with sodium methoxide in methanol.

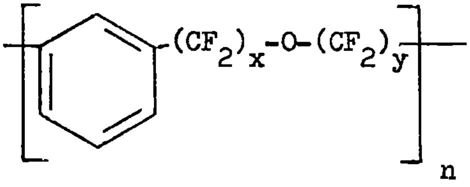
2,2,4-Trichloro-3,5,5-trifluoro-2,5-dihydrofuran (0•56g., 0•00248 mole) was placed in a round-bottomed flask (10 ml.) fitted with a magnetic stirrer, and sodium methoxide (0•14g., 0•00268 mole) in methanol (5 ml.) was added, and the mixture stirred 2 hr. The methanol was removed by transfer under reduced pressure, and the residue distilled under reduced pressure to give 2,2,4-trichloro-5,5-difluoro-3-methoxy-2,5-dihydrofuran (0•31g., 52%). Mass spectrum showed parent peak at $^m/e$ 238 with isotope pattern consistent with 2 Cl's. $\nu_{max.}$ 1700 ($>C=C<$), 1308, 1092, 1062 and 1007 $cm.^{-1}$ ^{19}F n.m.r. showed single peak at -96•7 p.p.m. from C_6F_6 as external reference and ^1H n.m.r. showed a single peak at 5•5τ.

CHAPTER IV.

THE PREPARATION OF POLYMERS CONTAINING A PERFLUORO-OXYDIMETHYLENE GROUP.

Introduction.

From the general introduction it can be seen that the work described in this thesis was instigated in an attempt to synthesise a polymer of type (I).



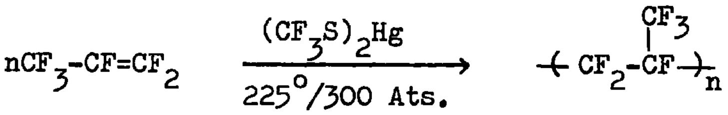
(I)

However, when all the attempted routes to this polymer failed, the aim of the work was modified to investigate the effect of the perfluoro-oxydimethylene group, $-CF_2OCF_2-$, on the thermal stability and the elastomeric properties of polymers. The preparation of polyesters incorporating a perfluoro-oxydimethylene link was achieved via polycondensation reactions using 3-oxa-2,2,4,4-tetrafluoropentane-1,5-diol, $O(CF_2CH_2OH)_2$ (XXXVII), and these polyesters were compared to analogous polymers prepared from hexafluoropentane-1,5-diol. However, before a discussion of the effects of the introduction of the perfluoro-oxydimethylene link on the physical properties of polymers, a brief resumé must be given of the factors which led to the decision to investigate these particular types of polymers.

Since the discovery of polytetrafluoroethylene, much work has gone into the synthesis of fluorinated polymers. Polytetrafluoroethylene (P.T.F.E.) shows remarkable resistance to acids, alkalis, and all common solvents, in addition to being thermally stable to temperatures greater than 250°C. This stability is attributed to the high carbon-fluorine bond strength and to the shielding effect that the highly electronegative fluorine atoms may have on the carbon chain. However, this shielding effect can explain the chemical stability but not the thermal stability, since this must be dependant on the strength of the carbon-carbon backbone. P.T.F.E. has a working temperature range from +250°C to -196°C, but its main limitation is that it cannot be moulded at relatively low temperatures, and when it is heated above its melting point (327°) it becomes an amorphous transparent gel that is mechanically weak and will not flow without fracture.

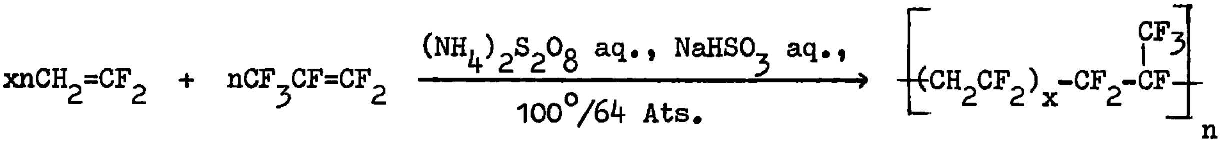
The copolymer of tetrafluoroethylene and hexafluoropropylene was found to be a random polymer containing mainly tetrafluoroethylene residues. It was found to have similar inertness to P.T.F.E., and a considerable advantage over P.T.F.E. in that it is a thermoplastic and can therefore be fabricated more easily.

Hexafluoropropylene is difficult to homopolymerise under free radical conditions and the preparation of the homopolymer involves the use of high temperatures and pressures:[91]



$$nCF_3\text{-}CF{=}CF_2 \xrightarrow[225^\circ/300\ \text{Ats.}]{(CF_3S)_2Hg} \left(CF_2\text{-}\overset{CF_3}{\overset{|}{CF}} \right)_n$$

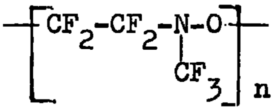
However, hexafluoropropene is readily copolymerised with vinylidene fluoride using an aqueous persulphate initiator system:[92]



$$xnCH_2{=}CF_2 \;+\; nCF_3CF{=}CF_2 \xrightarrow[100^\circ/64\ \text{Ats.}]{(NH_4)_2S_2O_8\ \text{aq., NaHSO}_3\ \text{aq.,}} \left[(CH_2CF_2)_x\text{-}CF_2\text{-}\overset{CF_3}{\overset{|}{CF}} \right]_n$$

This elastomeric copolymer (Viton A) is resistant to fuels, oils and solvents up to temperatures greater than 200°. The elastomeric character is probably due to the methylene groups introducing flexibility into the backbone whilst the pendant trifluoromethyl group may prevent close packing of the polymer chains so reducing the tendency of the polymer to crystallise. This polymer can be cross-linked via the methylene groups using peroxides, β-radiation or polyfunctional amines. The polymer can be used for short periods at temperatures up to 300°, and retains useful properties indefinitely at 200°. Its main drawback is the relatively high glass transition temperature (-19°).

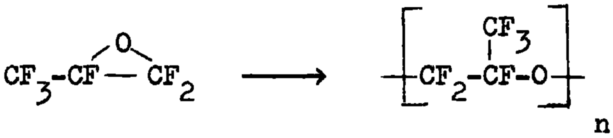
The copolymer of tetrafluoroethylene and trifluoronitrosomethane



$$\left[CF_2\text{-}CF_2\text{-}\underset{CF_3}{\underset{|}{N}}\text{-}O \right]_n$$

is also elastomeric to fairly low temperatures (-50°) but decomposes at temperatures greater than 200°.

Epoxides of fluorinated olefins have been polymerised to give perfluoropolyethers, as in the polymerisation of hexafluoropropylene oxide:[93]



Detailed information on the physical parameters of polymers of this type has not been published since most of the synthetic work is in the patent literature. However, it has been reported that poly(perfluoroalkylene oxides) having the repeating unit $\{O(CF_2)_n\}$, where n is between 4 and 20, prepared by pyrolysis of the metal salts

$$y[O(CF_2CF_2CO_2)_2Hg] \xrightarrow{\Delta} \{OCF_2CF_2CF_2CF_2\}_y$$

of perfluoro-oxydiacids,[94] are elastomeric to at least -80°, although no information has been given with respect to the upper temperature limit of stability.

Discussion.

The main factor which governs the usefulness of a flexible polymer as an elastomer is the glass transition temperature (Tg). For a particular elastomer to be useful, its glass transition temperature must be below the lowest temperature at which the polymer will be used, whilst the decomposition temperature should be well above the maximum temperature at which it is to be used. On a molecular scale, the Tg is considered to be that temperature at which the main polymer chain aquires long-range mobility i.e. for an amorphous polymer there is a narrow temperature range over which the rigid glass collapses to a highly viscous (usually elastic) fluid.

From information published[95] it seems that most polymers with Tg's below -20° contain aliphatic groups, and this causes the polymer to be oxidatively unstable above 200-250°. The replacement of the aliphatic hydrogen by oxygen or aromatic groups may improve the thermal stability but this usually leads to an increase in Tg also. Improvement in mechanical properties by structural modification and the use of groups to sterically hinder hydrolytic degradation both usually lead to an increase in Tg.

Since Tg is dependant on intermolecular forces, the cohesive energy density (c.e.d.), which is a measure of the attraction between polymer chains, must be kept as low as possible. For Tg's to be below -20°, it has been found that the c.e.d. should not exceed 90 cal./cc. since available data[95] shows that all polymers with c.e.d. values above this figure have Tg's above -20°.

Steric factors are also important due to their effects on Tg, large groups which interfere with the motion of the main-, or side-chains leading to high Tg's. However, if bulky groups can be arranged so as to exclude a large free volume, and so keep the polymer chains fairly widely separated, then Tg may be kept relatively low. Side chains may also be used to lower Tg provided that they do not hinder the movement of the main chain and that the length of the chain is optimised. For a number of identical groups in a sequence, it has been found that an odd number of groups confers a lower Tg than an even number. Other factors which influence the value of the glass transition temperature include the barriers to rotation about the links in the polymer backbone which should be kept as low as possible, the degree of crystallinity which should be kept to a minimum, and the molecular weight which should be as low as is consistent with retaining mechanical strength.

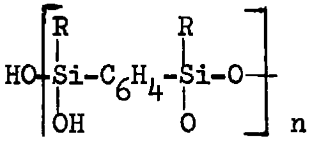
All these factors had to be borne in mind in order to attempt to postulate a structure which may have the elastomeric properties desired in addition to being thermally stable above approximately 250°.

Much work is being carried out in many fields in the search for an improved elastomer: for example a phosphonitrilic fluoroelastomer has been prepared by reaction of phosphonitrilic chloride polymer with polyfluoroalkoxides,[96] and is reported to have a Tg value of -77°:

$[NPCl_2]_n \xrightarrow{50:50\ NaOCH_2CF_3/NaOCH_2C_3F_7}$ polymer containing the three distinct units

$[NP(OCH_2CF_3)_2]$, $[NP(OCH_2C_3F_7)_2]$ and $[NP(OCH_2CF_3)(OCH_2C_3F_7)]$

whilst poly-silphenylenesiloxanes with the following structure[97] possess high thermal stability at 300°:



$$HO\!-\!\left[\underset{\displaystyle OH}{\overset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}}-C_6H_4-\underset{\displaystyle O}{\overset{\displaystyle R}{\overset{|}{\underset{|}{Si}}}}-O\right]_n$$

where R is methyl or phenyl

This project was concerned with attempting to solve the problem via organo-fluorine chemistry.

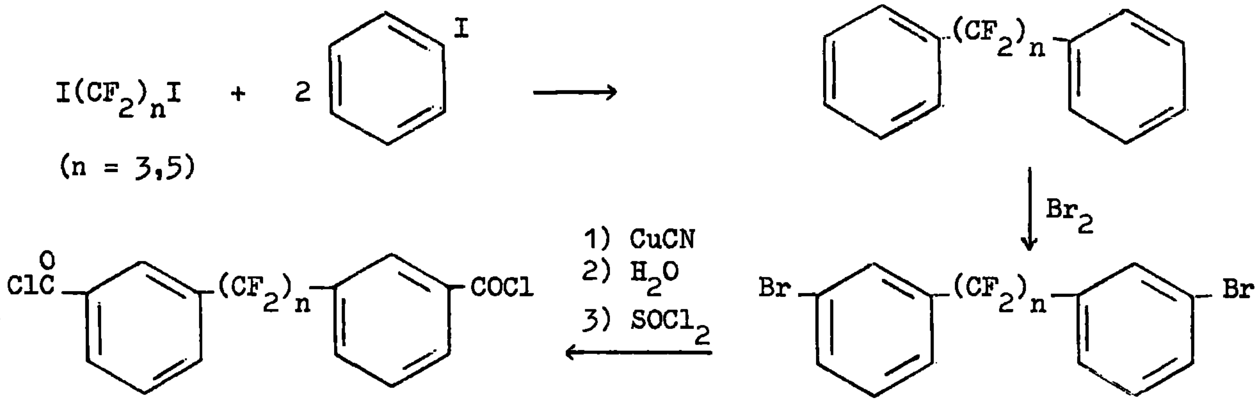
The initial model compound was taken as benzotrifluoride since this was found to have a cohesive energy density at 25° of 68 cal./cc., and the barrier for intramolecular rotation is believed to be about zero.[98] Possible structures can be written for the benzotrifluoride model:

$$-\left\{\left[(C_6H_4)_x(CF_2)_y\right]_n-[R]_z\right\}_q-$$

where C_6H_4 is o-, m-, or p-linked, R is a single bond or some linking group and x, y, z, n and q are variables.

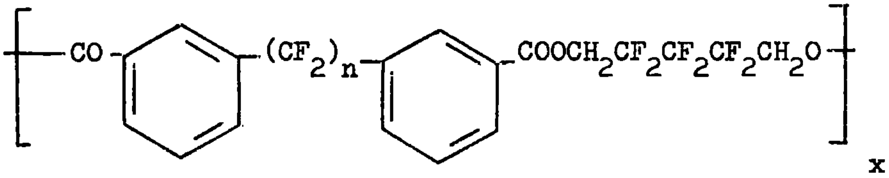
Substitution in the aromatic ring should be arranged so that the polymer has reversible elongation along its length, and that deformation of the main chain produces a change in the end to end distance. Hence, p-substitution can be ignored, and m-substitution would be preferred to ortho since there is less likelihood of steric hindrance in the main chain in this position. Consideration of the melting points of diphenyldifluoromethane and 1,2-diphenyl-1,1,2,2-tetrafluoroethane with values of -2 and +112·5° respectively[99] led to the suggestion that an odd value for y may produce a polymer with a lower Tg than an even value, since a lowering of melting point is usually accompanied by a lowering of Tg.

Using these theoretical considerations as the basis for polymer preparation, other workers prepared polymer precursors incorporating the hexafluorotrimethylene link $-(CF_2)_3-$.[1,46,100] These precursors were then polymerised by condensation methods, for example:



(LIII) (n = 3,5)

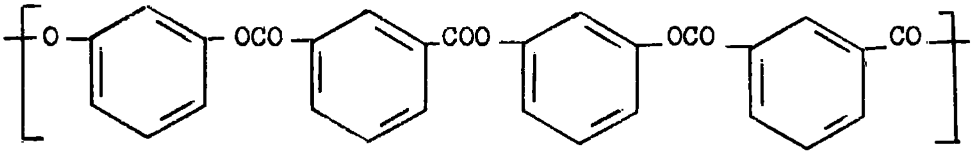
(LIII) was then polymerised with hexafluoropentane diol to give polyesters[100] of the type



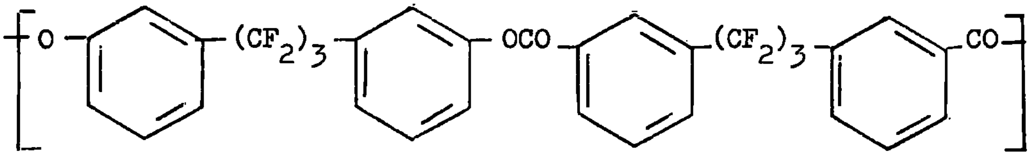
(LIV)

Additional polymers have been prepared by reaction of hexafluoropentane diol with other acid chlorides,[6,101] and thus the effect of introducing a perfluoroalkylene link in a polymer could be investigated.

It was found that replacement of an ester link by a perfluorotrimethylene group in the polyester from resorcinol and isophthalic acid (LV) produced a drop in Tg from 136° for (LV) to 71° for (LVI), whilst



(LV)

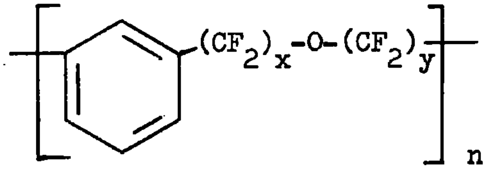


(LVI)

for polymers of type (LIV), the value for the Tg was 16° for both n,3 and n,5.[100] The effect of the introduction of the $-(CF_2)_3$ group on the Tg value was smaller than expected, although the thermal stability of the polymers was good.

The inclusion of an ether link into the perfluoropolymethylene group may impart more flexibility into the polymer backbone thus preventing the molecules packing closely together and this should result in a reduction of the Tg value. This work was carried out in an attempt to investigate the effect of the incorporation of a perfluoro-oxymethylene link in particular polymers.

As stated in the general introduction and Chapter II, attempts to prepare precursors for the synthesis of polymers of type (I) were unsuccessful.

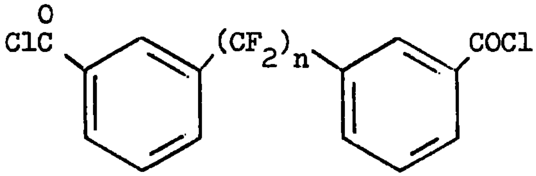


I

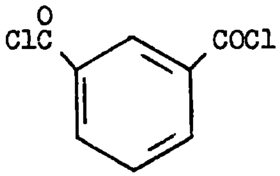
However, 3-oxa-2,2,4,4-tetrafluoropentane-1,5-diol, $O(CF_2CH_2OH)_2$, (XXXVII), was prepared and used in the synthesis of polyesters analogous to those derived from hexafluoropentane diol.

Three polyesters were prepared by melt condensation of 3-oxa-2,2,4,4-tetrafluoropentane-1,5-diol with 1,3-di(3-chlorocarbonylphenyl)-hexafluoropropane (LIII, n = 3), isophthaloyl chloride (LVII) and

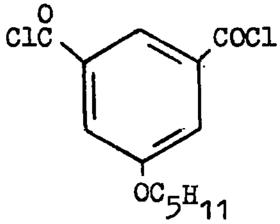
5-(n-amyloxy)isophthaloyl chloride (LVIII).



(LIII)

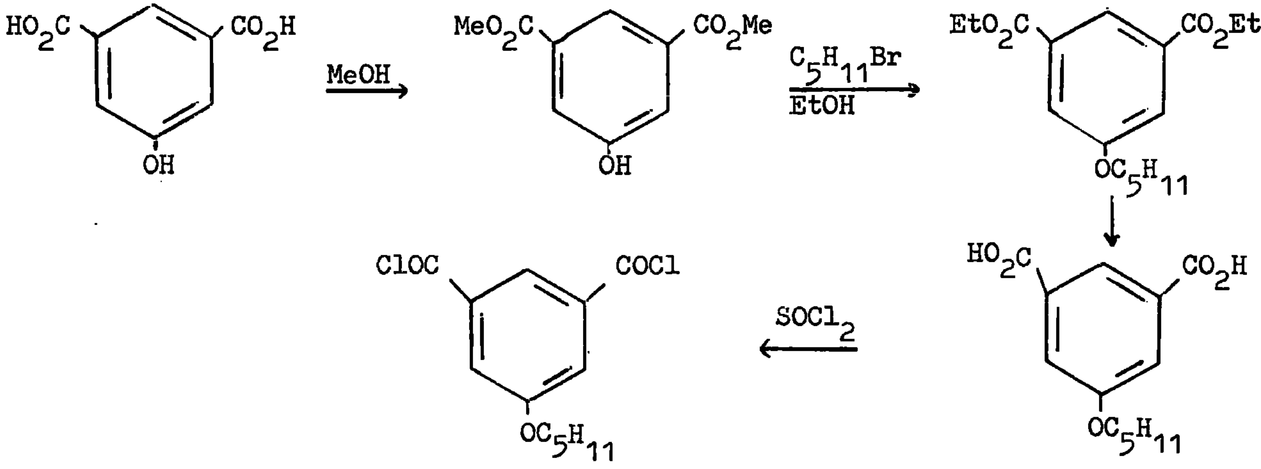


(LVII)



(LVIII)

5-(n-Amyloxy)isophthaloyl chloride was prepared by the method of Evers and Ehlers from 5-hydroxyisophthalic acid:[6]



(LVIII)

Experimental.

1,3-Di(3-chlorocarbonylphenyl)hexafluoropropane was obtained from Materials Department, R.A.E. Farnborough, and was purified by sublimation. Isophthaloyl chloride was used as received from Kodak Limited.

Preparation of 5-(n-amyloxy)isophthaloyl chloride from 5-hydroxyisophthalic acid.

(i) Dimethyl-5-hydroxyisophthalate.

5-Hydroxyisophthalic acid (10g., 0·048 mole), methanol (100 ml.) and concentrated sulphuric acid (2 ml.) were placed in a round-bottomed flask (200 ml.) and heated under reflux for 48 hr. Methanol (80 ml.) was removed by distillation, and the residual liquor added to sodium carbonate solution (40g./400 ml.). The precipitated solid was filtered and washed with water (3 x 20 ml.) and dried under vacuum to give dimethyl-5-hydroxyisophthalate (7·5g., 66%). Found: C, 57·1; H, 5·00; required for $C_{10}H_{10}O_5$: C, 57·14; H, 4·80. $\nu_{max.}$ 3425, 1740, 1715, 1252 and 758 $cm.^{-1}$.

(ii) 5-(n-Amyloxy)diethylisophthalate.

Dimethyl-5-hydroxyisophthalate (10g., 0·0325 mole), absolute ethanol (250 ml.) and n-amylbromide (14g., 0·093 mole) were heated under reflux for 90 hr. Ethanol (200 ml.) was removed by distillation, ether (200 ml.) added and the ethereal solution washed with dilute NaOH solution (100 ml.), water (2 x 100 ml.) and dried ($MgSO_4$). Removal of the ether followed by distillation under reduced pressure afforded 5-(n-amyloxy)diethylisophthalate (7•5g., 65%). Found: C, 66•5; H, 7•98; required for $C_{17}H_{24}O_5$: C, 66•2; H, 7•85. $\nu_{max.}$ 2950, 1733, 1340, 1317, 1238 and 1035 $cm.^{-1}$.

(iii) 5-(n-Amyloxy)isophthalic acid.

5-(n-Amyloxy)diethylisophthalate (2•0g., 0•0065 mole), NaOH (2N., 30 ml.) and methanol (130 ml.) were placed in a round-bottomed flask (250 ml.) fitted with a magnetic stirrer, and the solution stirred for 16 hr. The solution was acidified with concentrated HCl, the precipitate filtered off and washed with water (3 x 50 ml.) to give 5-(n-amyloxy)isophthalic acid (1•6g., 97%), m.227°. Found: C, 62•20; H, 6•20; required for $C_{13}H_{16}O_5$: C, 61•9; H, 6•39. $\nu_{max.}$ 1705, 1600, 1467 and 1280 $cm.^{-1}$.

(iv) 5-(n-Amyloxy)isophthaloyl chloride.

5-(n-Amyloxy)isophthalic acid (2•10g., 0•083 mole) and thionyl chloride (40 ml.) were heated under reflux for 19 hr. Excess thionyl chloride was removed by transfer under reduced pressure to leave a residue which on sublimation (82°/•001 mm.) and recrystallisation from n-hexane gave 5-(n-amyloxy)isophthaloyl chloride (2•24g., 93%), m.41•0°. Found: C, 54•30; H, 4•66; Cl, 24•8; required for $C_{13}H_{14}Cl_2O_5$: C, 54•0; H, 4•88; Cl, 24•5. $\nu_{max.}$ 1776, 1750, 1293, 1157, 1022, 1010 and 965 $cm.^{-1}$.

Preparation of polyesters.

General procedure:

An intimate mixture of 3-oxa-2,2,5,5-tetrafluoropentane diol and the diacyl chloride was placed in a cylindrical glass vessel (24 cm. x 3 cm. diam.) fitted with a sublimation adapter and a tube extending to the bottom of the vessel through which dry nitrogen could be passed. The vessel was placed in an oil bath and slowly heated until a homogeneous melt ensued. Dry oxygen free nitrogen was then slowly passed through the melt, whose viscosity gradually increased. The temperature of the oil bath was slowly raised when the melt became so viscous that the nitrogen could be passed only with difficulty. When the temperature of the oil bath reached 175-195°, the bath was kept at this temperature for several hours, followed by the slow application of reduced pressure to the vessel. The pressure was reduced to 0·05 mm. and this reduced pressure applied overnight. The polymer was then recovered by breaking the vessel.

(i) Reaction of 3-oxa-2,2,5,5-tetrafluoropentane diol with 1,3-di(3-chlorocarbonylphenyl)hexafluoropropane.

A mixture of 3-oxa-2,2,4,4-tetrafluoropentane diol (3·653g., 0·0205 mole) and freshly sublimed 1,3-di(3-chlorocarbonylphenyl)hexafluoropropane (8·783g., 0·0204 mole) was treated as above, duration of reaction 42 hr., to afford the polyester (LIV, n = 3), (10·62g., 97%). Found: C, 47·14;

H, 2·32; required for $C_{21}H_{12}F_{10}O_5$; C, 47·2; H, 2·27.

(ii) <u>Reaction of 3-oxa-2,2,5,5-tetrafluoropentane diol with isophthaloyl chloride</u>.

3-oxa-2,2,4,4-tetrafluoropentane diol (5·119g., 0·0289 mole) and isophthaloyl chloride (5·94g., 0·0293 mole) were reacted as above, duration of reaction 47 hr., to give the polyester (LIX), (8·85g., 99%). Found: C, 46·88; H, 2·57; required for $C_{12}H_8F_4O_5$: C, 46·76; H, 2·61.

(iii) <u>Reaction of 3-oxa-2,2,5,5-tetrafluoropentane diol with 5-(n-amyloxy)isophthaloyl chloride</u>.

3-oxa-2,2,4,4-tetrafluoropentane diol (4·033g., 0·0226 mole) and 5-(n-amyloxy)isophthaloyl chloride (6·743g., 0·0233 mole) were treated as above, duration of reaction 84 hr., to afford the polyester (LX), (6·66g., 70%). Found: C, 52·02; H, 4·56; F, 19·7; required for $C_{17}H_{18}F_4O_6$: C, 51·78; H, 4·6; F, 19·28.

CHAPTER V.

THE PHYSICAL PROPERTIES OF SOME POLYESTERS CONTAINING A PERFLUORO-OXYDIMETHYLENE LINK.

Introduction.

Considerable effort has gone into the investigation of polymer properties and into the methods used in these investigations. For direct comparison of polymers and their properties, methods of analysis had to be defined within fairly rigorous limits since to some extent the numerical value obtained for a particular physical property depends on the technique used to measure it.

Several methods have been devised for the determination of molecular weights of polymers, to give both absolute and relative values. Absolute molecular weight determinations usually involve the use of complex apparatus, as is the case with the ultra-centrifuge.[102] With this technique, the weight average molecular weight, Mw, is determined by allowing an equilibrium to be reached in which the polymer is deposited from a suspension, in a cell which is rotated. The deposit distribution is governed by the molecular weight and molecular weight distribution, the force of sedimentation on a species being just balanced by its tendency to diffuse back against the concentration gradient resulting from its movement in the centrifugal field. The major disadvantages of this method are that equilibrium is only reached after a fairly long time, and the solution of an integral equation is involved. A further absolute method for the determination of weight average molecular weights is light scattering.[103] This is based on the difference in refraction of light between pure solvent and the solvent plus some soluble material. Thus, from measurement of the increase in scattering and refraction change from solvent to solution, the weight average molecular weight of the polymer can be determined from standard equations.

End group analysis has also been used for the determination of molecular weight, but it has only limited application since the end group must be fairly easily determined (by, for example, titration for a carboxylic acid group[104]), and high sensitivity in analysis is required if high molecular weight materials are being analysed.

The most commonly used method for absolute molecular weight determinations is based on the colligative properties of polymer solutions. Osmotic pressure[103] is very sensitive since a 1% solution of polymer of molecular weight 20,000 might show an osmotic pressure of 20 cm. of solvent. The basic principle of operation is to measure the difference in osmotic pressure between pure solvent and a solution, since the pure solvent always has a higher osmotic pressure. With a membrane osmometer, equal amounts of solvent and solution are placed on opposite sides of the membrane and the system allowed to equilibrate. Transfer of solvent takes place from one side of the membrane to the other, and the difference in liquid levels is measured. From this, and the known density of the solvent, the number average molecular weight can be determined. An alternative way in which the colligative properties of dilute solutions can be used to obtain molecular weight data[105] is to measure the difference in rate of evaporation between a drop of pure solvent and a drop of solution in a closed chamber saturated with solvent vapour. Due to the difference in vapour pressure between the two drops and the saturated vapour, the rate of evaporation and condensation of the solvent on the solution drop will be different to the rate for the pure solvent drop. Hence, there will be a difference in temperature between the two drops, and this can be measured electrically. By reference to a standard, the observed temperature difference can be used to determine the number average molecular weight.

The most widely used method to give an indication of molecular weight is viscosity measurement, since the solution viscosity of a polymer is a measure of the size of a polymer molecule. Viscosity is measured as the time of flow of a known volume of the polymer solution through a capillary, the relative viscosity being the ratio of this to the time of flow of the same volume of pure solvent. The reciprocal of the relative viscosity is the specific viscosity, η_{sp}, which is related to the intrinsic viscosity, $[\eta]$, by the expression:

$$[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{C}$$

Intrinsic viscosity is related to molecular weight by an empirical equation developed by Mark and Houwink[106] from that of Standinger:[107]

$$[\eta] = kM^{\alpha}$$

where M is the molecular weight and k and α are constants for each particular polymer and solvent system. The values of k and α can be determined for a polymer from the plot of the logarithm of absolute molecular weight and the logarithm of intrinsic viscosity, when α is the slope and k the intercept. The values obtained can be used in the determination of molecular weights from viscosity measurements of structurally related polymers. The value obtained for α usually varies from 0·5 to 1·0, whilst k falls in the range 10^{-4} to 10^{-1}.

The thermal stability of polymers is normally recorded as either weight loss at a specific temperature over a definite period of time, or the temperature at which a standard amount of volatile material is lost. The data can be obtained from a thermobalance on which the sample is automatically heated and weighed, the results being recorded directly. These analyses can be carried out in any desired environment.

Differential thermal analysis (D.T.A.) analyses can be used to determine changes in physical properties of polymers with changes in temperature. The technique measures the difference in temperature between the sample and an inert reference material, whilst both are heated at the same uniform rate. Hence, for an endothermic change such as melting, the temperature of the reference sample would be higher than that of the test sample, this difference being continuously recorded.

This method of analysis can be used for the determination of temperatures at which changes in phase occur, decomposition temperatures, and any other physical transitions in the material which involve heat changes.

Differential scanning calorimetry (D.S.C.) is a method used for the investigation of polymer properties. It is similar to D.T.A. in that the sample is heated at a standard rate together with an inert reference sample, and the difference in heat content between the sample and reference can be measured quantitatively, by determination of the area under the curve produced on a recorder when a phase change occurred. This differs from D.T.A. since a heat content difference is measured with D.S.C. For the determination of heats of transitions D.S.C. is normally used, whilst for temperatures of transition, D.T.A. is used.

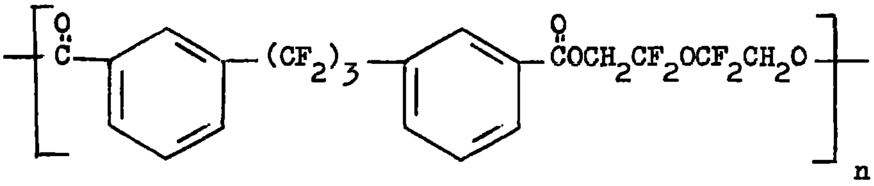
Discussion.

All polymers prepared by bulk polymerisation consist of a mixture of varying molecular weight materials when first prepared, and the properties of the bulk material can be adversely affected by the presence of a small amount of the low molecular weight material. It has been found that many physical parameters of polymers increase with increasing molecular weight, until a limiting value is reached. This limiting value represents the onset of the true bulk polymer properties since once this value is reached, increase in molecular weight does not produce any further change in these properties. In order to determine the true bulk properties of the polymers prepared each polymer was separated into discreet molecular weight fractions, and physical parameters were determined on each fraction. In this work it was found that all the polymer fractions had the same value for the glass transition temperature, except the residue where the value was much lower. This indicates that the limiting value, in terms of change of Tg with increase in molecular weight, had been reached.

To separate polymers into fractions of differing molecular weight, two main techniques have been used: elution of fractions from a packed column on which the polymer has been precipitated, with progressively better solvents, and fractional precipitation from a solvent by a non-solvent, in which the higher molecular weight material is precipitated first. This latter method was used for the polymers described herein, the solvent being chloroform and the non-solvent petroleum ether. Since molecular weights can be empirically related to viscosity by the Staudinger equation, and the values of the constants k and α will be

$$[\eta] = kM^{\alpha}$$

the same for fractions of the same polymer, then measurement of viscosity on the different fractions of a particular polymer would indicate whether fractionation had separated the high and low molecular weight material. From the results in Table 4, it can be seen that successive fractions have successively reduced intrinsic viscosities and hence some separation into fractions having differing molecular weight distributions had been achieved. Molecular weight determinations, by vapour pressure osmometry, on fractions 2 and 3 of the polymer from 1,3-bis(3-chlorocarbonylphenyl)hexafluoropropane and 3-oxatetrafluoropentane diol

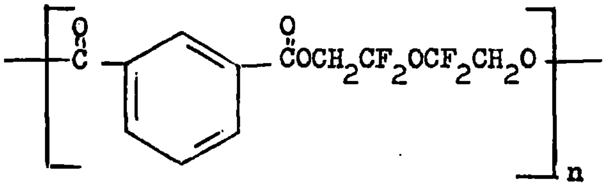


Polymer 1

(Polymer 1), and fractions 2 and 4 of the polymer from isophthaloyl chloride and 3-oxatetrafluoropentane diol (Polymer 2) gave values of

Table 4.

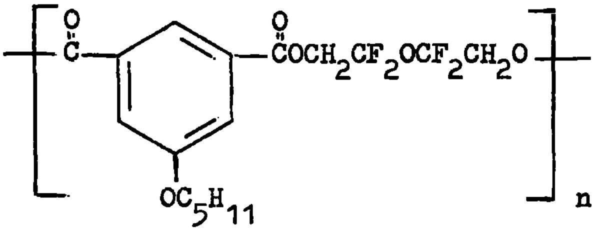
	Crude Polymer	Polymer Fractions						
		1	2	3	4	5	6	Residue
Polymer 1								
% Total		10	14	10				66
[η]	0·10	0·22	0·18	0·17				0·09
M.wt.	15,600		20,500	7,800				1,560
Dp	29		38	15				3
Polymer 2								
% Total		9	22	10	23	23		
[η]	0·21	0·23	0·19	0·21	0·14	0·14		0·08
M.wt.			3,300		1,500			
Dp			11		5			
Polymer 3								
% Total		7	14	10	12	32	14	11
[η]		0·24	0·23	0·22	0·15	0·03	0·02	0·001



Polymer 2

20,500, 7,800, 3,300, and 1,500 respectively, corresponding to degrees of polymerisation (Dp) values of 38, 15, 11 and 5 respectively. Consistent values could not be obtained using this instrument with, presumably, the highest molecular weight fractions (fraction 1) which would have molecular weights in excess of the values quoted above. However, the instrument is only reliable for maximum molecular weight values of approximately 20,000, and so it is assumed that the molecular weights of the first fractions for both polymers are in excess of this figure.

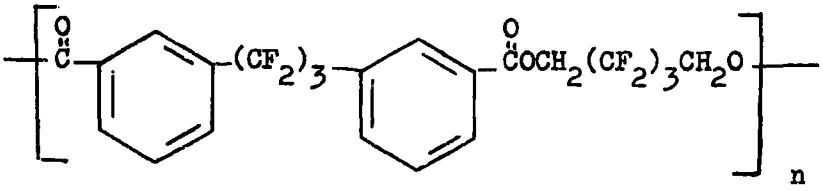
Molecular weight determinations on the separated fractions of the polymer from 5-(n-amyloxy)isophthaloyl chloride and 3-oxatetrafluoropentane diol (Polymer 3) could not be achieved due to malfunction of the



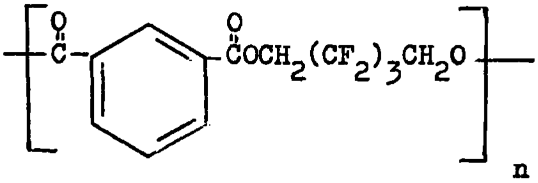
Polymer 3

instrument, but if it is assumed that the values of the constants k and α in the Staudinger equation are identical for polymers 2 and 3, then the values of the molecular weights for the first two fractions of polymer 3, would be in excess of 20,000.

As stated earlier, the main aim of this research work was the investigation of the effects of the introduction of the perfluoro-oxydimethylene link on the physical properties of polymers. Thermal stability data were obtained using thermogravimetric analysis (T.G.A.), the analyses being carried out in both nitrogen and air from room temperature to about 600°C. In order to attempt to determine the effect of the introduction of the perfluoro-oxydimethylene link, analyses were also carried out on the polymers from 1,3-bis(3-chlorocarbonylphenyl)-hexafluoropropane, and isophthaloyl chloride, with hexafluoropentane diol, (LXI) and (LXII) respectively.



(LXI)



(LXII)

Figure (i) - **Comparative T.G.A. for Polymer 1.**

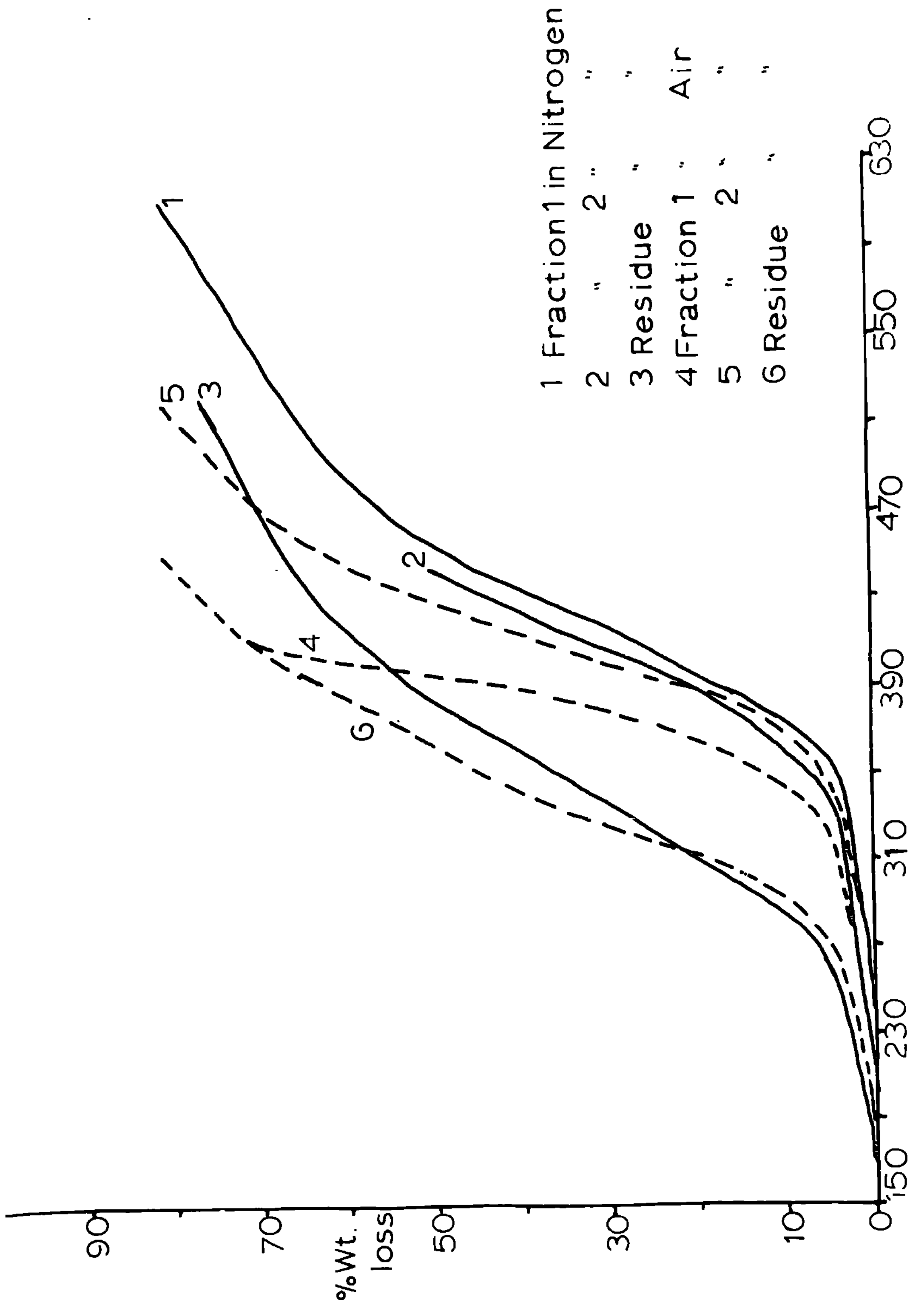


Figure (ii) - Comparative T.G.A. for Polymer 2.

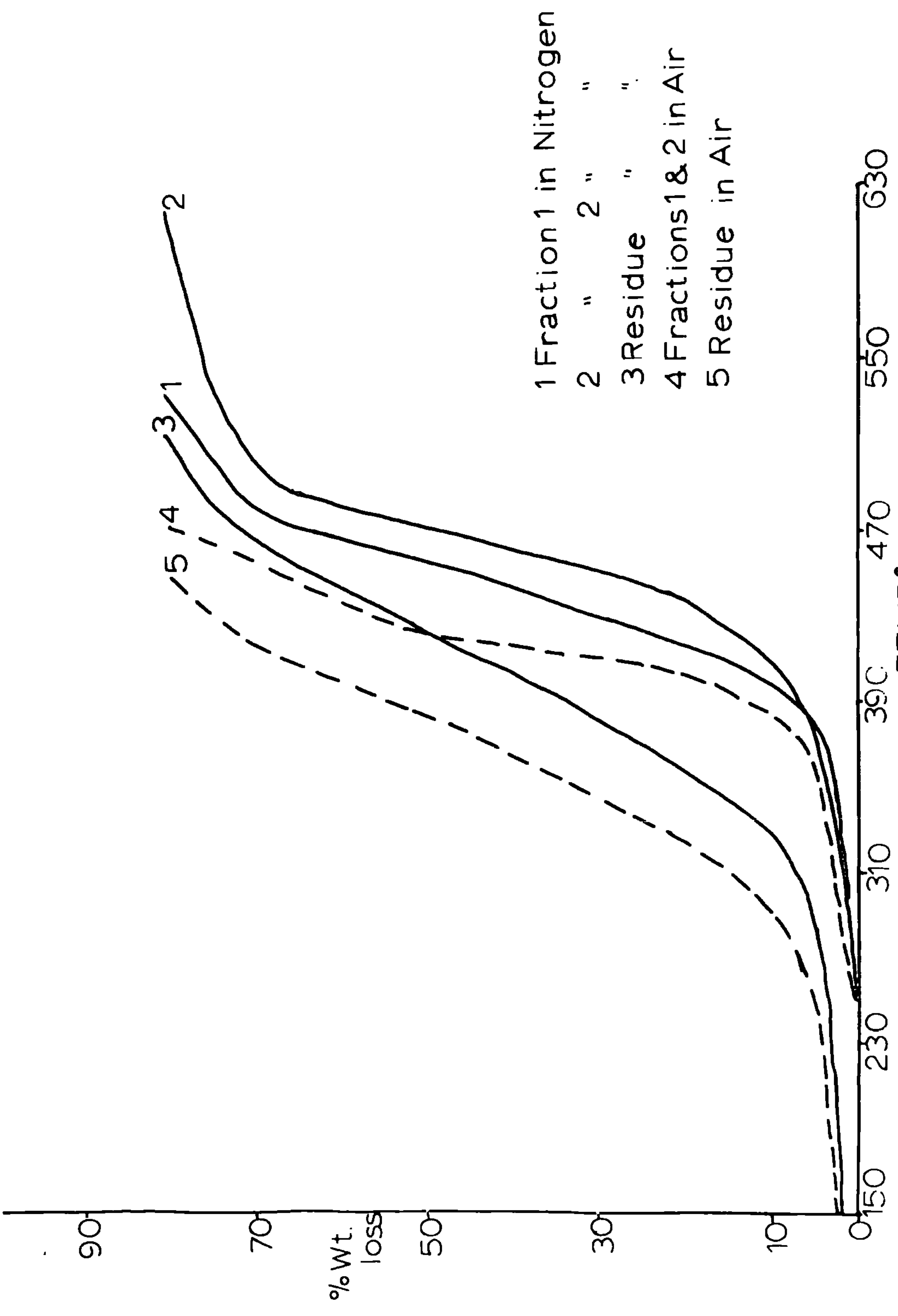


Figure (iii) - Comparative T.G.A. for Polymer 3.

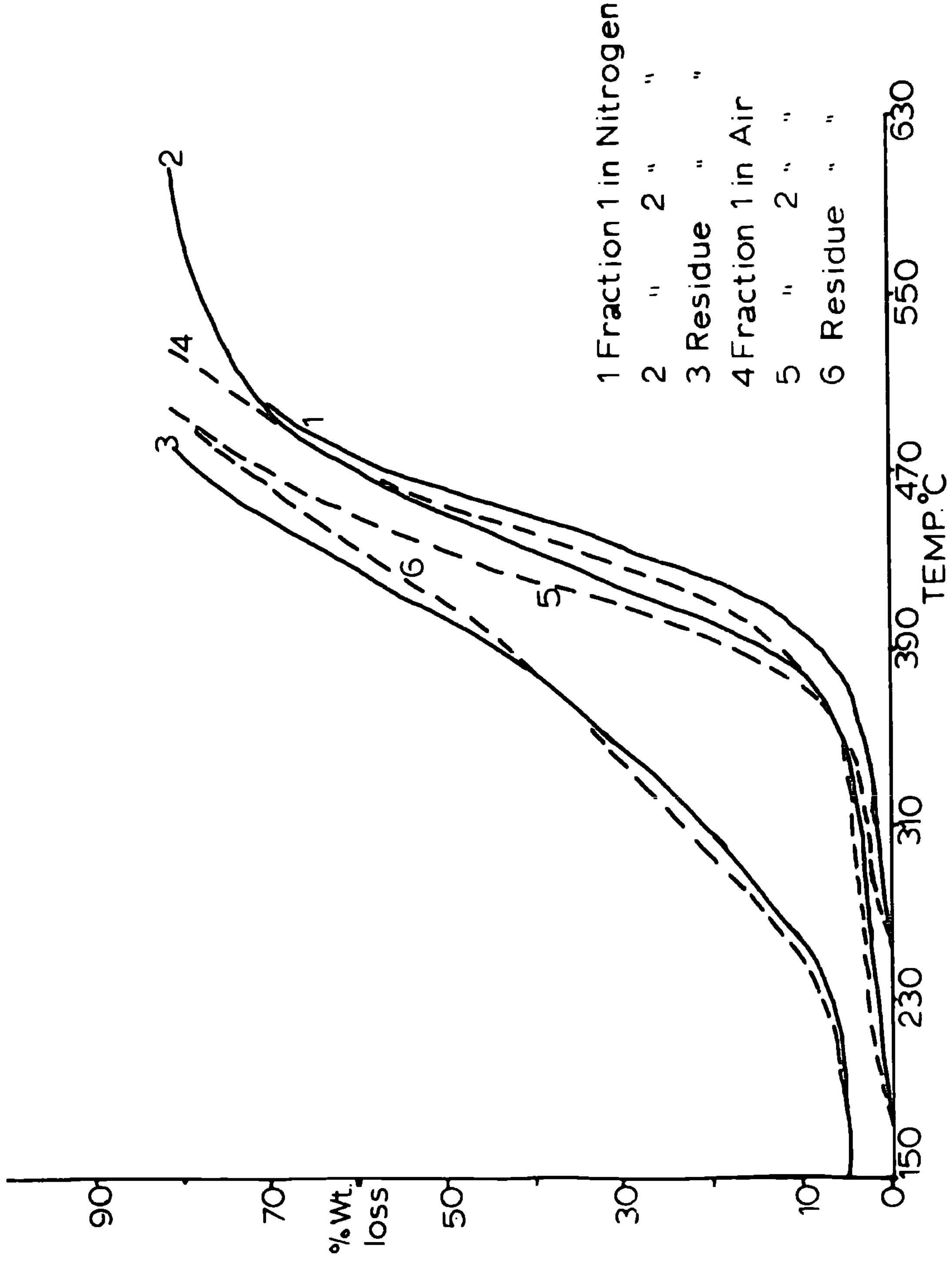


Figure (iv) -

Comparative T.G.A.'s in N_2 for Polymers 1, 2, 3, (LXI) and (LXII)

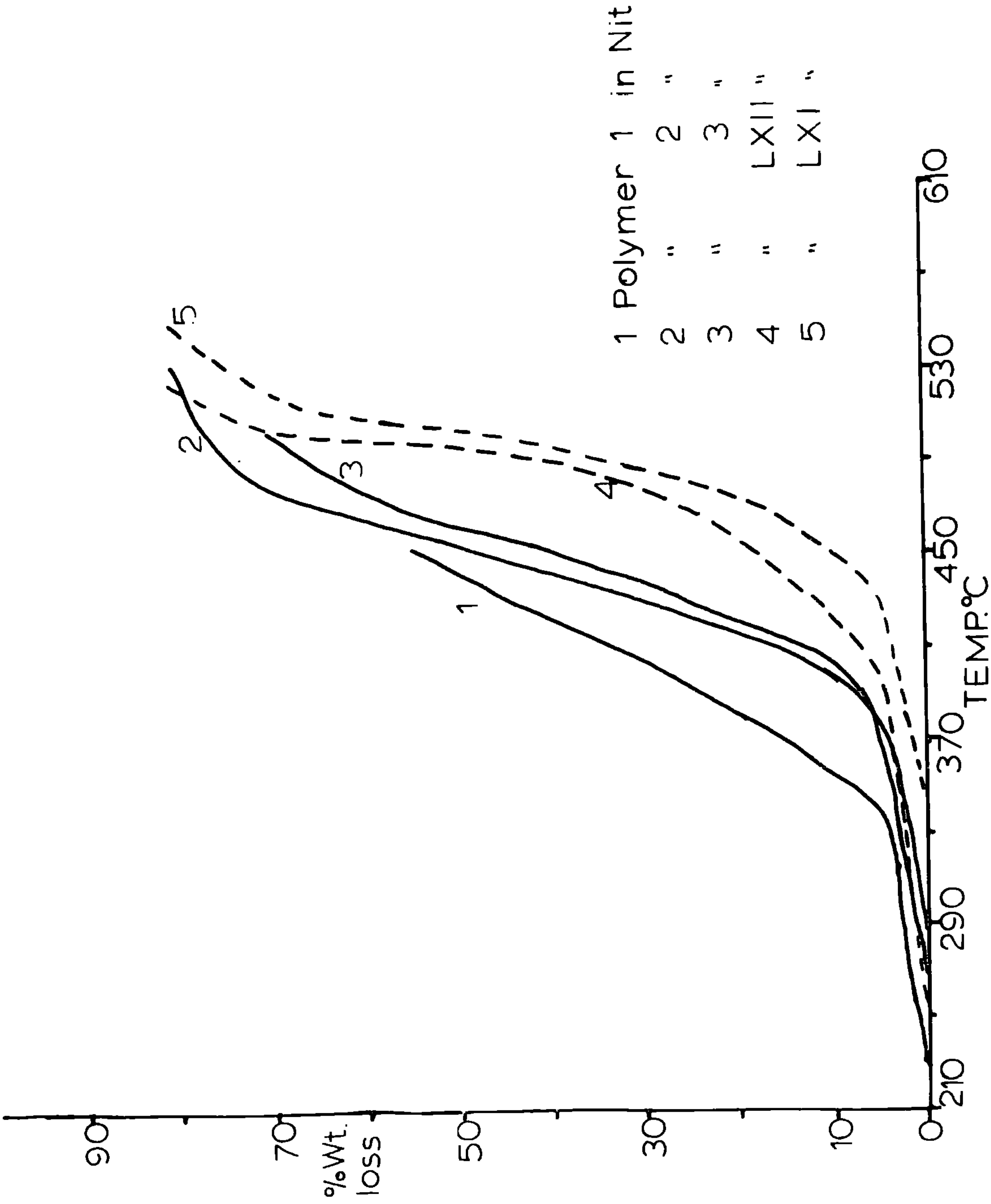
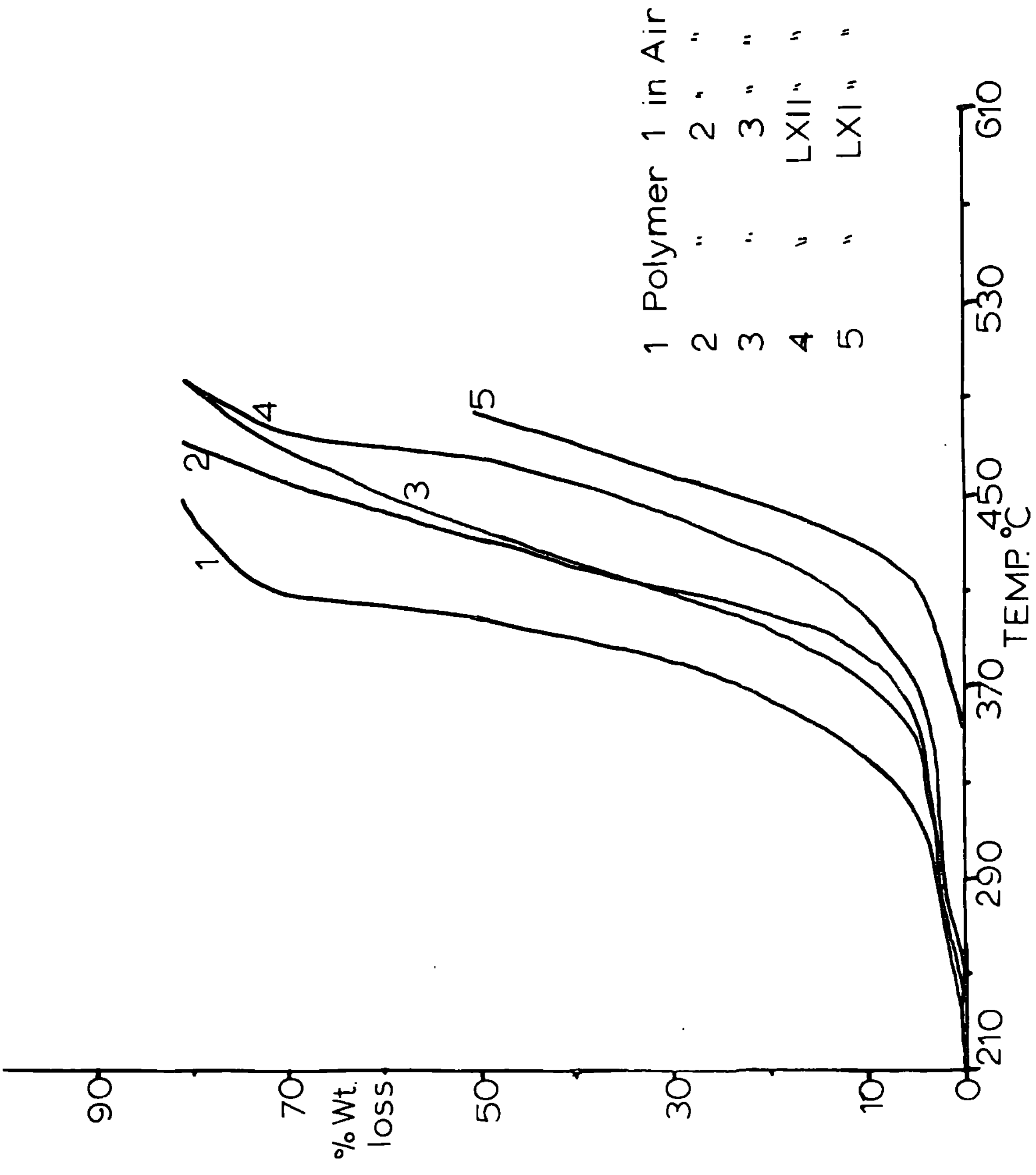


Figure (V) - Comparative T.G.A.'s in air for Polymers 1, 2, 3, (LXI) and (LXII)



The data obtained for polymers 1, 2 and 3 are given in figures (i), (ii) and (iii) respectively, from which it can be seen that the highest molecular weight material is more thermally stable than that of lower molecular weight. The residue fractions are the lowest molecular weight fractions and they decompose at lower temperatures than the other fractions. The polymers are also found to be more thermally stable in nitrogen than air, presumably since initial weight loss in air will be due to oxidation of the methylene group, followed by thermal decomposition, whilst in nitrogen oxidation cannot occur and hence the polymer will be more stable. Figures (iv) and (v) compare polymers 1, 2 and 3 with (LXI) and (LXII) in nitrogen and air respectively. It was found that polymer 1 was the least thermally stable of all, with weight loss beginning at *ca.* 230°C both in air and nitrogen.

Polymers 2, 3 and (LXII) were of comparable thermal stability as indicated by the onset of decomposition, but polymer (LXII) appeared to undergo the final rapid degradation (indicated by the steep part of the graph) at a temperature some forty degrees higher than polymers 2 and 3. Polymer (LXI) was significantly better than any of the other materials as regards both onset of decomposition and the temperature of final rapid degradation.

It has been reported[108] that onset of rapid decomposition in polyesters resulting from fragmentation of ester bonds usually occurs in the temperature range 280-325°C; the data being derived from T.G.A. under nitrogen with a temperature rise rate of 150° per hour. This higher than expected stability found for polymers 1, 2, 3, (LXI) and (LXII) may in part be due to the faster heating rate of 240° per hour employed in this work. However, a more significant factor may have been the purity of the polymer samples used in the earlier work; it has been noted (see figures (i), (ii) and (iii)) that the observed thermal stability depends markedly on the molecular weight distribution. Much of the data in the literature[108] is derived from measurements on unfractionated polymer samples which probably contain a high proportion of low molecular weight materials hence giving a misleading indication of thermal stability.

With so few examples, it is difficult to draw firm conclusions regarding structure stability relationships. However, comparing analogous systems containing either a perfluorotrimethylene or a perfluoro-oxydimethylene link, that is polymer 1 compared to polymer (LXI) and polymer 2 compared to polymer (LXII), it can be seen that the polymers containing the perfluoro-oxydimethylene links are less stable than those containing perfluorotrimethylene links.

An arbitrary numerical value can be placed on this decreased stability by a comparison of the temperatures at which 10% of the weight is lost; in the two examples cited above this amounts to a drop in thermal stability, under nitrogen, of 100° and 40° respectively.

The other physical property of importance was the glass transition temperature (Tg), below which the polymer is a rigid glass. The data were obtained for the polymers using differential scanning calorimetry, the glass transition temperature being taken as the mid-point of the curve showing a change of slope for the heat content of the polymer as compared to a reference sample. The data obtained were compared with those for polymers (LXI) and (LXII), the Tg value for (LXI) being reported as 16°C measured by dilatometry[100] and 24°C measured by D.S.C.,[46] and that for (LXII) being reported as 25°C[46] and 22°C[6]. The latter authors[6] also found that the introduction of a 5-(n-amyloxy)substituent in the aromatic ring of (LXII) produced a decrease in the Tg value to -30°C. The values of Tg found for polymers 1, 2 and 3 were 30°C, 28°C and 14°C respectively, the latter value confirming the reduction of the glass transition temperature by introduction of the internal plasticiser unit, the 5-(n-amyloxy)substituent, the reduction not being as great as that found in the case of polymer (LXII). However, a comparison of the data shows that far from producing a decrease in the glass transition temperature, replacement of a perfluoro-trimethylene unit by a perfluoro-oxydimethylene unit seems to give an increase in Tg. This would indicate that the perfluoro-oxydimethylene link, in this particular environment, produces an increase in intermolecular interaction which outweighs any additional flexibility gained by the incorporation of the ether link. However, it should be noted that the values of Tg obtained for particular polymers are dependant on the rate of heating in the determination, although differences are only of the order of a few degrees.[109]

The results obtained from the analyses of the physical properties of the prepared polymers, indicate that the replacement of a perfluorotrimethylene group by a perfluoro-oxydimethylene group in this particular environment, does not produce the expected lowering of the glass transition temperature. Indeed, the results suggest that the opposite effect occurs, an increase in Tg being found, in addition to a substantial reduction in thermal stability. The conclusion to be drawn from the work up to the present, is that it is unlikely that a polymer containing a perfluoro-oxydimethylene group adjacent to an ester link, would be a thermally stable elastomer over the required temperature range -20°C to +250°C.

Experimental.

Fractional precipitation of the polymers was carried out by successive addition of petroleum ether (80-100) to a 2% solution of the polymer in chloroform. The successive immiscible lower layers were separated and heated under reduced pressure ($100^{\circ}/0{\cdot}01$ mm./6 hr.) to remove volatile material. The residue was then used for the analyses reported.

Viscosity determinations were carried out with an Ubbelohde viscometer immersed in a water-bath thermostatted at $30 \pm 0{\cdot}01^{\circ}C$. An accurately known solution of about 1% concentration of the polymer in methyl ethyl ketone was made up, and the time of flow of the solution through the viscometer was determined until 3 consecutive results within 0•2 secs. were obtained. Successive dilution of the polymer solution in the viscometer was then carried out in order that determinations could be made at different concentrations.

Molecular weight measurements were made using a Mechrolab Vapour Pressure Osmometer, model 301A, operating at $30^{\circ}C$.

Thermogravimetric analyses were carried out with a DuPont 950 Thermogravimetric Analyser using a heating rate of 4°/min., the determinations being carried out in nitrogen and air.

Differential Scanning Calorimetry measurements were made using a Perkin Elmer Differential Scanning Calorimeter programmed at 32°/min. heating rate from $200^{\circ}K$ to decomposition temperature.

APPENDIX I.

General Apparatus.

This is a summary of the apparatus and instruments used for obtaining the results in the Experimental sections.

Infrared spectra. Spectra were recorded on Perkin Elmer 137 and 157, Grubb Parsons Spectromaster and Grubb Parsons GS2A spectrophotometers.

Ultraviolet spectra. Unicam SP800 u.v. spectrophotometer.

N.M.R. spectra. Perkin Elmer R10 and Varian A56/60 spectrometers, operating at 56·46 MHz. for ^{19}F and 60 MHz. for ^{1}H spectra. ^{1}H shift values are expressed as τ with reference to tetramethylsilane as external reference.

Analytical g.l.c. A Perkin Elmer 452 with a variety of stationary phases using hydrogen as carrier gas and a hot wire detector were used. Column designations were:

Column A: 2·2 m. x 7 mm. diam., di-n-decylphthalate/Celite.

Column O: 2·2 m. x 7 mm. diam., silicone grease/Celite.

Column L: 2·2 m. x 7 mm. diam., acetonylacetone/Celite.

Preparative g.l.c. All instruments used nitrogen as carrier gas and were either

4·9 m. x 75 mm. diam., dinonylphthalate/Celite, 1:1; flow rate *ca.* 60 l/hr, or Perkin Elmer F21 Präparativer Gaschromatograph, 4·5 m. x 9·5 mm. diam., di-n-decylphthalate/ Chromosorb P, 1:4; flow rate *ca.* 12 l/hr.

APPENDIX II.

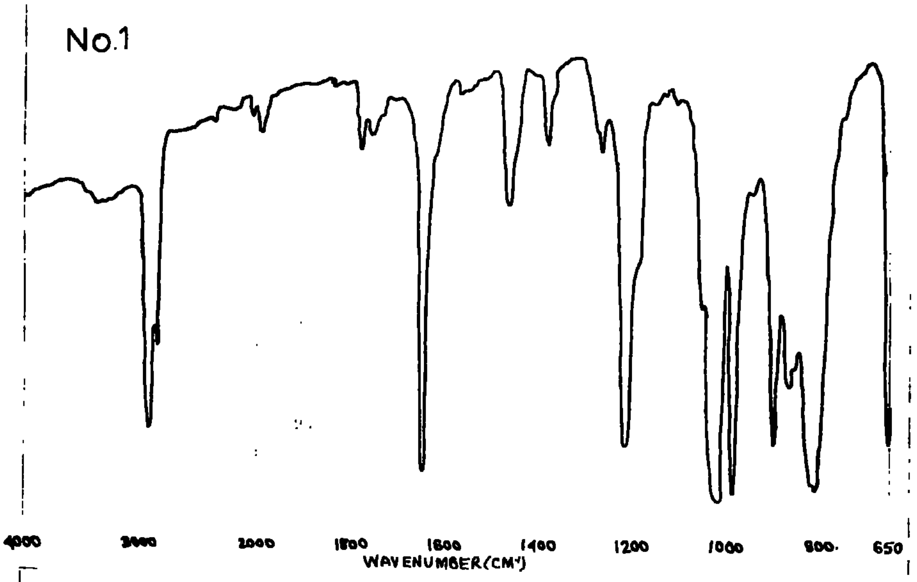
Infrared Spectra.

1.	Perchloro-2,5-dihydrofuran.	(n)
2.	3,4-Dichloro-2,2,5,5-tetrafluoro-2,5-dihydrofuran.	(g, 12 mm.)
3.	2,3,4-Trichloro-2,5,5-trifluoro-2,5-dihydrofuran.	(cf)
4.	2,2,4-Trichloro-3,5,5-trifluoro-2,5-dihydrofuran.	(cf)
5.	Perfluoro-oxydiacetyl chloride.	(g, 20 mm.)
6.	Monomethyl perfluoro-oxydiacetyl chloride.	(cf)
7.	Perfluoro-oxydiacetic acid.	(n)
8.	Dianilinium perfluoro-oxydiacetate.	(d)
9.	Dimethyl perfluoro-oxydiacetate.	(cf)
10.	Perfluoro-oxydiacetic anhydride.	(cf)
11.	Dipiperidinium perfluoro-oxydiacetate.	(d)
12.	Diethyl perfluoro-oxydiacetate.	(cf)
13.	Perfluoro-oxydiacetamide.	(d)
14.	1-Aza-4-oxa-3,3,5,5-tetrafluorocyclohexa-2,6-dione.	(d)
15.	Monomethyl perfluoro-oxydiacetate.	(cf)
16.	5-Phenyl-3-oxa-perfluoropentanoic acid-5-one.	(cf)
17.	2,2,4,4-Tetrafluoro-3-oxapentane diol.	(d)
18.	2,2,4,4-Tetrafluoro-3-oxapentane-1,5-dibenzoate.	(d)
19.	4-Hydroxy-2,3-dichloro-4,4-difluoro-2-butenoic acid γ-lactone.	(cf)
20.	Difluorotetrachloro-2,5-dihydrofurans.	(cf)

21.	2-Fluoro-2,3,4,5,5-pentachloro-2,5-dihydrofuran.	(cf)
22.	Perfluoro-2,5-dihydrofuran.	(g, 10 mm.)
23.	4-Chloro-3-methoxy-2,2,5,5-tetrafluoro-2,5-dihydrofuran.	(cf)
24.	Chlorodimethoxy-2,2,5,5-tetrafluorotetrahydrofuran.	(cf)
25.	Dichloroethoxy-2,5,5-trifluoro-2,5-dihydrofuran.	(cf)
26.	2,2,4-Trichloro-3,5,5-trifluoro-2,5-dihydrofuran.	(cf)
27.	Polyester from 1,3-di(3-chlorocarbonylphenyl)-hexafluoropropane and 2,2,4,4-tetrafluoro-3-oxapentane diol. (Polymer 1).	(cf)
28.	Polyester from isophthaloyl chloride and 2,2,4,4-tetrafluoro-3-oxapentane diol. (Polymer 2).	(d)
29.	Polyester from 5-(n-amyloxy)isophthaloyl chloride and 2,2,4,4-tetrafluoro-3-oxapentane diol. (Polymer 3).	(cf)

(n) - nujol mull.
(cf) - contact film.
(d) - KBr disk.
(g) - gas sample, followed by pressure in mm.

No.1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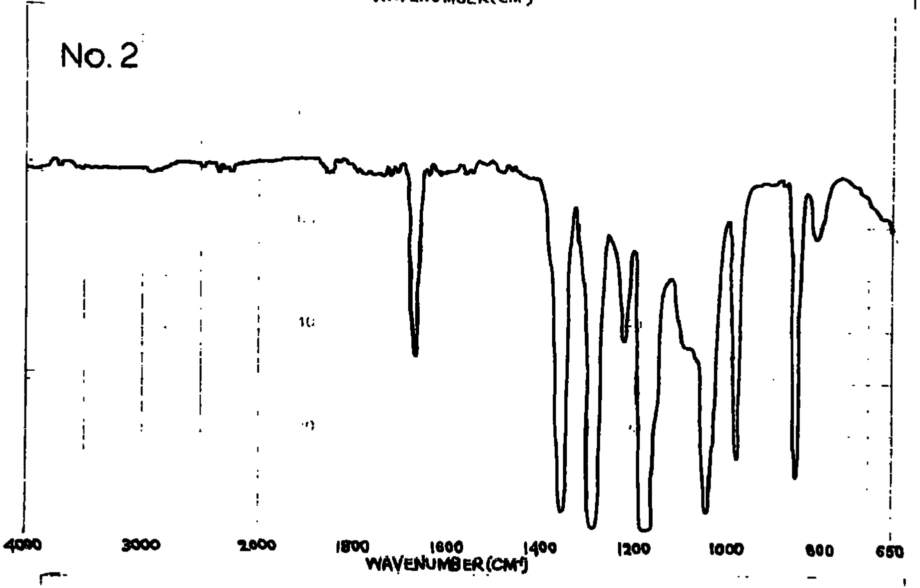
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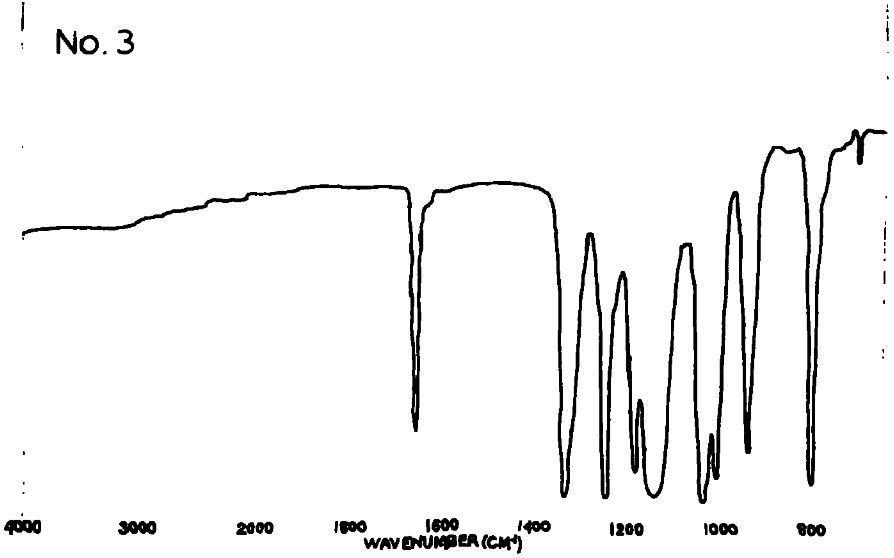
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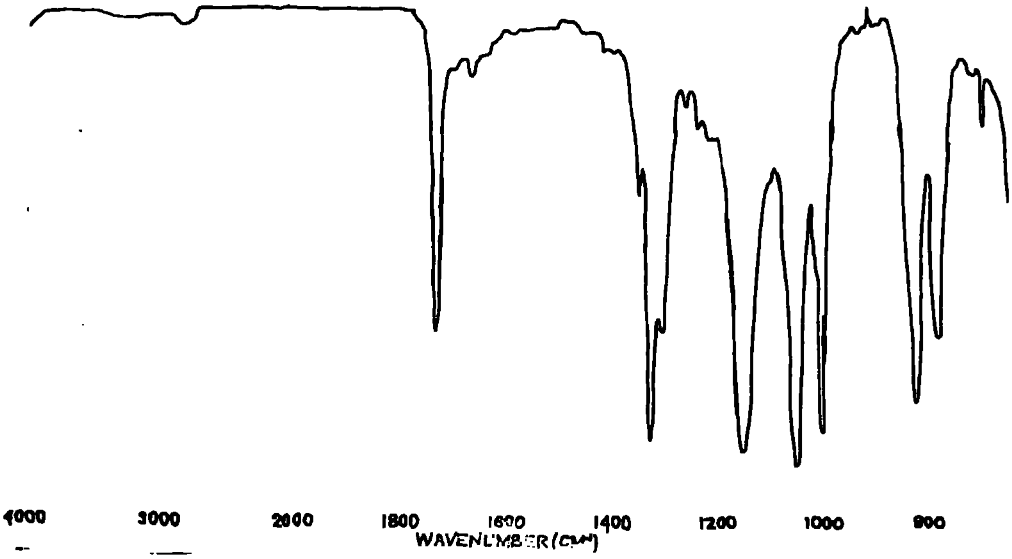
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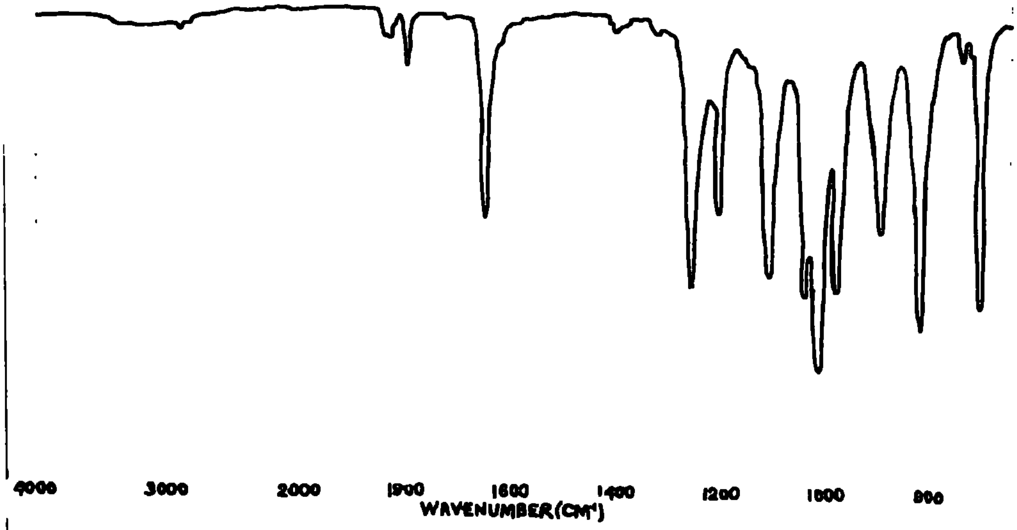
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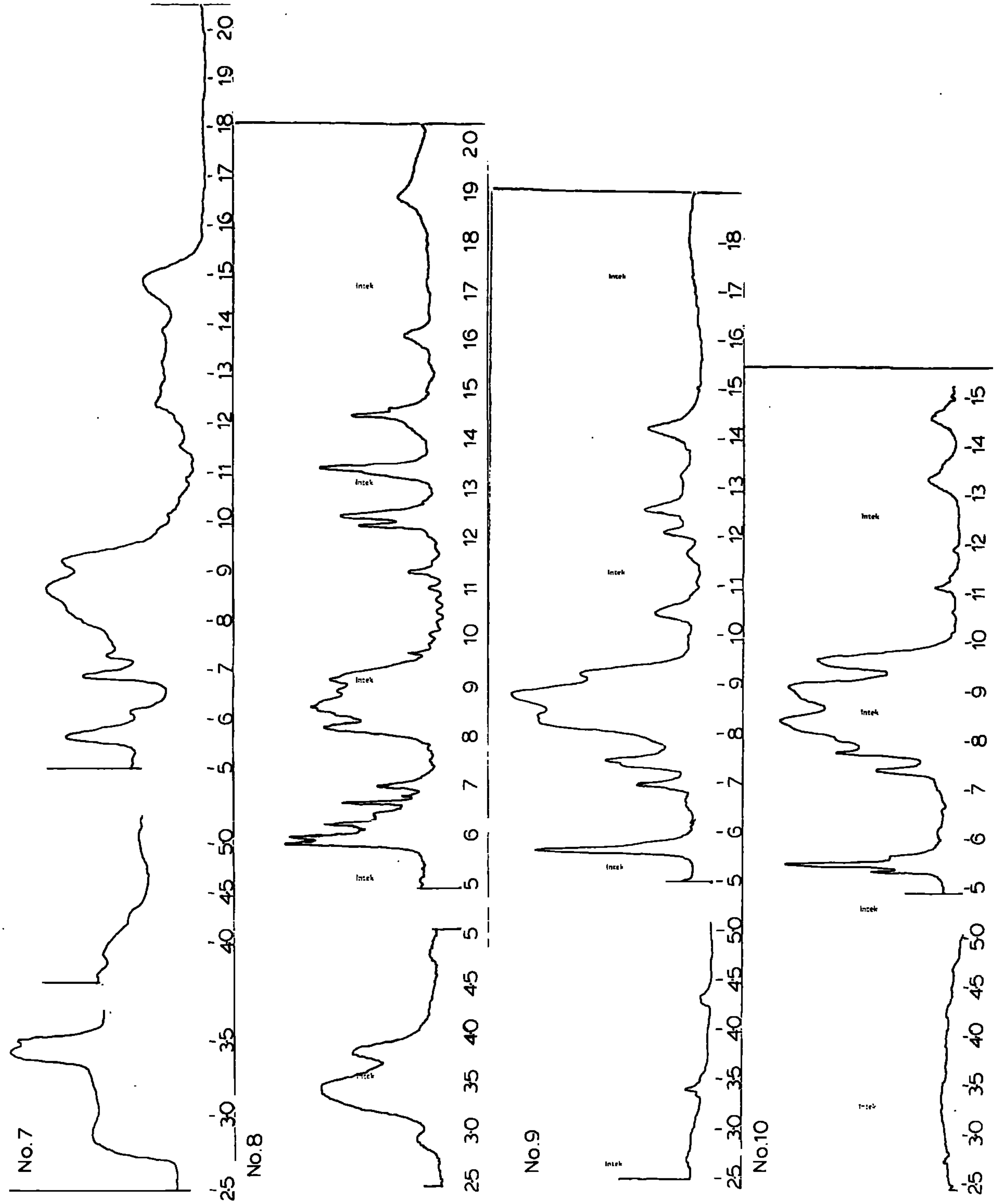
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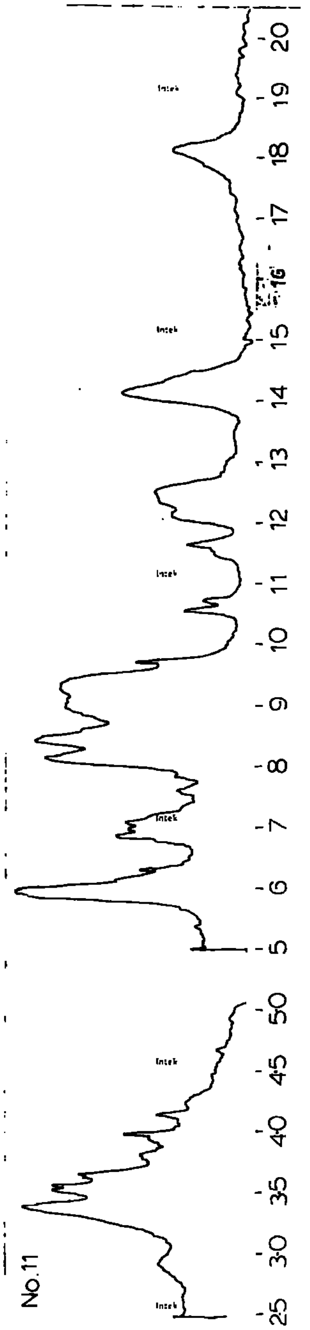

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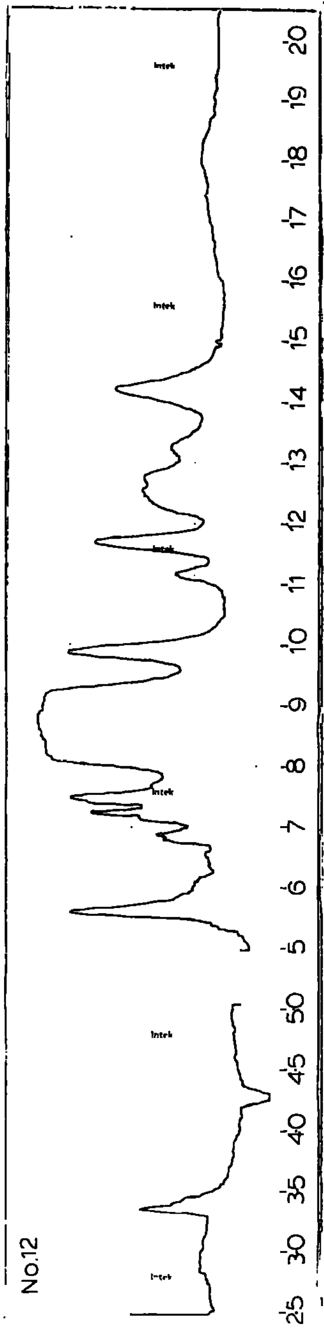

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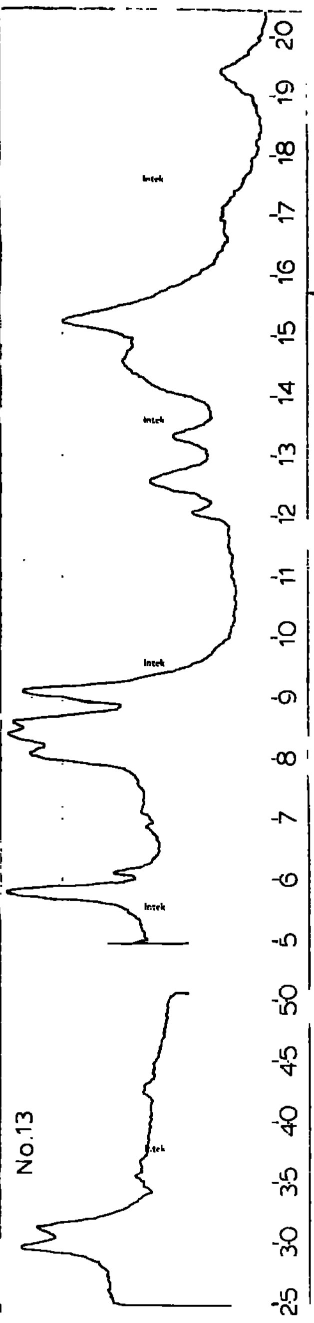

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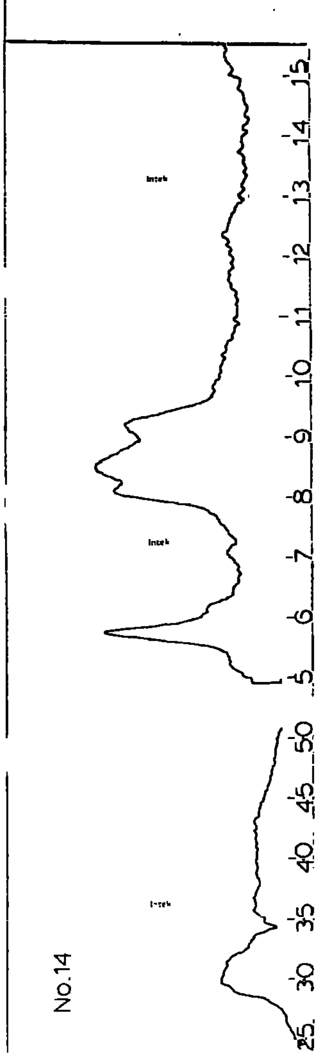

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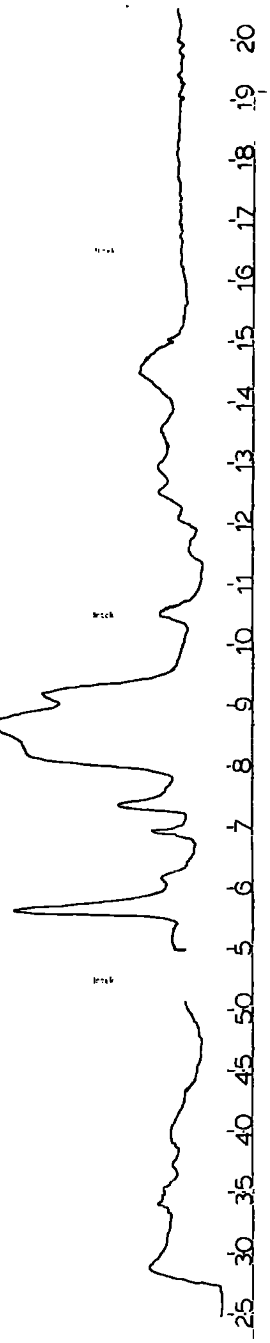

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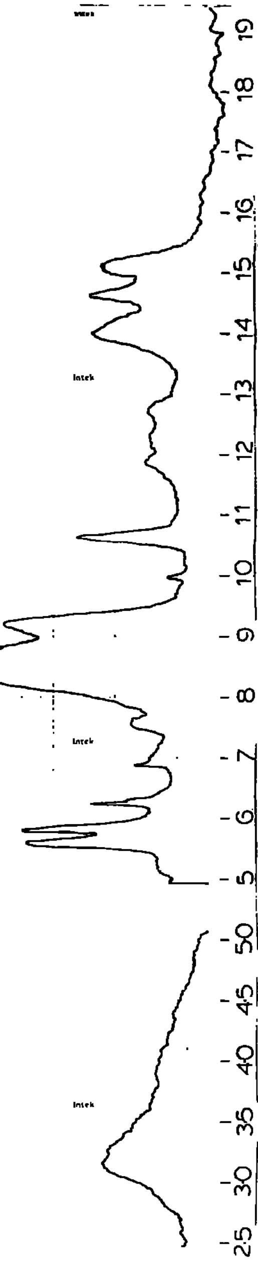

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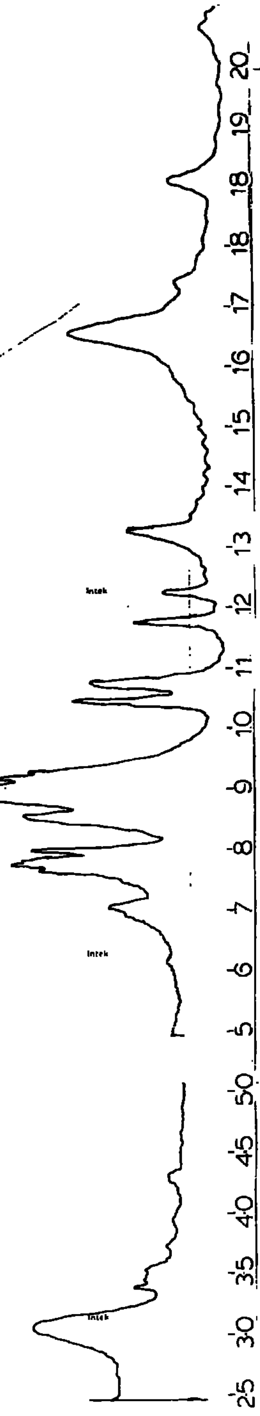

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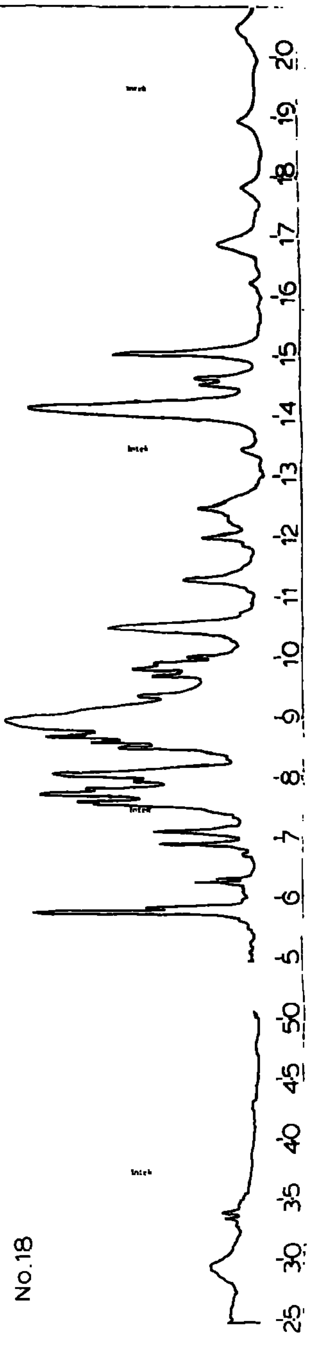

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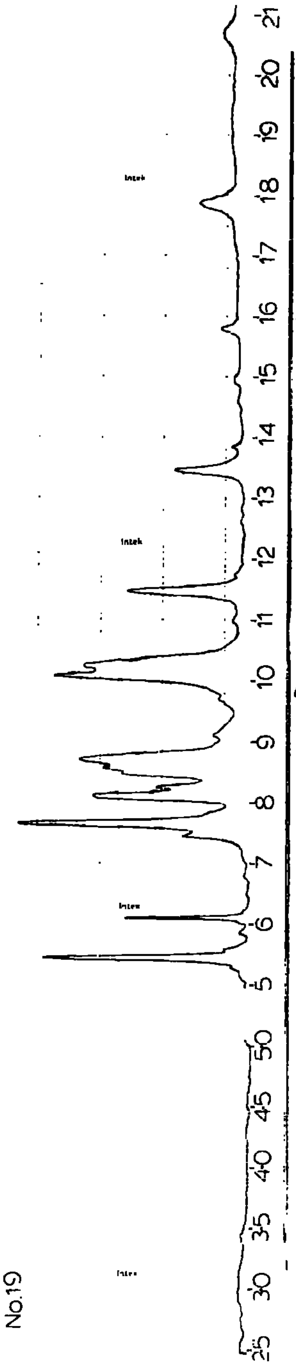

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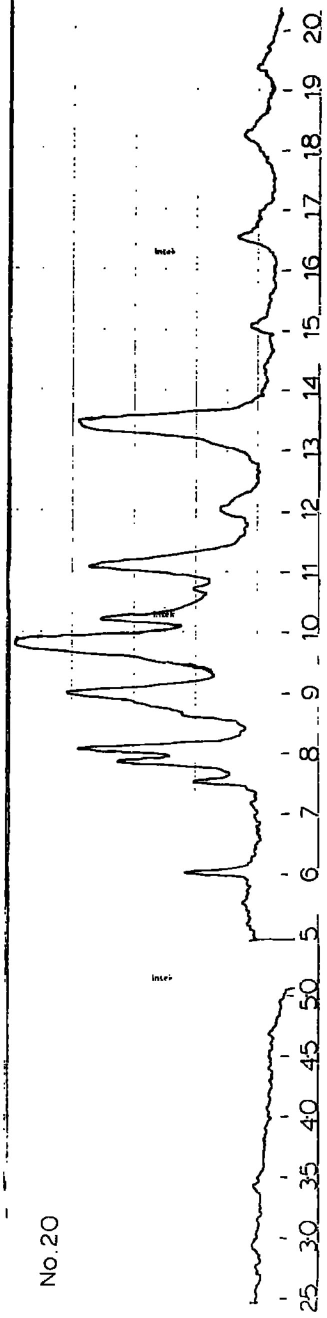

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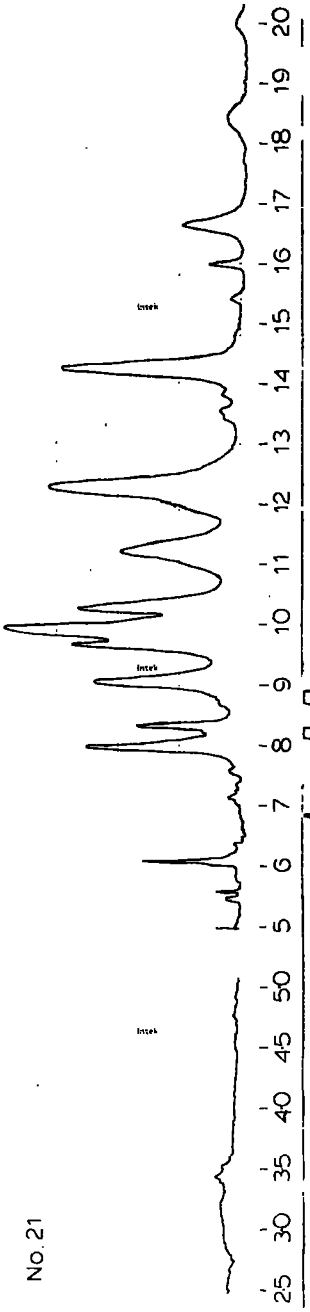

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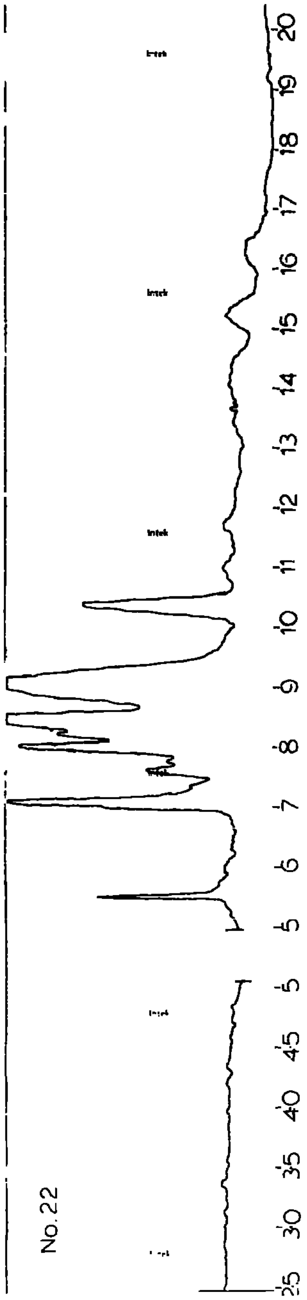

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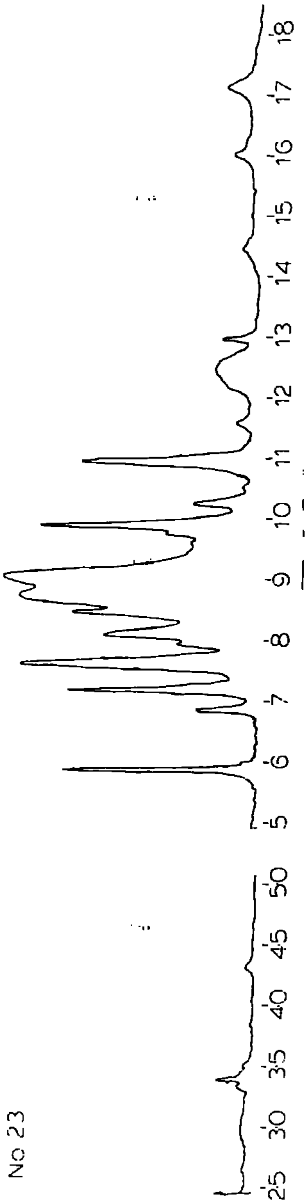

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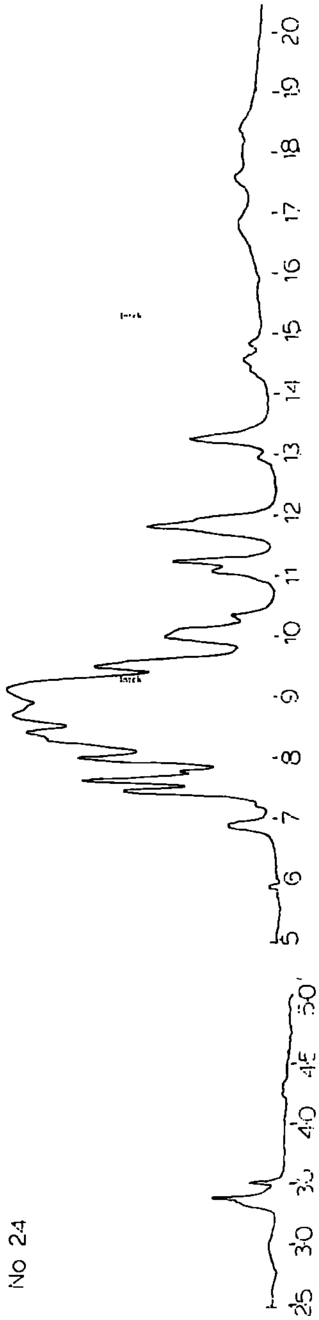

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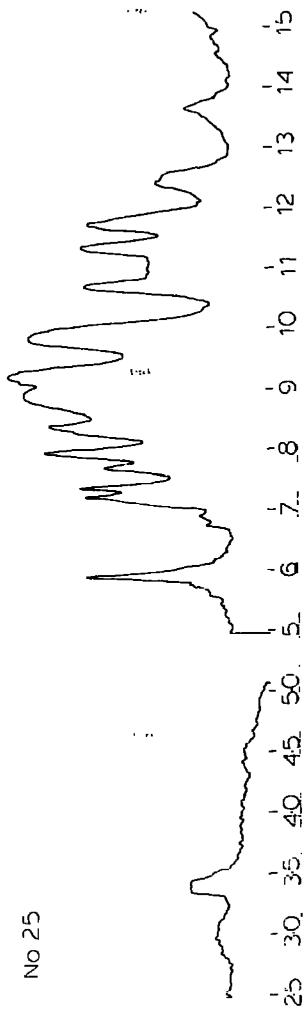

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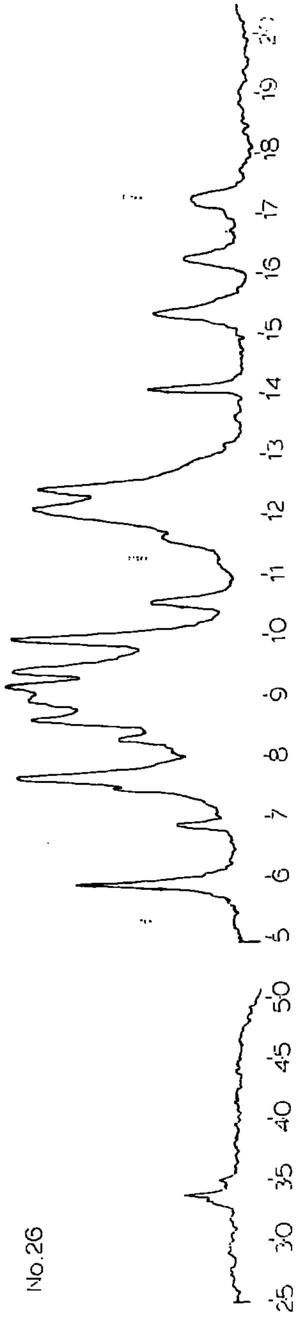

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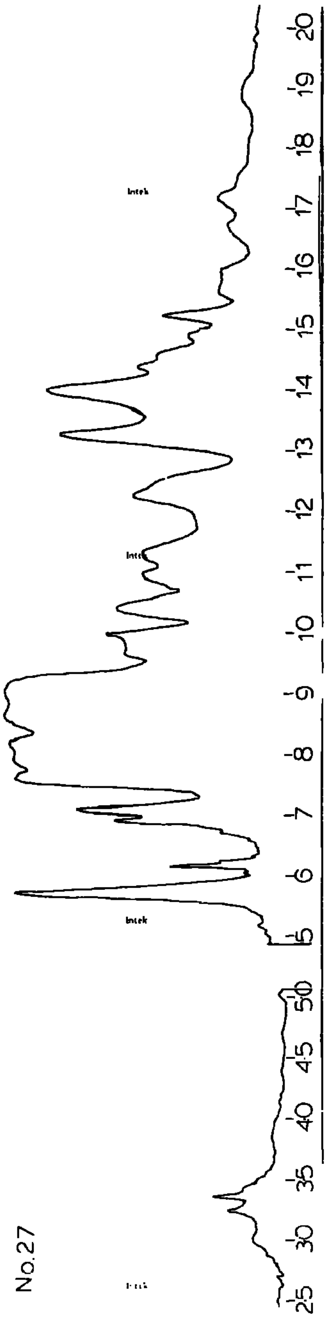

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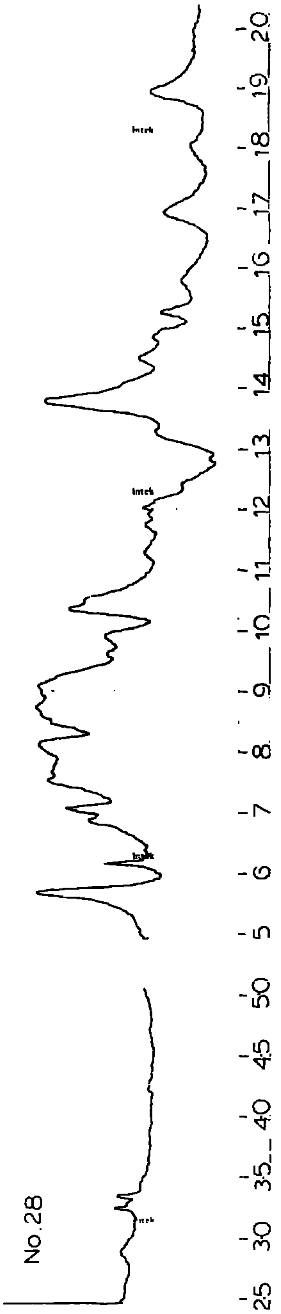

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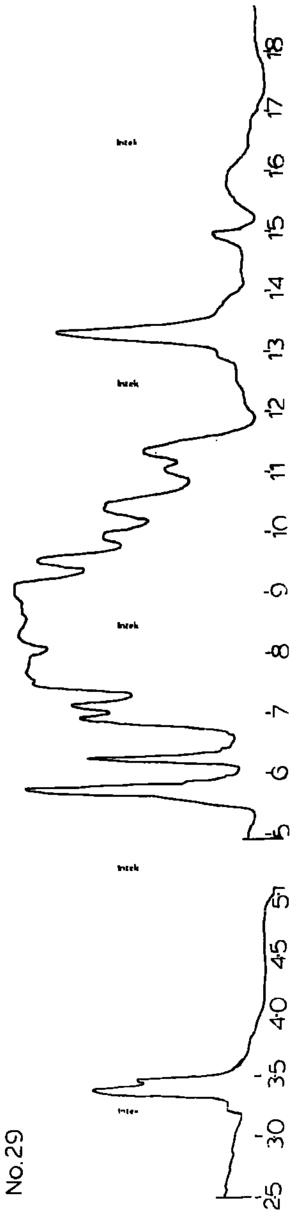

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