Chemistry of some model compounds related to fluorinated polymers

Odello, Paolo

UNIVERSITY OF DURHAM

A THESIS
entitled

CHEMISTRY OF SOME MODEL COMPOUNDS RELATED TO FLUORINATED POLYMERS

submitted by

PAOLO ODELLO B. Sc.

(St. Mary's College)

A thesis submitted for the degree of
Doctor of Philosophy
of the
Universisty of Durham

May 1993

A mia madre Maria Assunta,
a mio padre Franco e
a mio fratello Maurizio

ACKNOWLEDGEMENTS

I would like to thank Professor Richard D. Chambers for his continuous advice and encouragement throughout the course of this work.

I would also like to thank the technical staff in the Department for their invaluable help. In particular Dr. M Jones, Mr. V. McNeilly, Miss L.M.Turner, (Mass Spectrometry); Mrs Cox and Mrs J Dostal (Elemental Analysis); Mr D. Hunter (High Pressure Facilities); Mr L. Lauchlan (Chromatography and Italian Soccer Results); Mr. R. Hart and Mr G. Haswell (Glass Blowing); Dr R. Matthews and Dr A. Kenwright (Nuclear Magnetic Resonace Spectroscopy); and last but not least Mr T.F.Holmes (who consumed about 12 Kg (4,500,000 mol) Italian chocolate) for his endless and heartfelt help with practical chemistry and father-like suggestion to enjoy my stay in Durham.

I would also like to mention the lads in the laboratory for making this period so enjoyable actively contributing to the improvement of my English "vocabulary" and knowledge of beers.

Finally I would like to thank Ausimont S.p.A - Italy for their financial support.

MEMORANDUM

The work described in this thesis was carried out in the university of Durham between January 1990 and December 1992. This thesis is the work of the author, except where acknowledged by reference, and has not been submitted for any other degree.

Part of this work is the sugject of papers in print, and has been presented by the author at:

11th ACS Winter Fluorine Synposium, St. Petersburg, Florida, U.S.A; January 1993.

ABSTRACT

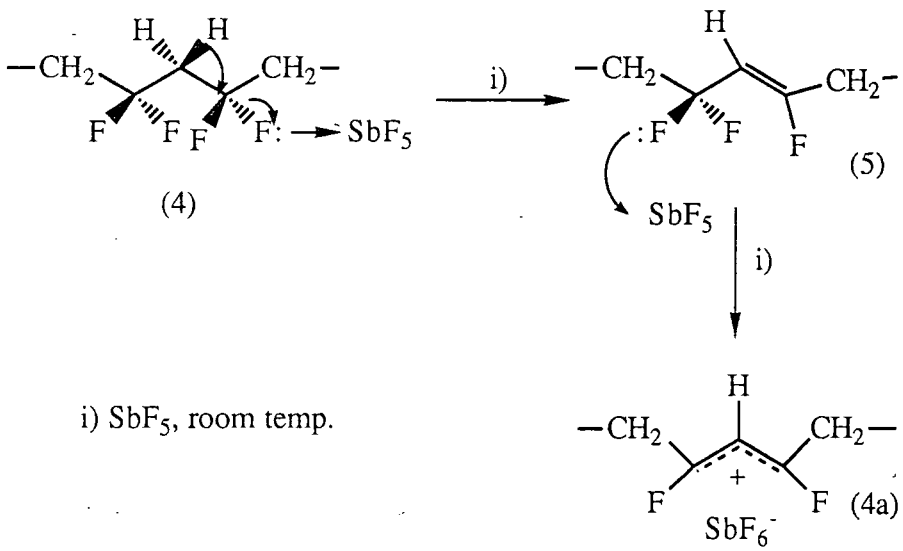
CHEMISTRY OF SOME MODEL COMPOUNDS RELATED TO FLUORINATED POLYMERS

by

Paolo Odello

The work described in this thesis is concerned with three areas which are the generation of stable carbocations from saturated model compounds related to poly-vinylidenefluoride, the development of synthetic routes to fluoro-organo-phosphazenes with intention of obtaining some potential additives for perfluoropolyether fluids operating at elevated temperatures, and pericyclic reactions involving fluorinated olefins.

1. We reported that some remarkable conjugated cations, and di-cations (4a) are obtained by reaction of hydrofluorocarbon precursors (4) with an excess of antimony pentafluoride. Cations (4a) bear the fluorine atoms at the charged sites, which of course, leads to stabilisation of the systems.



[4]

We investigated the effect of both re-hybridisation and charge on ^{13}C, ^{19}F, ^{1}H n.m.r. chemical shifts and we applied the empirical criterion of ^{13}C chemical shifts additivity to these systems to confirm the structure of some carbo-mono-cations and -di-cations.

2. The mechanism of displacement reactions in halophosphazenes was rationalised by reacting the systems in study with selected nucleophiles in competition reactions.

Some fluoro-organo-phosphazenes were synthesised using halophosphazenes as starting materials. Different methodologies were used and their effectiveness was limited

by the reactivity of the halophosphazenes towards the fluoroalkylating agents. The methodologies used include nucleophilic displacement of the halogen with fluorinated alcohols (R_FCH_2OH), and perfluoroalkylating agents (eg.: CF_3SiMe_3); perfluoroalkylation of organo-phosphazene using hexafluoropropene under gamma ray irradiation.

Potential stabilising agents for perfluoropolyether fluids were synthesised and their effectiveness was tested.

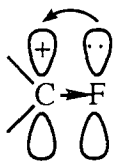
3. Some pericyclic reactions of heptafluorobut-2-ene and hexafluorobut-2-ene with dienes have been studied in an attempt to synthesise a series of benzenoid and heteroaromatic compounds containing two trifluoromethyl groups in high yields.

CONTENTS

CHAPTER 1
STUDIES AND CALCULATIONS ON FLUORINATED CARBOCATIONS

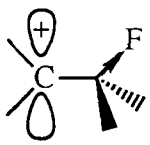
1.A Introduction

The following work concerns fluorinated carbocations. Olah and coworkers were the first to report on the subject[1,2], showing the effect of fluorine atoms on carbocation stabilities. It was found that when fluorine is at the charged site (1a), its inductive electron withdrawing effect is offset by back-donation of the non bonded electron pairs into the vacant p orbital of carbon, resulting in overall stabilisation. On the contrary, when fluorine is at the adjacent position (1b), it is strongly electron-withdrawing, and therefore, destabilising.



(1a)

- I = destabilising, +M = stabilising resulting in stabilisation

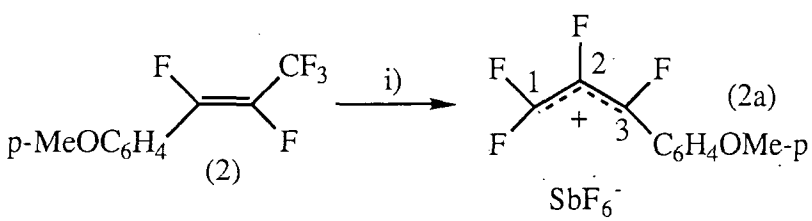


(1b)

-I = destabilising

[1]

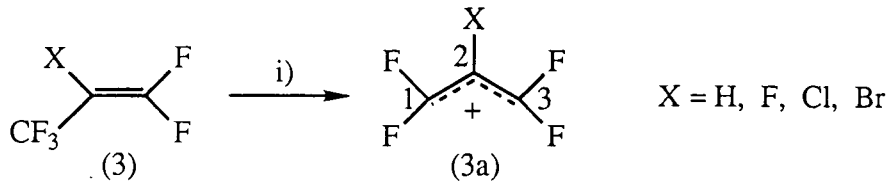
In particular we are interested in delocalised systems similar to the ones previously described by Chambers and co-workers.[3,4] They reported that fluorinated propenes of type CF_3-CF=CFX gave fluorinated allyl cations, when treated with antimony pentafluoride in sulphur dioxide at low temperatures (-30°C). When X = p-$MeOC_6H_4$ (2), a long-lived carbocation (2a) was formed, and when X = OMe, a C-1 - C-3 interaction was observed. However, in both cases, the allyl cations showed the positive charge delocalised principally at carbons C-1 and C-3.



i) SbF_5, SO_2, -30°C

[2]

Later, German and co-workers[5,6] showed that the existence of allylic cations of type (3a) could be confirmed by ^{19}F and ^{13}C n.m.r. data. These cations were easily obtained reacting CF_3-CX=CF_2 (3) (X= H, F, Cl, and Br) with antimony pentafluoride at low temperature.



(3) (3a)

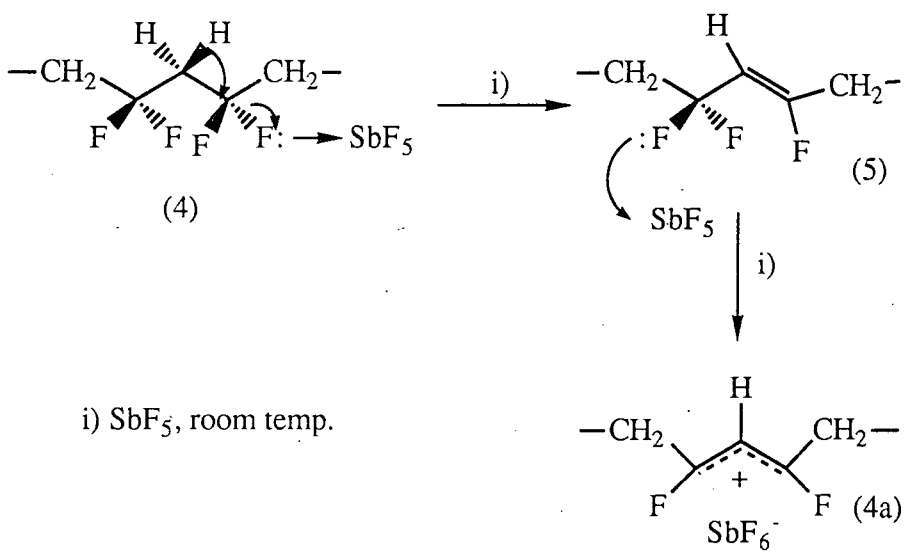
i) SbF_5, SO_2ClF, -30°C

[3]

Particularly interesting was ion (3a), X = F, where the fluorine atom was at the nodal point (destabilising); this ion could only be observed at -30°C, and in presence of SO_2ClF, because at room temperature it would undergo dimerisation with hexafluoropropene (3) X = F. They compared[5,6] the ^{13}C n.m.r. data for all cations (3a) and their corresponding precursors (3), and observed that the carbon atoms at the charged sites (C-1), (C-3), underwent a relatively large deshielding, as opposed to the one at the nodal position (C-2) which did not appear to be effected by the presence of the charge. Furthermore, they noticed that the values of the carbon-fluorine coupling constants at (C-1), (C-3), increased in going from the precursors (3) to the cations (3a).

1.B Results and discussion

The present work has its origins in an early study[7] with the Ausimont S.p.A. company (Italy), on model compounds related to polyvinylidenefluoride chemistry[8]. It has been shown that some remarkable conjugated cations, and di-cations are obtained by reaction of hydrofluorocarbon precursors (4) with an excess of antimony pentafluoride. In the first stage antimony pentafluoride induces dehydrofluorination to produce alkenes (5), followed by abstraction of a fluorine atom and formation of carbocations (4a). Cations (4a) bear the fluorine atoms at the charged sites, which of course, leads to stabilisation of the systems.



(4)

[4]

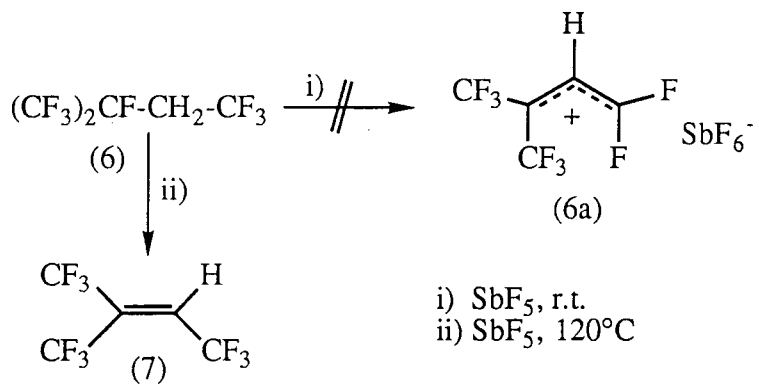
The synthesis of hydrofluorinated saturated model compounds and their unsaturated derivatives is dealt with in the second part of this chapter, while the generation of conjugated mono-cations and di-cations is described hereafter.

1.B.1 Formation of carbocations.

Carbocations are simply generated by mixing precursors (4) with antimony pentafluoride at room temperature, in all these reactions antimony pentafluoride acts both as a Lewis acid and as a solvent. Once formed, cations (4a) are stable for a considerably long period of time. Indeed, analysis by ^{13}C n.m.r. did not show any change in the spectra after several weeks of storage at room temperature in a sealed n.m.r. tube, and undoubtedly, these are conditions that hydrocarbon systems could not stand up to, without extensive fragmentation.

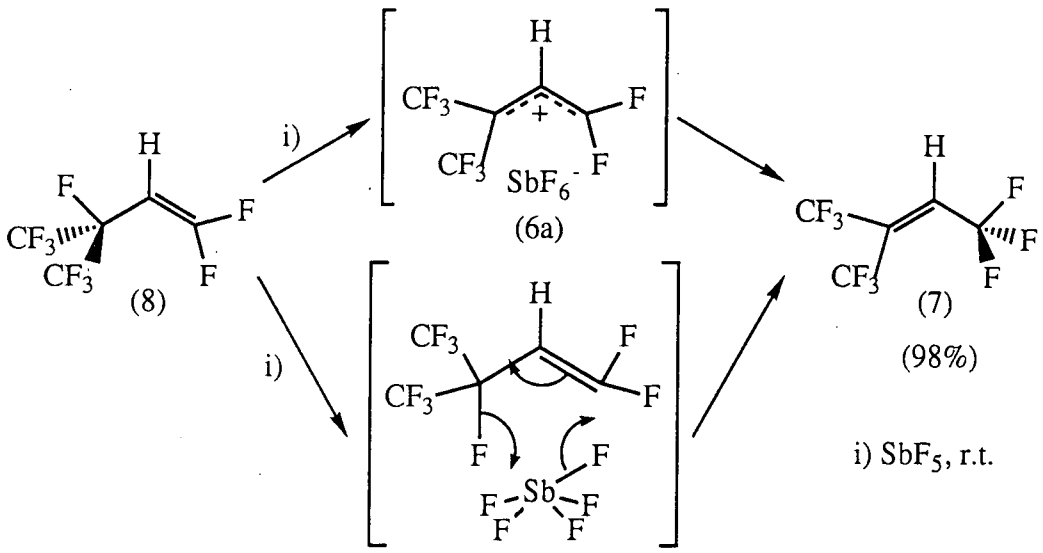
1.B.2 Mono-cations.

Quite surprisingly, reaction of antimony pentafluoride with model compound (6) did not give the corresponding cation (6a), and heating to 120°C was required to induce dehydrofluorination and obtain the corresponding alkene (7).



[5]

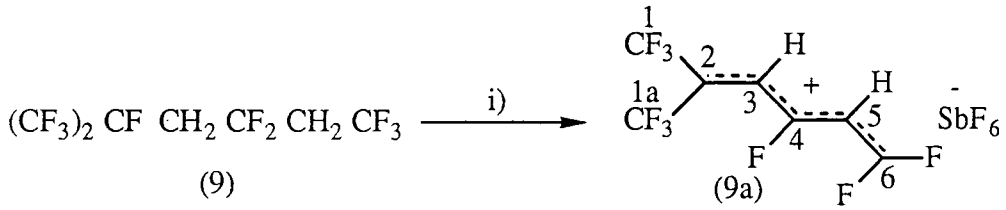
In addition, isomerisation of alkene (8) to (7) also occurred in this medium at room temperature [6], indicating that (7) is obtained under thermodynamic control, because, generally, those isomers most substituted at the double bond by perfluoroalkyl groups rather than fluorine, are the most stable.[9] This stems from the greater resultant electron-withdrawing ability of perfluoroalkyl groups compared to fluorine atoms, because the latter can induce Iπ-repulsion by interaction of the non-bonded electron-pairs with the π electrons of the double bond. This argument may account for the fact that the preferred path for dehydrofluorination of (6) leads to (7), where no fluorine is at the double bond. However, so far, we have not been able to ascertain whether alkene (7) is obtained directly from (6) by abstraction of the fluorine at the tertiary carbon or via formation of (8) followed by rapid isomerisation. Also, we are not sure whether isomerisation of (8) proceeds via formation of the allyl cation (6a) or via formation of the cyclic transition state (6b).



(8) (6a) (6b) (7) (98%)

[6]

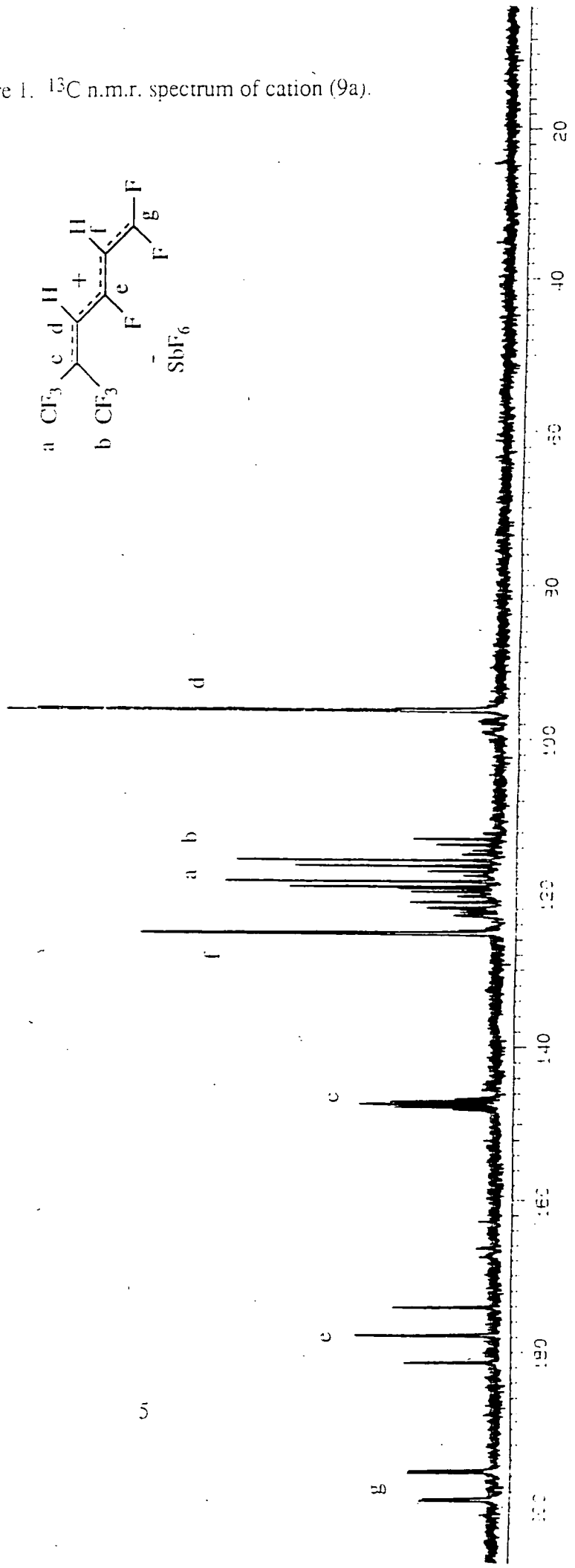
However, when compound (9) was dissolved in antimony pentafluoride at room temperature, and the system allowed to stand, then the ^{13}C n.m.r. spectrum of the solution showed that, not only had elimination occurred to give a conjugated system, but a stable carbocation (9a) was produced! This is a remarkable system in that the conjugation is extended to C-2, a position adjacent to two trifluoromethyl groups, which would normally be considered to be strongly destabilising in their effect on a carbocation centre[9].



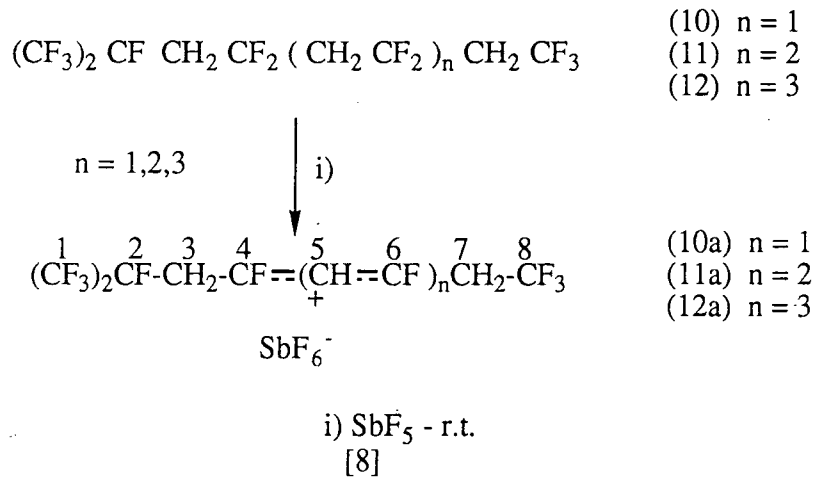
[7]

Furthermore, unlike other systems described hereafter, the conjugation is also extended to include a terminal difluoromethylene, which appeared in the ^{19}F n.m.r. spectrum as a pseudo AB system ν_a at +34.7, ν_b at +35.3 ppm J = 274 Hz, complicated by additional coupling with the fluorine at C-4 and the proton at C-5. These coupling constants depend on the conformation and were measured as $J_{Fa\text{-}Fc}$ = 62.8 Hz, $J_{Fb\text{-}Fc}$ = 142.2 Hz, $J_{Fa\text{-}Hd}$ = 0 Hz, $J_{Fb\text{-}Hd}$ = 17.6 Hz. The vinylic fluorine at C-4, appeared at ca. +16 ppm and these three signals are obviously massively deshielded from the corresponding positions in the starting material. The ^{13}C n.m.r. spectrum for (9a) is also very revealing because the splitting due to spin-spin coupling and their magnitude are consistent with the assignments (Figure 1). The absence of fluorine at C-2 and the large deshielding from the corresponding signal in the starting material (9), clearly demonstrates that conjugation is extended to this site.

Figure 1. ^{13}C n.m.r. spectrum of cation (9a).



We have also established that a regular series of ions (10a)-(12a) can be generated from the series of precursors (10)-(12), and the ions have increasing conjugation in the series. N.m.r. data for ions (10a)-(12a) are given in the appropriate section.



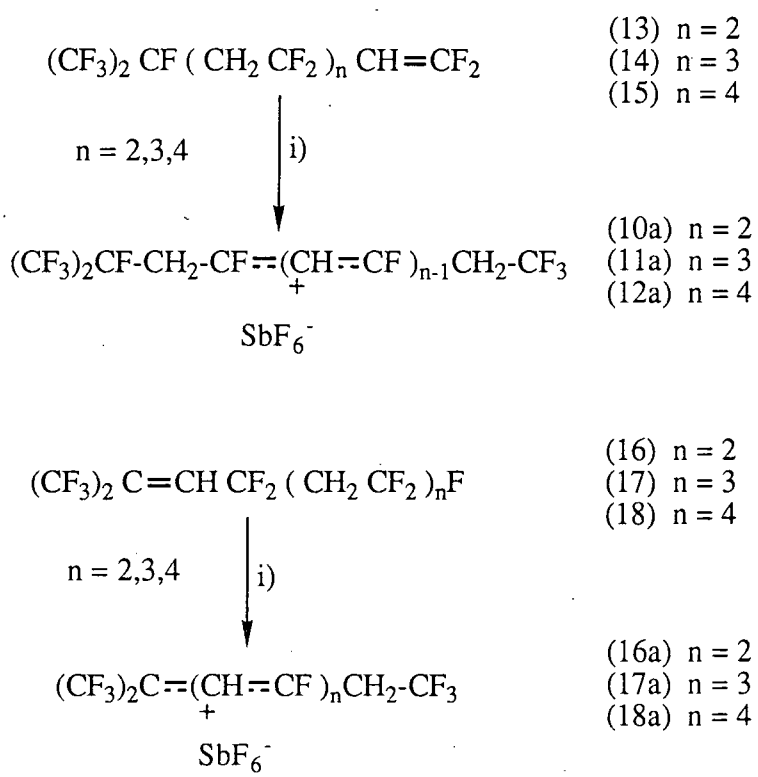
i) SbF_5 - r.t.
[8]

The chemical shift range for these ions is dramatically wide, from -182 ppm, for the tertiary fluorine, to +58 ppm for the fluorine atoms bonded at the charged sites (C-4 and C-6). Thus, there is a massive down-field shift for the fluorines at the charged sites compared to the fluorines at the more remote positions, whose shifts are very similar to those for the neutral precursor (10). The same effects are reflected in the ^{13}C n.m.r. data.

An up-field trend for the ^{19}F and ^{13}C chemical shifts for the charged sites is observed in comparing data for ions (10a)-(12a); ^{19}F n.m.r. chemical shifts have range of +8 to 0 ppm for (10a) and -13 to -30 ppm for (12a) and the ^{13}C n.m.r. shows peaks at 190 and 195 ppm for (11a) and 179, 184, 186, and 191 ppm for (12a). These trends are, of course, understandable as the charge is delocalised over a greater number of carbon atoms. Indeed, as we would expect, the magnitude of the de-shielding falls off with increasing delocalisation of the charge.

Furthermore, there is an extremely interesting contrast between ion (9a) and the series (10a) - (12a) because, in the latter, there is clearly some potential for further extension of the conjugation, as exists in (9a). Instead, however, each of the cations (10a)-(12a) presents a conjugated system terminated at each end by a methylene group, which also separates the destabilising perfluoroalkyl groups from the charged system. It is possible to conclude, therefore, that systems (10a)-(12a) provide a relatively deep energy well and no such analogous system is available for any ion derived from (9). In a further investigation of this point, we used two series of unsaturated precursors, (13)-(15) and (16)-(18) in attempts to extend the conjugation beyond that observed in (10a)-(12a). The series (13)-(15), gave only the ions (10a)-(12a), which were obtained from the saturated precursors (10)-(12). However, systems (16)-(18) gave a new series of ions (16a)-(18a) where the conjugation is extended to include the position attached to

the trifluoromethyl groups (destabilising). Thus, we have a puzzling series of apparent contradictions, which we are not wholly able to resolve on the results available. Nevertheless, the latter result demonstrates that there is a kinetic barrier, at some stage, to extending the conjugation in ions (10a)-(12a) to that observed in (16a)-(18a), and it seems clear that the most difficult step is the last elimination of hydrogen fluoride. We have demonstrated that the conversion of terminal olefins such as (8) into the internal olefin (7) in presence of antimony pentafluoride occurs rapidly and therefore, we would expect (13)-(15) to isomerise to give the internal olefins, which would then react further with antimony pentafluoride similarly to (10)-(12). Conversely, conversion of (16)-(18) to the corresponding isomers with the double bond at C-3 does not occur, thus explaining the formation of ions (16a)-(18a). Furthermore, the fact that ions (16a)-(18a) are not formed from the saturated precursors (10)-(12), probably finds its explanation in that the acidity of the medium diminishes as the hydrogen fluoride content of antimony pentafluoride increases.[10]



i) SbF_5 - r.t.

[9]

1.B.3 Di-cations.

As a natural extension to these studies, we attempted the generation of di-cations, with some surprising results. We showed earlier that most saturated model compounds (10)-(12) tend to give carbocations flanked by two methylene groups. As a consequence, we thought we could get di-cations simply by putting together two of these elemental structures. Thus, reaction of the couple precursor (19) with antimony pentafluoride gave an ion that was easily assigned as a di-allyl-di-cation (19a).

$$(CF_3)_2CF(CH_2CF_2)_3\text{-}(CF_2CH_2)_3CF(CF_3)_2 \quad (19)$$

$$\downarrow \text{i)}$$

$$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{=}CFCH_2CF_2\text{-}\ CF_2CH_2CF{=}\overset{+}{C}H{=}CFCH_2CF(CF_3)_2$$

$$SbF_6^- \qquad\qquad SbF_6^-$$

(19a)

i) SbF_5, r.t.
[10]

The ^{13}C n.m.r. spectrum (Figure 2) clearly shows that we are dealing with a symmetric system, where the signal of the carbons bearing the positive charge, and the fluorines at the charged sites are shifted up-frequency.

Apsey[8] reported about the generation of a di-cation from precursor (20). Here, remarkably, the data quite clearly point to a contiguous di-allyl-di-cation of structure (20a) and we are unaware of any analogous ion described in the literature. The structure (20a) follows essentially from its relative simplicity and hence symmetry. Only two low-field vinylic fluorine signals are observed, and there is only one set of signals for the perfluoroisopropyl groups; the same symmetry is reflected in the ^{13}C spectrum (Figure 3). Again, the magnitude of the deshielding, which is larger than in (19a), clearly demonstrates the carbocation character of this species, consisting with a structure showing two positive charges delocalised over six carbon atoms.

$$(CF_3)_2CF(CH_2CF_2)_2\text{-}(CF_2CH_2)_2CF(CF_3)_2 \quad (20)$$

$$\downarrow \text{i)}$$

$$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{=}CF{=}CF{=}\overset{+}{C}H{=}CFCH_2CF(CF_3)_2$$

$$SbF_6^- \qquad\qquad SbF_6^-$$

(20a)

i) SbF_5, r.t.
[11]

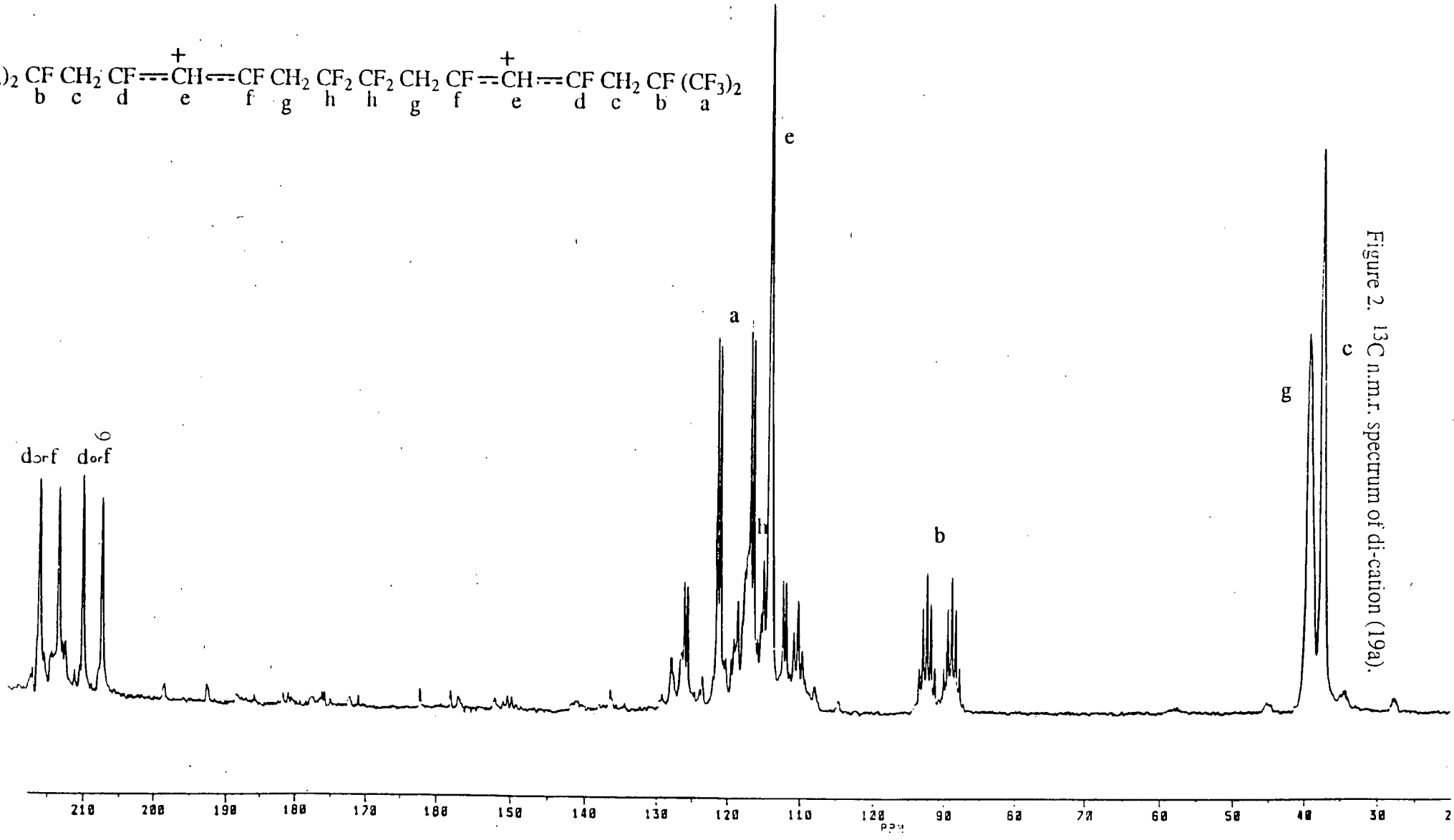


Figure 2. ^{13}C n.m.r. spectrum of di-cation (19a).

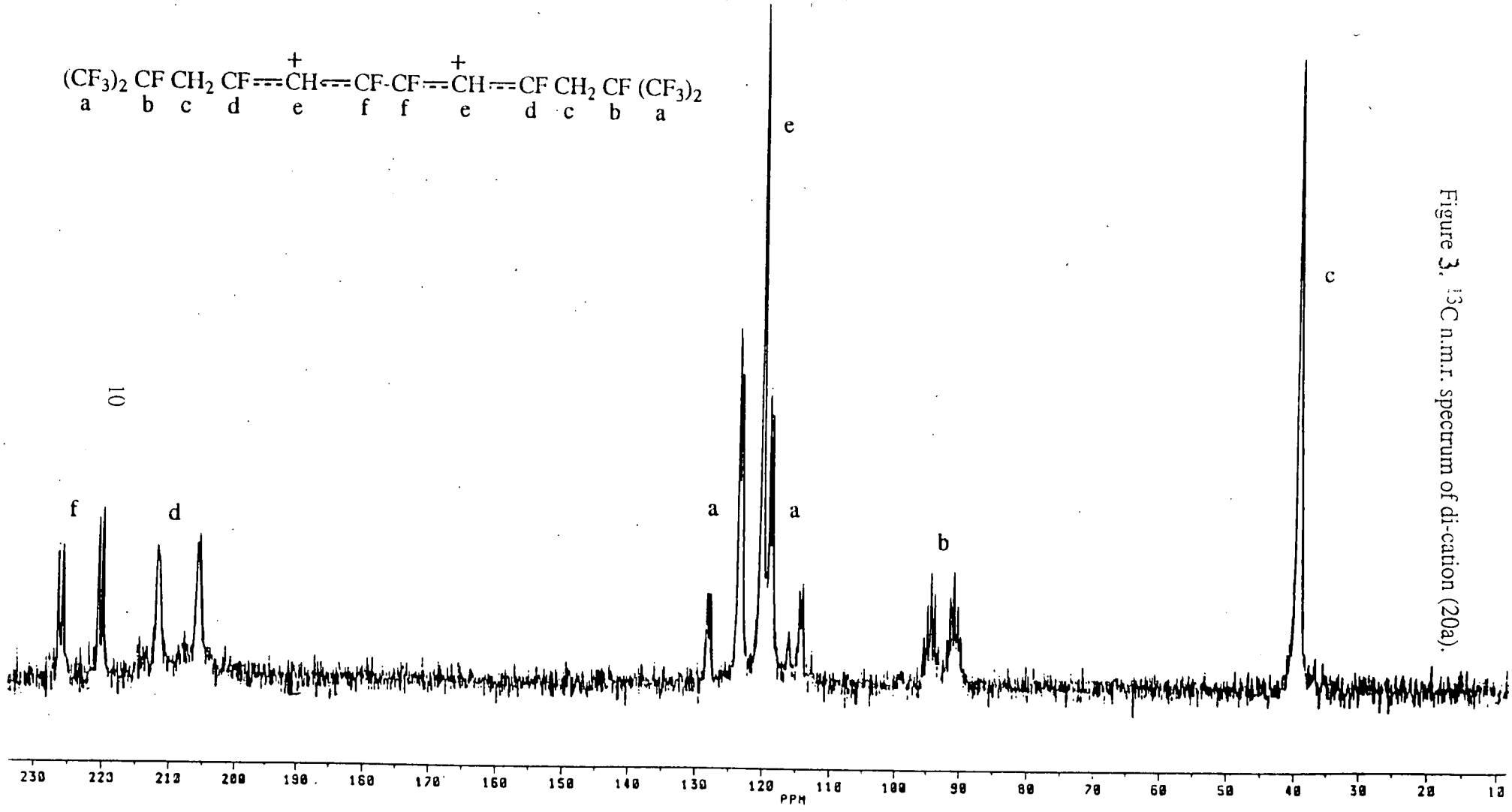
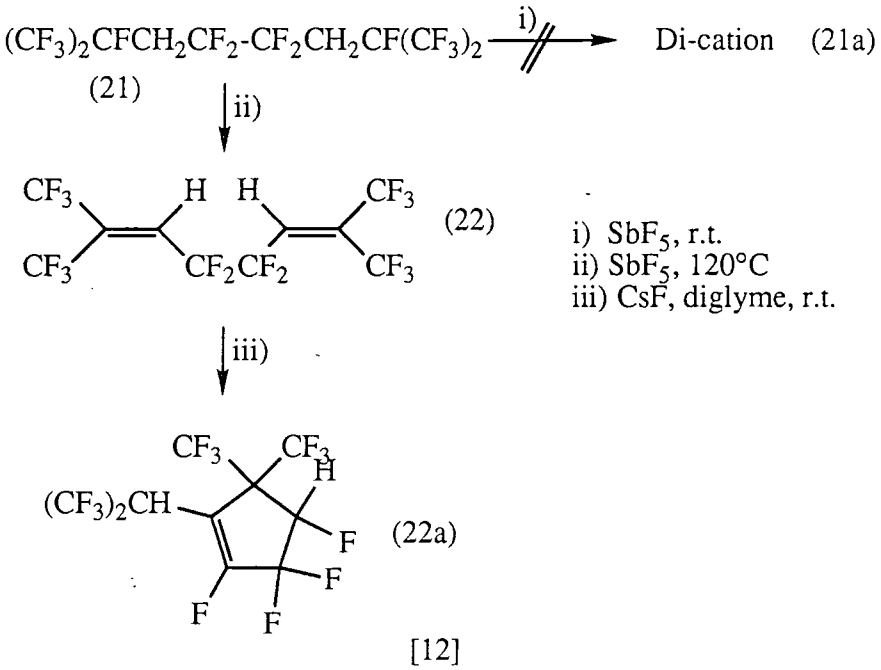


Figure 3. ^{13}C n.m.r. spectrum of di-cation (20a).

The ^{13}C n.m.r. spectrum reported by Apsey (Figure 3) is very neat and of high quality, which we did not reproduce exactly. Carbocation (20a) was obtained, but in a more complicated mixture. We noted that the ^{13}C n.m.r. spectrum changed with the history of antimony pentafluoride, whose content in hydrofluoric acid is a variable very difficult to control.

As for its equivalent non-coupled product (8), antimony pentafluoride did not react with precursor (21) at room temperature, nevertheless formation of a very interesting non conjugated diene was observed when the reaction was carried out at 120°C.



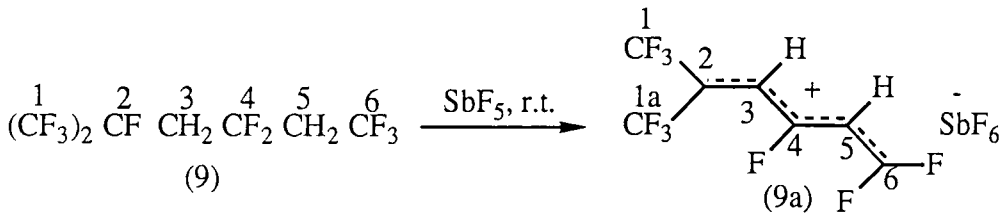
[12]

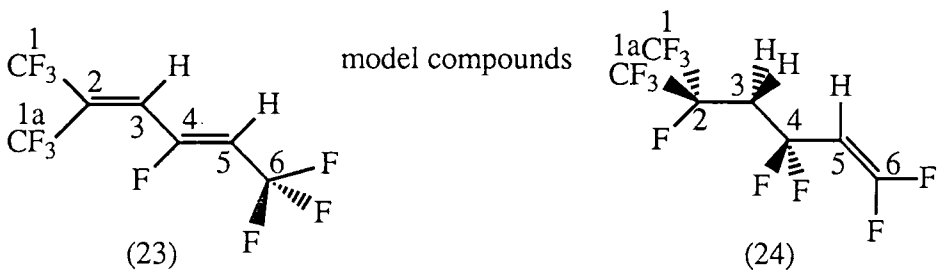
Formation of (22) is particularly significant because it is not possible to isolate this compound in a base-induced process[8], where (22a) is formed instead. Nevertheless it has been demonstrated[8] that the isolated di-ene (22) undergoes transformation to (22a) extremely rapidly in the presence of fluoride ion.

1.B.4 Determination of re-hybridisation and charge effects.

At this point we wanted to investigate the effect of both re-hybridisation and charge on ^{13}C, ^{19}F, ^{1}H n.m.r. chemical shifts. To this end, we considered the saturated precursor (9) and its ultimate conversion to (9a) and attempted to separate the effects of re-hybridisation and formation of charge, at each of the positions in (9) and (9a). We have achieved this by a process of comparison with model compounds, which may be considered as "intermediate" in the conversion of (9) to (9a). Thus, comparison of the n.m.r. data for di-ene (23) and precursor (9) allows us to establish the effects of re-hybridisation at positions 2, 3, and 4 and a comparison of mono-ene (24) with (9) allows the effect of re-hybridisation to be established for positions 5 and 6, for ^{13}C, ^{1}H, ^{19}F spectra, as appropriate. Furthermore, comparisons of (23) and (24) with the

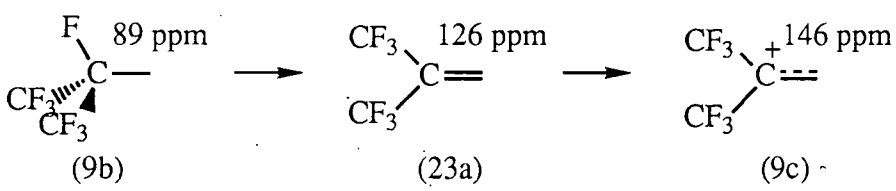
carbocation (9a), then allows us to establish the effects of charge, on chemical shift values, for position 2-6.





[13]

For example a comparison of ^{13}C chemical shifts is illustrated by the sequence (9b), (23a), (9c). Proceeding from (9b) to (23a) leads to a chemical shift change of +35 ppm due to re-hybridisation, and proceeding from (23a) to the carbocation (9c) gives a change of +20 ppm due to formation of charge. Furthermore, we have summarised similar comparisons for other positions and these data are contained in Table 1. For ^{13}C chemical shifts, it is quite clear that the effect of charge is actually less important than the effect of re-hybridisation, and this is in complete contrast to the analogous observations for hydrocarbon systems, where the effect of charge is considerably greater.[11]



Re-hybridisation Δ =+37 ppm Charge Δ = +20 ppm

Effect on ^{13}C chemical shifts	sp^3 -> sp^2 re-hybridisation (ppm)	charge (ppm)
2 CF- to C=	+37	+20
4 CF_2- to CF=	+41	+42
6 -CF_3 to =CF_2	+36	+20
3,5 CH_2- to CH=	+70 - +90	-5

Table 1. Incremental effects on ^{13}C chemical shifts, values for re-hybridisation and charge

Table 2 shows the corresponding incremental effects on fluorine chemical shifts and here the trend is completely reversed from the ^{13}C data shown in Table 1. We see gradual deshielding of all sites but, remarkably, the values for re-hybridisation are much less than for introducing a charge; the latter are very large indeed and thus, clearly indicating that much of the charge in the carbocation (9a) actually resides on fluorines, as illustrated by (9d), (9e).

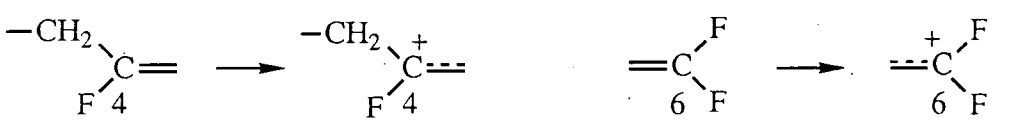
Effect on ^{19}F chemical shifts	sp^3 -> sp^2 re-hybridisation (ppm)	charge (ppm)
4 CF_2- to CF=	+16	+100
6 CF_3 to =CF_2	+13	+110

(9d) (9e)

Table 2. Incremental effects on ^{19}F chemical shifts, values for re-hybridisation and charge

Analogous effects on ^{1}H chemical shifts have also been deduced; for re-hybridisation, a value of ca. 4 ppm is observed, but essentially no increment associated with charge is evident!. Furthermore, we note from the ^{13}C chemical shifts reported in Table 1, that C-3 and C-5 undergo only small changes associated with the formation of charge, and as a consequence, these two observations taken together are understandable because the hydrogenated sites 3 and 5 are at the nodal points in cation (9a) and therefore, they would be associated with much less charge, if any, than the other sites 2,4, and 6.

Analysis of C-F coupling constant was also of considerable interest. We found that very little change in the values occurred on re-hybridisation, nevertheless, there was a remarkable increase in going from sp^2 neutral to sp^2 charged carbon atoms for both internal and terminal C-F bonds (Δ ca. 70-80 Hz)[14].



J_{C-F} = 276 Hz J_{C-F} = 354 Hz J_{C-F} = 290 Hz J_{C-F} = 365 Hz

(23) (9b) (24) (9b)

[14]

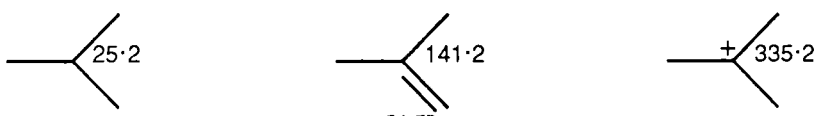
This significant increase in coupling constants has also to be associated with bond shortening due to back donation (9d), (9e), which provides further evidence for the stabilising effect of fluorine at charged sites.

1.B.5 Calculations using Olah and Schleyer' s ^{13}C additivity criterion

At this point we asked ourselves whether we could obtain further evidence and information for the conjugated carbocations (9a)-(20a), and, in particular, for the remarkable di-cation (20a), and this lead us to the approach that Olah and Schleyer adopted for hydrogenated systems [12]. They reported that information on the structure of carbocations could be derived using the additivity criterion of ^{13}C chemical shifts. This is merely an empirical approach and consists in taking the sum of the observed chemical shifts for all carbon atoms of a given carbocation and subtracting the sum of all the carbon chemical shifts for the corresponding hydrogenated precursor. Classical carbocations show chemical-shift differences typically of 350 ppm or more, and this value is roughly constant. Deviations from such values are due to a higher coordination at carbon (bridged or non classical structures) displaying differences which are often hundreds of ppm less.

For example, the sum of chemical shift (vs. Me_4Si) for 2-methyl-2-propyl cation is 478 ppm (335.2 ($\delta\ ^{13}C_2$) + 3 x 47.5 ($\delta\ ^{13}C_{1,3,4}$))[11], for 2-methyl-2-methane this sum is 98 ppm[11]. Thus in going from 2-methyl-2-propane to 2-methyl-2-propyl cation, a total deshielding of 478 - 98 = 380 ppm is observed. This total deshielding can be rationalised in the following way [13]: the large 335.2 - 25.2 = 310 ppm change can be attributed partly to sp^3 to sp^2 hybridisation change (116 ppm) and partly to formation of the positive charge (194 ppm).

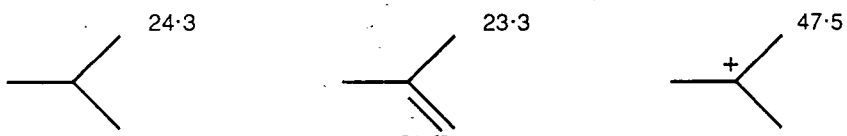
Carbon-13 chemical shifts



[15]

The remaining 380 - 310 = 70 ppm of the total deshielding is then due to charge delocalisation to the remaining carbons.

Carbon-13 chemical shifts



[16]

It is worthwhile noting that for these systems the deshielding due to the charge formation (194 ppm) exceeds that due to re-hybridisation (116 ppm).

It has also been shown carbo-di-cations exhibit values which were double those typical of classical monocations.

The aims of the following calculations are to show how this empirical rule applies to fluorinated systems; what information can be derived by careful analysis of ^{13}C and ^{19}F n.m.r. data; to determine whether in the presence of a di-carbocationic

species the chemical shift difference values are double the one for corresponding monocations. The results are shown in Tables 3-5. In these tables, we have grouped similar carbocations, differing just in the number of carbon atoms involved in the conjugation. Table 3, shows that the difference values ($\Delta\Sigma\delta$) increase with the extent of conjugation, and, as we would expect, the magnitude of the increment falls off with increasing delocalisation, and this is consistent with the effect of one positive charge being spread over an increasing number of centres.

CARBOCATIONS	$\Sigma_i \delta_i$ ^{13}C	PRECURSORS	$\Sigma_i \delta_i$ ^{13}C	$\Delta\Sigma\delta$
$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CFCH_2CF_3$ (10a)	**1053**	$(CF_3)_2CF(CH_2CF_2)_3F$ (10)	**816**	**237**
$(CF_3)_2CFCH_2CF{=}(\overset{+}{C}H{-}CF)_2CH_2CF_3$ (11a)	**1322**	$(CF_3)_2CF(CH_2CF_2)_4F$ (11)	**970**	**352**
$(CF_3)_2CFCH_2CF{=}(\overset{+}{C}H{-}CF)_3CH_2CF_3$ (12a)	**1582**	$(CF_3)_2CF(CH_2CF_2)_5F$ (12)	**1145**	**437**

Table 3. ^{13}C chemical shifts difference values for mono-cations.

CARBOCATIONS	$\Sigma_i \delta_i$ ^{13}C	PRECURSORS	$\Sigma_i \delta_i$ ^{13}C	$\Delta\Sigma\delta$
$(CF_3)_2C{=}(\overset{+}{C}H{-}CF)_2CH_2CF_3$ (16a)	**1199**	$(CF_3)_2CF(CH_2CF_2)_3F$ (16)	**816**	**383**
$(CF_3)_2C{=}(\overset{+}{C}H{-}CF)_3CH_2CF_3$ (17a)	**1462**	$(CF_3)_2CF(CH_2CF_2)_4F$ (17)	**970**	**492**
$(CF_3)_2C{=}(\overset{+}{C}H{-}CF)_4CH_2CF_3$ (18a)	**1710**	$(CF_3)_2CF(CH_2CF_2)_5F$ (18)	**1145**	**565**

Table 4. ^{13}C chemical shifts difference values for mono-cations.

However, we were particularly interested in the di-cations shown in Table 5; it is extremely interesting that di-cation (19a) ($\Delta\Sigma\delta$ = 499 ppm) shows an incremental value almost exactly twice the value shown for mono-cation (10a) ($\Delta\Sigma\delta$ = 237 ppm). Now, if we were to bring together the two allylic cations in (19a) so to extend the conjugation of the two positive charges over 6 carbon atoms, as for di-cation (20a), we would expect a higher incremental value than that shown for (19a), which is what we see ($\Delta\Sigma\delta$ = 596 ppm). Furthermore, this is quite consistent with the trend shown in Tables 3 and 4 which clearly indicate that as we extend the length of the conjugated system, then the incremental value gradually increases. Thus, all of the data in Table 5 are consistent with our earlier characterisation of di-cation (20a).

CARBOCATIONS	$\Sigma_i \delta_i$ ^{13}C	PRECURSORS	$\Sigma_i \delta_i$ ^{13}C	$\Delta\Sigma\delta$
$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CFCH_2CF_3$ (10a)	**1053**	$(CF_3)_2CF(CH_2CF_2)_3F$ (10)	**816**	**237**
$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CF_2CH_2CF_2$ $(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CF_2CH_2CF_2$ (19a)	**2113**	$[(CF_3)_2CF(CH_2CF_2)_3]_2$ (19)	**1614**	**499**
$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CF$ $(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CF$ (20a)	**1879**	$[(CF_3)_2CF(CH_2CF_2)_2]_2$ (20)	**1283**	**596**

Table 5. ^{13}C chemical shifts difference values for a mono-cation and di-cations.

1.B.6 Calculations using the ^{19}F additivity criterion.

At this point we asked ourselves whether we could obtain information on the conjugated cations using a new approach, based on the additivity of the ^{19}F chemical shifts.

In the first place we examined the range of the ^{19}F chemical shifts in cations (9a)-(12a), (20a) (Table 6), and compared it to the trend shown in Tables 3-5. It is clear that the decreasing of the magnitude of the increments ($\Delta\Sigma\delta$) is accompanied by a parallel decreasing of the charge effect for each fluorine atom involved in the delocalisation.

Type of carbocation	^{19}F chemical shifts (range ppm)
(10a) 1+ over 3 carbons	+60
(9a) 1+ over 5 carbons	(+ 45) - (+10)
(11a) 1+ over 5 carbons	0 - (-10)
(12a) 1+ over 7 carbons	(-10) - (-30)
(20a) 2+ over 6 carbons	+40

Table 6. ^{19}F chemical shift range for some cations

However, this consideration does not enable us to determine the overall effect on the ^{19}F chemical shifts in going from the saturated precursors to the corresponding cations. Thus, we added up all the observed chemical shifts for all the fluorine atoms of a given cabocation and subtracted the sum of the chemical shifts for the same number of

fluorine atoms in the respective positions of the corresponding precursor (Tables 7-8). We found that it is very important to limit addition of the fluorine chemical shifts for the starting material to the number of fluorine atoms present in the corresponding cation. For instance, we considered the conversion of the saturated precursor (9) into its final conversion (9a) via the formation of "intermediate" (23), with the intention of separating the total effects of re-hybridisation and development of charge. The sum of all ^{19}F chemical shifts for precursor (9) is -1008 ppm, for (23) this sum is -701 ppm and for (9a) this sum is -315 ppm, thus in going from (9) to (9a) a total deshielding of -315 - (-1008) = 693 ppm is observed of which -701 - (-1008) = 307 ppm are due to re-hybridisation and -315 - (-701) = 386 ppm are due to charge formation. Conversely, the sum of the ^{19}F chemical shifts for precursor (9) limited to the number of fluorine atoms present in ion (9a) is -671 ppm, and for (23) this sum is -635 ppm. Therefore, in going from (9) to (9a) a total deshielding of -315 - (-671) = 356 ppm is observed of which only -635 - (-671) = 36 ppm are due to re-hybridisation and -315 - (-635) = 320 ppm to the development of charge. Therefore, redundancy due to the two additional fluorine atoms has to be eliminated to allow us to determine the real effect of re-hybridisation and charge in agreement with what was shown in section 1.4.A.

The results of the calculations are shown in Tables 7-8. In this tables we have gathered similar carbocations, differing just in the number of carbon atoms involved in the delocalisation of the charge. Tables 7 shows that the difference values ($\Delta\Sigma\delta$) decreases with the extent of conjugation and this is consistent with a minor interaction of the fluorine p orbitals with the extended π^* orbitals in an increasing conjugated system.

CARBOCATIONS	$\Sigma_i \delta_i$ ^{19}F	PRECURSORS	$\Sigma_i \delta_i$ ^{19}F	$\Delta\Sigma\delta$
$(CF_3)_2CFCH_2CF{=}{=}\overset{+}{C}H{=}{=}CFCH_2CF_3$ (10a)	**-728**	$(CF_3)_2CF(CH_2CF_2)_3F$ (10)	**-1029**	**301**
$(CF_3)_2CFCH_2CF{=}{=}(\overset{+}{C}H{=}CF)_2CH_2CF_3$ (11a)	**-862**	$(CF_3)_2CF(CH_2CF_2)_4F$ (11)	**-1123**	**261**
$(CF_3)_2CFCH_2CF{=}{=}(\overset{+}{C}H{=}CF)_3CH_2CF_3$ (12a)	**-931**	$(CF_3)_2CF(CH_2CF_2)_5F$ (12)	**-1219**	**288**

Table 7. ^{19}F chemical shifts difference values for mono-cations.

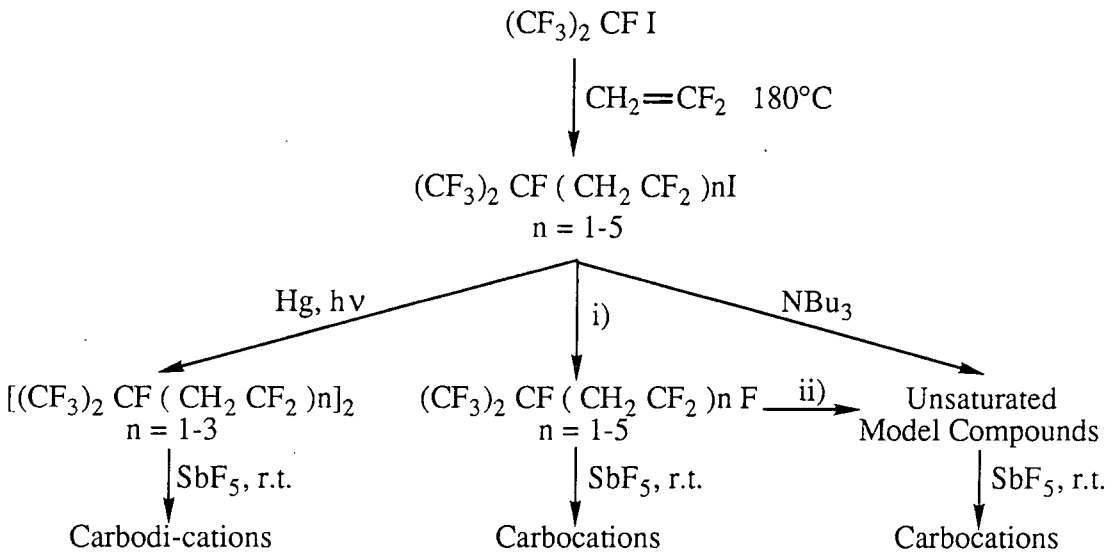
Table 8 shows for di-cation (19a) an incremental value which is almost twice the value for mono-cation (10a), and thus, following the trend shown in Table 7, when the conjugation of the two positive charges is extended over 6 carbon atoms (di-cation (20a)) the incremental value decreases.

CARBOCATIONS	$\Sigma_i \delta_i$ ^{19}F	PRECURSORS	$\Sigma_i \delta_i$ ^{19}F	$\Delta\Sigma\delta$
$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CFCH_2CF_3$ (10a)	**-728**	$(CF_3)_2CF(CH_2CF_2)_3F$ (10)	**-1029**	**301**
$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CF_2CH_2CF_2$ (19a)	**-1496**	$[(CF_3)_2CF(CH_2CF_2)_3]_2$ (19)	**-2124**	**628**
$(CF_3)_2CFCH_2CF{=}\overset{+}{C}H{-}CF$ (20a)	**-1148**	$[(CF_3)_2CF(CH_2CF_2)_2]_2$ (20)	**-1722**	**574**

Table 8. ^{19}F chemical shifts difference values for a mono-cation and di-cations.

1.C Synthesis of fluorinated model compounds.

Model compounds as precursors for the generation of carbocations were synthesised by telomerisation of vinylidene fluoride using heptafluoroisopropyl iodide as a telogen. The telomers obtained were isolated by fractional distillation under reduced pressure, and further treated to achieve coupling and dehydrohalogenation, as shown in Scheme 1.



i) SbF_5, R-113, 0°C ii) CsF, Sulpholane, 130°C

Scheme 1. Synthesis of model compounds as precursors for the carbocations

1.C.1 Synthesis of fluoroalkyl iodides

1.C.1.a Heptafluoro-2-iodopropane

Heptafluoro-2-iodopropane (25) was synthesised by reacting hexafluoropropene with a mixture of iodine and iodine pentafluoride, using proportions equivalent to IF stoichiometry.[8].

$$CF_3\text{-}CF{=}CF_2 + IF_5 + I_2 \xrightarrow{\text{i)}} (CF_3)_2\,CFI \quad (100\%)$$
(25)

i) 150°C, 24 hours
[17]

The reaction was carried out using a stainless steel autoclave under autogenous pressure and it proceeded quantitatively; *caution in scaling up the reaction must be taken because of the exothermicity of the reaction!*

1.C.1 b Telomerisation of vinylidene fluoride using perfluoroisopropyl iodide as telogen.

Heptafluoro-2-iodopropane is a source of tertiary fluorinated radicals at carbon, at elevated temperature (180°C), homolytic cleavage of the carbon-iodine bond occurs and the so formed radical undergoes successive additions of vinylidene fluoride (26) to give a mixture of telomer iodides of the type $(CF_3)_2CF(CH_2CF_2)_nI$ (27) where n = 1-5, with the respective isolated yields of n = 1, (27a) 30%; n = 2, (27b) 44%; n = 3, (27c) 7%; n = 4, (27d) 4%; n = 5 (27e) traces[8].

$$\underset{(25)}{(CF_3)_2CFI} + \underset{(26)}{CH_2=CF_2} \xrightarrow{i)} \underset{\substack{(27a)\ n=1;\ (27b)\ n=2;\ (27c)\ n=3;\\ (27d)\ n=4;\ (27e)\ n=5.}}{(CF_3)_2CF(CH_2CF_2)nI} \quad (100\%\ conv.)$$

i) 180°C, 24 hours

[18]

The mechanism for the telomerisation reaction is outlined in Scheme 2; the free-radical addition of the propagating fluoroalkyl radical (25a) to vinylidene fluoride proceeds preferentially at the methylene unit, and after addition of "n" units (25b), chain transfer to the telogen (25) occurs to terminate telomers and start a new chain. Since heptafluoro-2-iodopropane is a very efficient chain transfer agent, chains containing more than 5 vinylidene fluoride units are not found among the products of telomerisation when the heptafluoroisopropyl iodide (25) / vinylidene fluoride (26) molar ratio is approximately 1 / 2.. On the contrary, it was noticed that when vinylidene fluoride (26) was added in a larger excess, then, telomers with higher molecular weight were obtained.

Initiation

$$\underset{(25)}{(CF_3)_2CFI} \xrightarrow{\Delta} \underset{(25a)}{(CF_3)_2CF^{\cdot}} + I^{\cdot}$$

Propagation

$$\underset{(25a)}{(CF_3)_2CF^{\cdot}} + (n+1)\ CH_2=CF_2 \longrightarrow \underset{(25b)}{(CF_3)_2CF(CH_2CF_2)_nCH_2CF_2^{\cdot}}$$

Chain Transfer

$$\underset{(25b)}{(CF_3)_2CF(CH_2CF_2)_nCH_2CF_2^{\cdot}} + \underset{(25)}{(CF_3)_2CFI} \longrightarrow \underset{(27)}{(CF_3)_2CF(CH_2CF_2)_nCH_2CF_2I} + \underset{(25a)}{(CF_3)_2CF^{\cdot}}$$

Scheme 2. Suggested mechanism for the telomerisation of vinylidene fluoride, using heptafluoroisopropyl iodide as a telogen

However, the influence of the perfluoroisopropyl iodide/vinylidene fluoride molar ratio on the chain length of telomers formed, has already been investigated.[14,15]

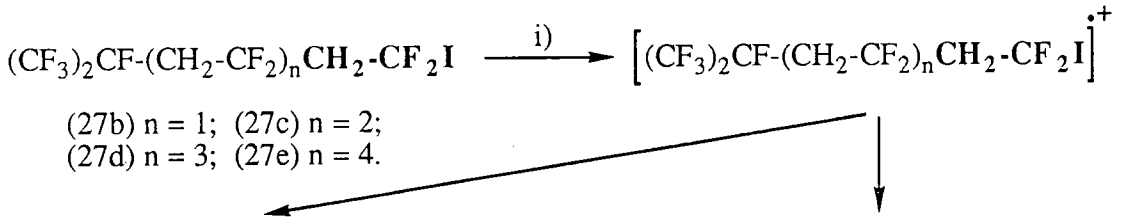
Of course, the preferred addition of the propagating radical is at the methylene site because the so formed difluoromethylene radical (CF_2·) is more stable than the correspondent methylene radical (CH_2·). This is because the difluoromethyl radicals (25b) are stabilised by mesomeric effect (+M) of fluorine which is able to conjugate its non bonded electron pair into the p orbital of carbon, containing an unpaired electron.

However, careful GC/MS analysis showed that every telomer where n>1 (27b)-(27e) was formed together with their structural isomers(27b')-(27e') in a ca. 10:1 ratio, but, remarkably, only the end groups showed this regio inversion.

$(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_n\mathbf{CH_2\text{-}CF_2I}$ $\quad$ $(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_n\mathbf{CF_2\text{-}CH_2I}$

(27b) n = 1; (27c) n = 2; (27d) n = 3; (27e) n = 4. $\quad$ (27b') n = 1; (27c') n = 2; (27d') n = 3; (27e') n = 4.

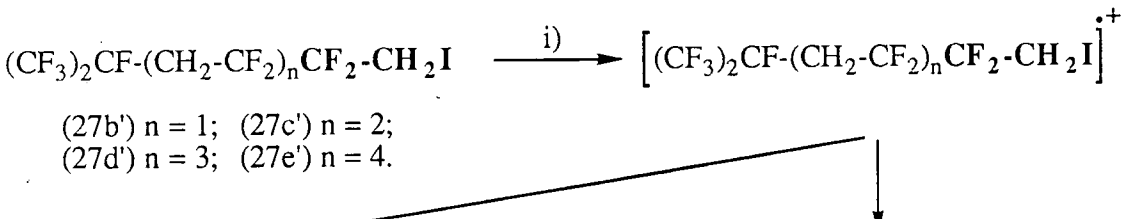
[19]



(25b) $(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_nCH_2\text{-}CF_2$· + I^+ (m/z^+ 127)

(25b') $(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_nCH_2\text{-}CF_2^+$ (M-127) + I·

[20]



(25b) $(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_{n-1}CH_2\text{-}CF_2$· + I-$CH_2$-$CF_2^+$ (m/z^+ 192) (28)

(25b') $(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_{n-1}CH_2\text{-}CF_2^+$ (M-192) + I-CH_2-CF_2·

[21]

i) ionisation using an electron beam

Scheme 3. Typical GC/MS fragmentation pattern of regio-isomers (27).

Evidence was obtained from the different fragmentation patterns. Typically, the preferred fragmentation (Scheme 3) for (27b)-(27e) was characterised by loss of iodine (m/z^+ 127) [20] and subsequent loss of vinylidene fluoride to give peaks at interval of 64 (CH_2CF_2) units. On the contrary, telomers (27b')-(27e') showed intense peaks at m/z^+ M-192 and m/z^+ 192 (CF_2-$CH_2I^{\cdot+}$) [21] associated with the cleavage of the

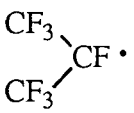
R-$\mathbf{CF_2}$-$\mathbf{CF_2}$-CH_2I bond. In both circumstances the fragmentation of the molecular ion is consistent with the formation of the most stable cations (25b') and (28).

Since there is a significant separation on a GC column between the two terminal regio-isomers (detected as two sharp peaks), we would have anticipated a very complex chromatogram if such regio-isomerism occurred along the chain. However for telomers (27) where n > 2 there was no indication to suggest the presence of other additional structural isomers. This poses the question of why regio-isomerism should occur only at the end of the chains and we believe that this is connected to the presence of the difluoromethylene-iodide ($-CF_2I$) and methylene-iodide groups ($-CH_2I$) at the end of the telomer chain (29), (30). The former is known to be much more reactive in telomerisation reactions, and therefore, the propagation of the telomerisation must cease when a methylene-iodide group is produced.

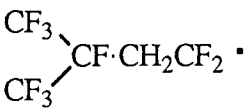
$$\underset{(29)}{-CF_2I} \xrightarrow{CH_2=CF_2} \underset{(29a)}{-CF_2-CH_2-CF_2I} \qquad \underset{(30)}{-CH_2I} \xrightarrow{CH_2=CF_2} \underset{(30a)}{-CH_2-CH_2-CF_2I}$$

[22]

Furthermore the presence of only one structural isomer for the telomer (27a) suggested that radical (25a) was more selective (and therefore less reactive) than radical (25b) n =1.



(25a)



(25b) n = 1

[23]

1.C.2 Fluorodeiodination of the telomer iodides.

Many reagents have been reported to effect the fluorodeiodination of fluoroalkyl iodides[15-19]. They include the use of HF, CoF_3, Hg_2F_2, SbF_3Cl_2. Among those antimony pentafluoride (SbF_5) was the most convenient to use at room temperature in an inert solvent. Reactions were then carried out with an excess of SbF_5 at temperatures below 0° C in 1,1,2-trichloro-1,2,2-trifluoroetane (R-113).

$$\underset{\text{(27a)-(27e) n = 0-4}}{(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_nCH_2\text{-}CF_2I} \xrightarrow{\text{i)}} \underset{\text{(6) n = 0; (9)-(12) n = 1-4}}{(CF_3)_2CF\text{-}(CH_2\text{-}CF_2)_nCH_2\text{-}CF_3}$$

i) SbF_5, r.t., R- 113 yields = 60 - 80%

[24]

Temperature was a crucial parameter for these reactions: in fact above 10°C the model compounds are underwent further reactions with antimony pentafluoride to give unsaturated products and eventually carbocations. Also, reactions carried out in absence of solvent were very exothermic.

1.C.3 Coupling reaction of telomer iodides.

A relevant amount of work has been published about the coupling of fluoroalkyl iodides which can be achieved either using Mercury and ultra-violet light,[8,16,20,21] or by reaction with zinc in a suitable solvent.[20,22,23]

1.C.3. a Coupling with mercury.

Hydrofluoroalkyl iodide (27a) reacted in presence of mercury and ultra-violet radiation to give the corresponding coupled derivative (21) in high yields, and a mixture of (31) and (8) in comparable amounts (according to GC integration).

$$\underset{(27a)}{(CF_3)_2CFCH_2CF_2I} \xrightarrow{i)} \underset{(21)}{[(CF_3)_2CFCH_2CF_2]_2} \quad (82\%)$$

+

by-products

$$\underset{(31)}{(CF_3)_2CFCH_2CF_2H} + \underset{(8)}{(CF_3)_2CFCH{=}CF_2}$$

i) Hg, h. ν.

[25]

Similar treatment of telomer (27b) led to the formation of the corresponding coupled product (20), but in lower yield. By-products (32) and (24) were also obtained (50%) in comparable amounts (according to GC integration).

$$\underset{(27b)}{(CF_3)_2CF(CH_2CF_2)_2I} \xrightarrow{i)} \underset{(20)}{[(CF_3)_2CF(CH_2CF_2)_2]_2} \quad (42\%)$$

+

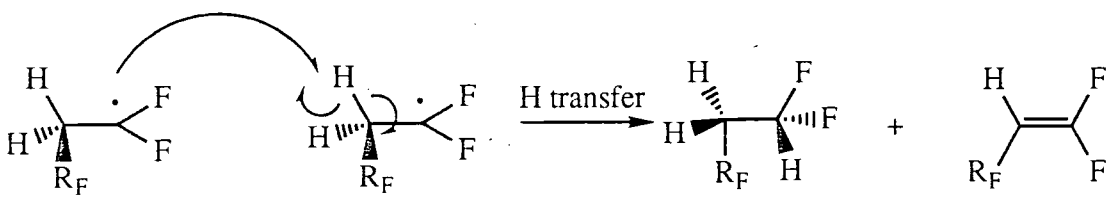
by-products

$$\underset{(32)}{(CF_3)_2CF(CH_2CF_2)_2H} + \underset{(24)}{(CF_3)_2CFCH_2CF_2CH{=}CF_2}$$

i) Hg, h. ν.

[26]

By-products of the two former reactions were probably formed by the disproportionation of the two radicals (25b): the difluoromethylene $CF_2\cdot$ radical underwent intermolecular proton abstraction to give the terminal difluoromethyl group ($-CF_2H$; MS: peak at m/z^+ 51) and the terminal alkene (IR: band at 1750 cm^{-1}).



(25b) (25b) (31) or (32) (8) or (24)

[27]

Trimer (27c) was also coupled in presence of mercury and ultra-violet light to give (19) in relatively low yield, and some by products whose composition was not investigated.

$$(CF_3)_2CF(CH_2CF_2)_3I \xrightarrow{\text{i)}} [(CF_3)_2CF(CH_2CF_2)_3]_2 \quad (45\%)$$
(27c) (19) + by-products

i) Hg, h. ν.
[28]

Agitation of the Carius tubes proved to be fundamental for the success of the reactions. Apparently coupling occurred only when agitation was carried out by keeping the tube in the horizontal position gently rolling along its axis.

1.C.3.b Coupling with zinc.

Some attempts were also made explore alternative routes leading to the coupled derivatives (19)-(21) in higher yields. Reaction of telomer iodide (27a) with activated zinc in acetic anhydride showed to be promising giving the desired coupled product in good yields.

$$(CF_3)_2CFCH_2CF_2I \xrightarrow{\text{i)}} [(CF_3)_2CFCH_2CF_2]_2 \quad (85\%)$$
(27a) (21)

i) Zn, Ac_2O
[29]

Similar treatment of telomer (27b) afforded the product of reduction (32) (10%), the coupled product (20) (58%) and the hydrofluoroalkylmethylketone (33), (32%), derived from alkylation of acetic anhydride (Ac_2O). We believe that zinc induces a single electron transfer reaction (SET), which in some cases proceeds further to give the hydrofluoroalkyl zinc derivative and this, in its turn, alkylates the carboxyl group. Reduction of the iodide occurred primarily, when dioxane was used as a solvent. This seems to indicate that, the greater the ability of the solvent to solvate the organo zinc derivative, the more reduction takes place.

$$(CF_3)_2CF(CH_2CF_2)_2I \xrightarrow{\text{i)}} \begin{cases} (CF_3)CF(CH_2CF_2)_2H & (10\%) \\ \quad (32) & \\ [(CF_3)_2CF(CH_2CF_2)_2]_2 & (58\%) \\ \quad (20) & \\ (CF_3)_2CF(CH_2CF_2)_2C(O)CH_3 & (32\%) \\ \quad (33) & \end{cases}$$
(27b)

i) Zn, Ac_2O
[30]

1.C.4 Synthesis of unsaturated model compounds

1.C.4.a Synthesis of 2-unsaturated derivatives ($(CF_3)_2C=CH-CF_2-$).

Elimination of hydrofluoric acid from saturated fluorohydrocarbon provides a general route to unsaturated model compounds[24,25]. It has been reported that bases such as potassium hydroxide, lithium alkyls, and amines react with the saturated model compounds to give extensive decomposition and tar. This is due to the reaction of the base, which also acts as a nucleophile, with the readily formed fluoro-olefins. In some cases cyclic products of defined structure are also obtained.[8] The use of fluoride ion as a strong base has been well documented in the past[26], and more recently it has been proved[8] that heating saturated model compounds in presence of caesium fluoride gave good yields of the corresponding alkenes derived from the dehydrofluorination at the tertiary carbon.

Therefore, we followed this procedure to obtain model compounds containing an unsaturated site at the position adjacent to the two trifluoromethyl groups.

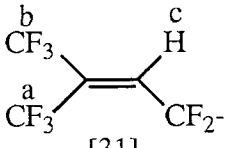
$$(CF_3)CF(CH_2CF_2)_nF \xrightarrow{\text{i)}} (CF_3)_2C=CH(CF_2CH_2)_{n-1}CF_3$$

(6) n = 1	(7) n = 1
(9) n = 2	(24a) n = 2
(10) n = 3	(16) n = 3
(11) n = 4	(17) n = 4
(12) n = 5	(18) n = 5

i) CsF, Sulpholane, 130°C

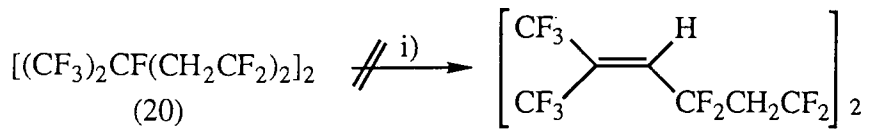
[30]

The structural unit $(CF_3)_2C=CH-CF_2-$ was characterised in detail by n.m.r. spectroscopy and typically showed a triplet for the proton (c) at ca 7.2 ppm, a triplet of quartets for trifluoromethyl groups (CF_3) (b) at ca. -64 ppm (accidental degeneration occurred, the coupling constants being respectively 18 Hz and 9 Hz), and a quartet for trifluoromethyl group (a) at ca. -70 ppm.



[31]

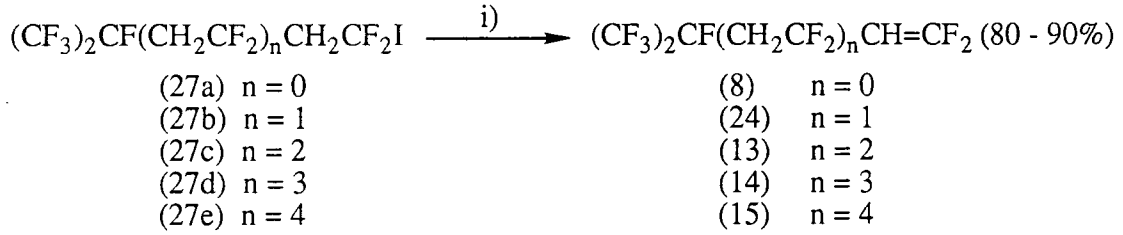
In an attempt to induce dehydrofluorination a the tertiary site, saturated model compound (20) was reacted with caesium fluoride, in sulpholane at 130°C. The reaction gave a complex mixture of products which were not investigated further.



i) CsF, sulpholane, 130°C
[32]

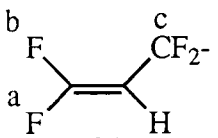
1.C.4.b Synthesis of α-β unsaturated model compounds (-CF_2-CH=CF_2)

Fluorohydroalkyl iodides are known to give the corresponding polyfluorinated-alkenes by elimination of hydrogen iodide in the presence of a base. For our purposes the elimination reactions were simply carried out by mixing the iodides and tributylamine in the absence of solvent, which made the work up of the reactions and the purification of the products easier.



i) NBu_3, r.t
[33]

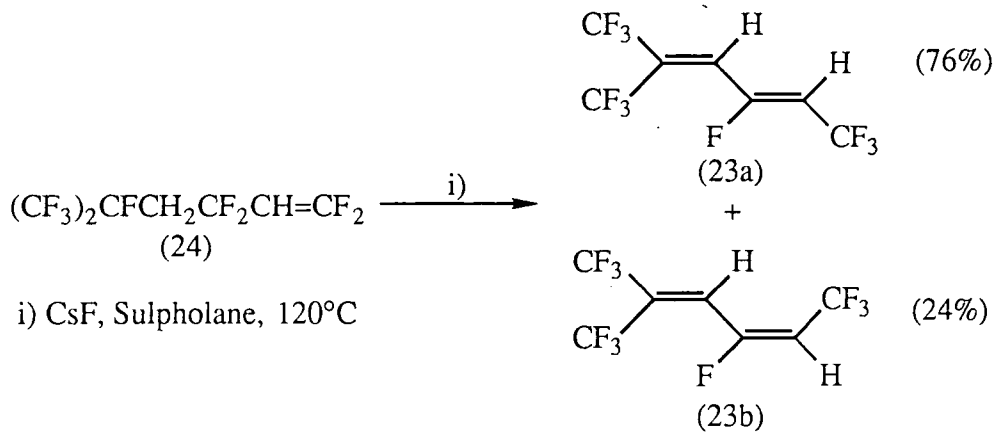
The structural unit -CF_2-CH=CF_2 was characterised in detail by n.m.r. spectroscopy and typically showed a doublet of triplets of doublets for proton (a) at ca. 5.2 ppm, a doublet of doublets of triplets for fluorine (b) at -80 ppm, and a doublet of triplets of doublets for fluorine (c) at -84 ppm. Accidental degeneration occurred in the n.m.r. signal for both proton (a) and F (b) because of similarity in the coupling constants.values.



[34]

Reaction of saturated compounds (27) with a large excess of tributylamine led to dehydrofluorination and subsequent decomposition (tarring).

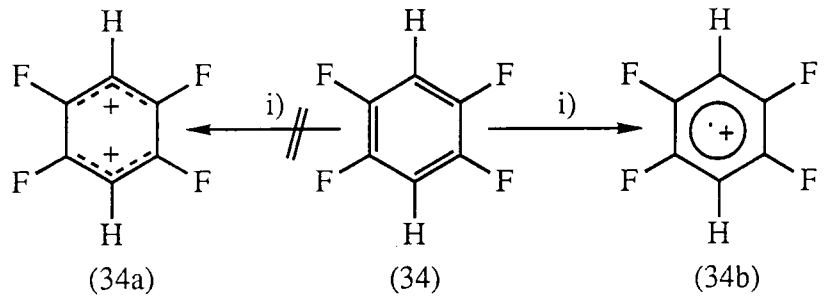
The reaction of (24) with caesium fluoride was particularly interesting: not only did isomerisation of the double bond from the terminal position occur, but this was also accompanied by dehydrofluorination, thus, di-enes (23a) and (23b) were obtained and these were valuable reference compounds for the calculations on carbocations which we discussed before. Of the two isomers the (Z,Z) (23a) appeared to be thermodynamically more stable than the (Z,E) (23b), as we observed comparing the corresponding yields: 76 and 24%.



[35]

1.C.5 Attempts at the preparation of novel model compounds as precursors for fluorinated carbocations

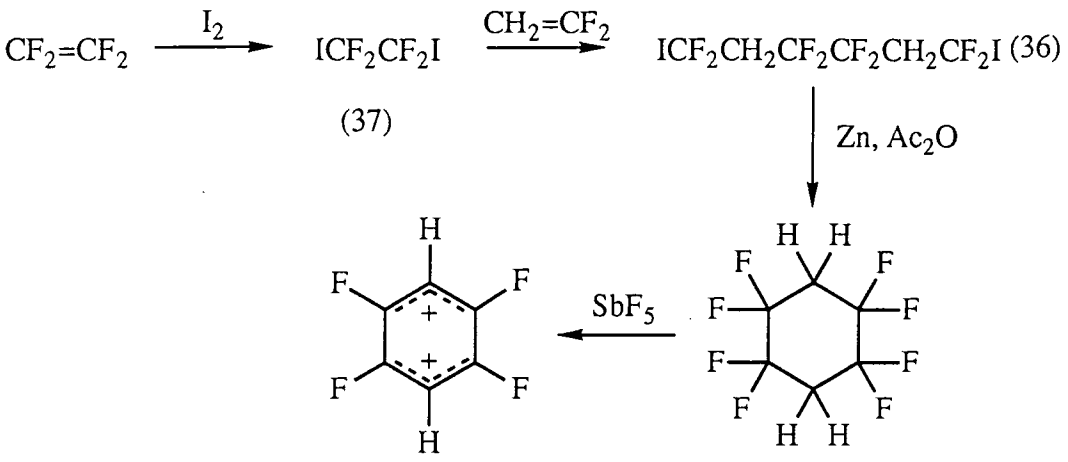
It has been reported that treatment of 1,2,4,5-tetrafluorobenzene (34) with an excess of antimony pentafluoride afforded the formation of radical cation (34b) rather than di-cation (34a).[8]



i) SbF_5, r.t.

[36]

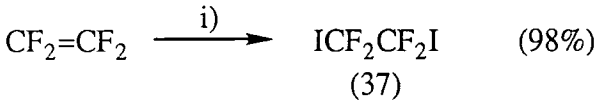
It occurred to us that, maybe, 1,1,2,2,4,4,5,5-octaflurocyclohexane (35) would have been a better precursor for di-cation (34a). Possibly, antimony pentafluoride would have induced dehydrofluorination and, at the end, extraction of an additional fluorine atom would have led to (34a). Retrosynthetic approach to a potential precursor indicated that intramolecular coupling of di-iodide (36) was the most direct route to (35) since (36) could have easily been obtained by addition of vinylidene fluoride to 1,2-diiodotetrafluoroethane (37).



[37]

1.C.5.a Synthesis of 1,2-diiodotetrafluoroethane

1,2-Diiodotetrafluoroethane was synthesised by reacting tetrafluoroethylene with iodine.



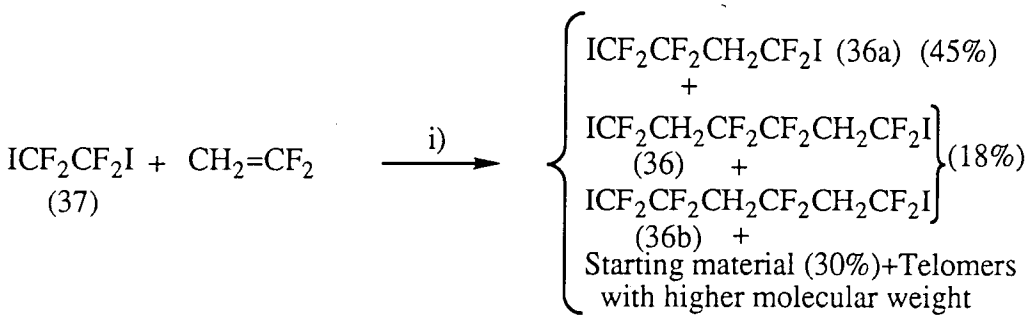
i) I_2, 150°C, 24 hours

[38]

The reaction was carried out in a stainless steel autoclave under autogenous pressure and proceeded almost quantitatively. *Attention!, scaling up the reaction may be dangerous because polymerisation of tetrafluoroethylene may occur explosively at pressures above 17 atm !!!.*

1.C.5.b Telomerisation of vinylidene fluoride using 1,2-diiodotetrafluoroethane as a telogen.

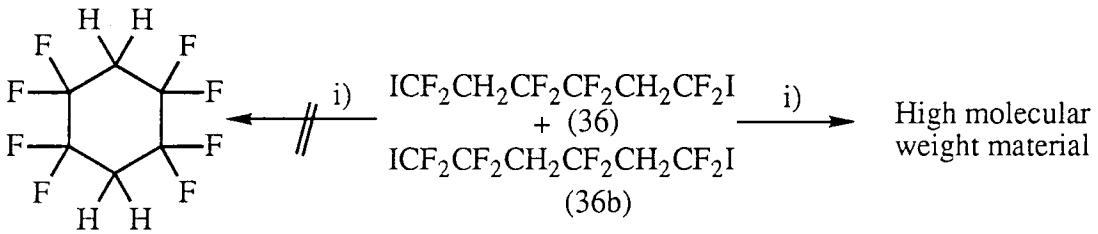
1,2-Diiodotetrafluoroethane (37) is a source of fluorinated radicals at carbon at elevated temperature (200°C); homolytic cleavage of the C-I bond occurs and the so formed radicals undergo successive additions of vinylidene fluoride to give a mixture of ICF_2CF_2I (37) ca. 30%, $ICF_2CF_2CH_2CF_2I$ (36a) ca.45% and a 1:1 mixture of $ICF_2CH_2CF_2CF_2CH_2CF_2I$ (36) and $ICF_2CF_2CH_2CF_2CH_2CF_2I$ (36b) ca. 18%.



i) 200°C, 36 hours
[39]

The mechanism for the telomerisation reaction is similar to the one outlined in Scheme 2. Separation of the structural isomers containing two units of vinylidene fluoride (36), (36b) could not be achieved by distillation under reduced pressure. TLC showed that separation by chromatography would not have been possible because of the identical Rf values.

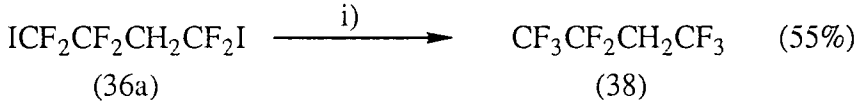
Coupling with zinc in acetic anhydride was then attempted on the mixture of (36)and (36b). Repeated trials showed that intermolecular coupling was preferred to intramolecular, even in highly diluted systems.



i) Zn, Ac_2O
[40]

1.C.5.c Preparation of $CF_3CF_2CH_2CF_3$.

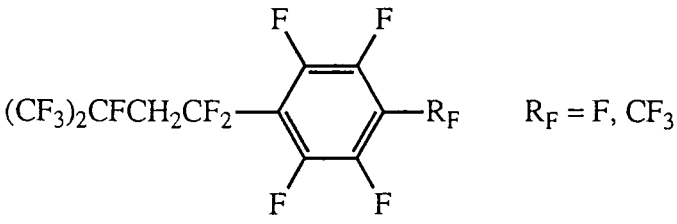
$ICF_2CF_2CH_2CF_2I$ was reacted with antimony pentafluoride to replace iodine for fluorine. The reaction was carried out in triclhorotrifluoroethane (R-113) in moderate yields.



i) SbF_5, 0°C, R-113
[41]

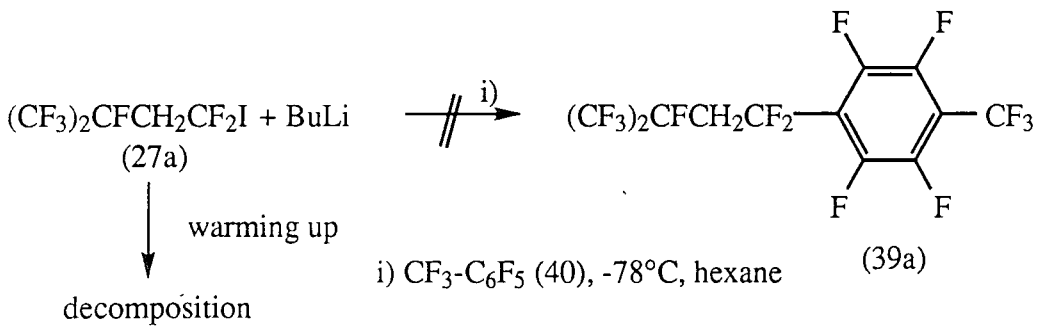
1.C.6 Attempted preparation of perfluoro-aromatic derivatives.

It was also our intention to investigate the effect of perfluoro-aromatics on carbocation stabilisation. Thus in the first instance our target molecules were precursors of type (39).



(39)
[42]

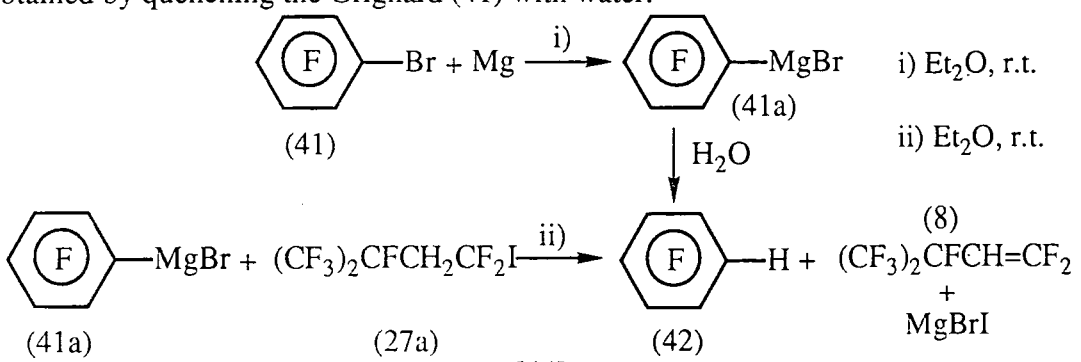
Numerous methods have been attempted for the preparation of (39), but, unfortunately, they were not successful. Our original intention was to generate fluoroalkyl metal derivatives of $(CF_3)_2CFCH_2CF_2I$ (27a) to induce nucleophilic aromatic substitution on perfluorotoluene (40). We first tried to obtain the lithium derivative using butyl lithium, and react it with perfluorotoluene (40) in situ. ^{19}F n.m.r. monitoring showed that no reaction occurred at -78°C and that extensive decomposition took place on allowing the temperature to raise to room temperature. However, perfluorotoluene (40) was unaffected.



[43]

Reaction of (40) with the fluoroalkyl zinc derivative of (27a) in dioxane was also unsuccessful, leading, mainly, to the formation of product of reduction (31).

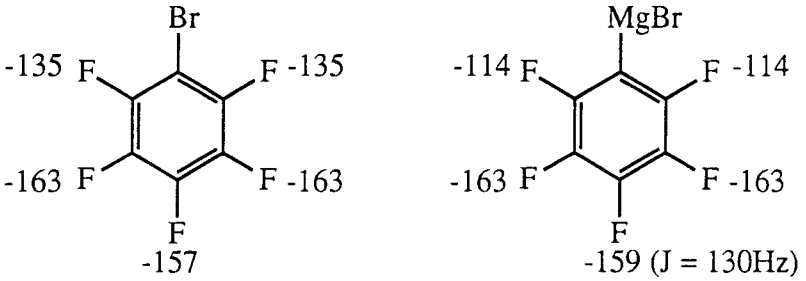
We then tried a different approach. We took bromopentafluorobenzene (41), formed the Grignard (41a), and reacted it with $(CF_3)_2CFCH_2CF_2I$ (27a). Pentafluorophenyl magnesium bromide (41a) acted mainly as a base (rather than a nucleophile), inducing elimination of HI to form pentafluorobenzene (42) and alkene (8) (GC integration: 70% overall). The mixture was analysed by means of GC/MS. Pentafluorobenzene (42) showed a typical peak at m/z^+ 168 (M^+). The product was also identified by comparison of the ^{19}F n.m.r. chemical shifts with the product obtained by quenching the Grignard (41) with water.



[44]

It is interesting to note that the ^{19}F chemical shift signal for the p-fluorine appeared as a singlet at 157 ppm in bromopentafluorobenzene (41) and as a doublet at -160 ppm (J = 130 Hz) in the Grignard (41a). Also the fluorines at the ortho position were shifted by about 21 ppm down-field.

^{19}F chemical shifts (values in ppm)

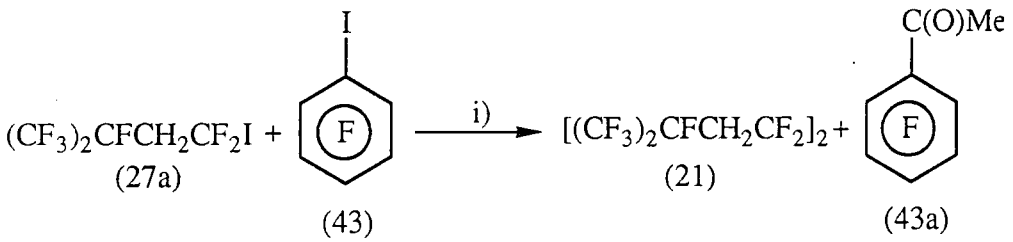


(41) (41a)

[45]

Variation using Pd(PPh3)4 and CuI as catalysts led to identical results.

The former attempts having failed, we turned to explore the mixed coupling of an aromatic with an aliphatic iodide. To this end, iodopentafluorobenzene (43) was reacted with $(CF_3)_2CFCH_2CF_2I$ (27a) in presence of activated zinc in acetic anhydride as a solvent. Analysis showed that mainly homo-coupling of (27a) and formation of pentafluorophenylmethylketone (43a) had occurred. Ketone (43a) was easily detected by GC/Ms showing peaks at m/z$^+$ 210 (M^+), 195 (M^+ - 15) .

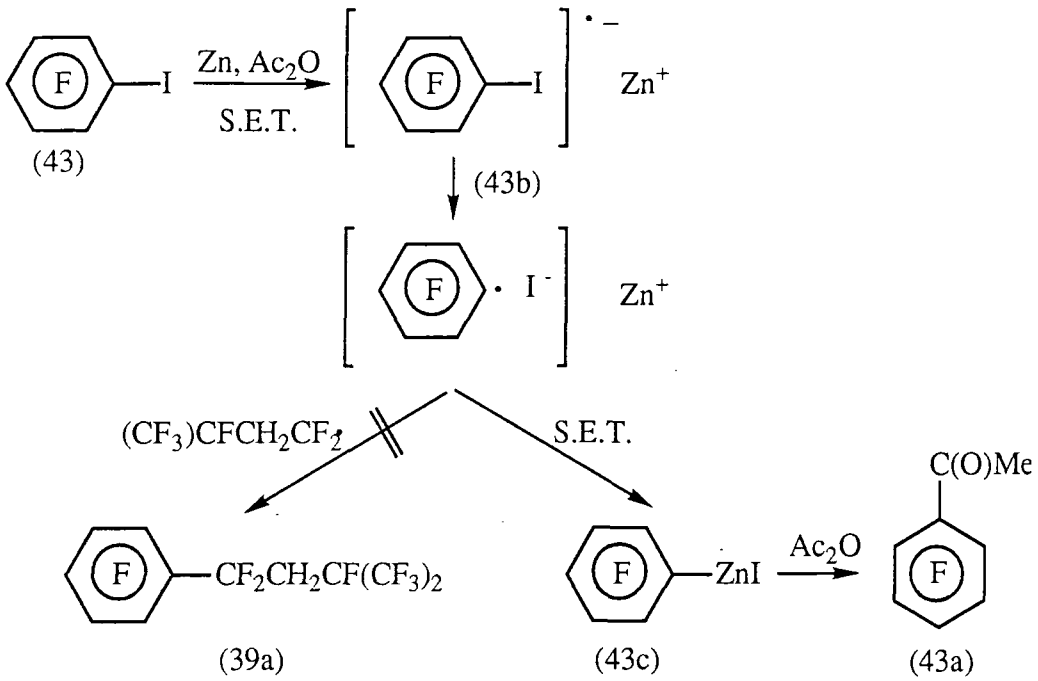


(27a) (43) (21) (43a)

i) Zn, Ac_2O

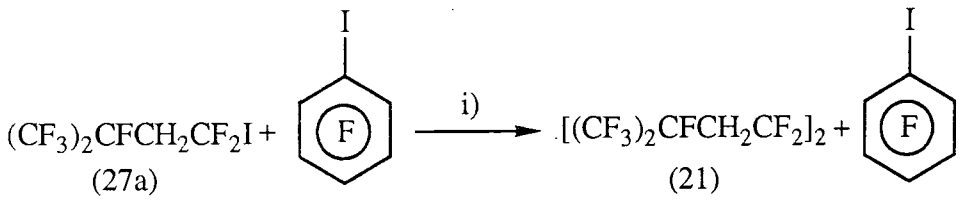
[46]

The aforementioned results suggest that the reaction proceeds via SET to form radical anion (43b), which undergoes cleavage to give iodide ion and perfluorophenyl radical. At this point the second electron transfer takes place to form the perfluorophenyl zinc derivative (43c), and this process seems to be much faster than the coupling reaction to form (39b).



[47]

Reaction in presence of Cu metal at 150°C (no solvent) or in presence of Hg under ultra-violet light irradiation (r.t.) afforded only the coupling of the alkyl iodide, leaving iodopentafluorobenzene unaffected.

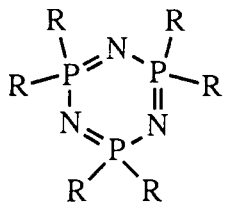


[48]

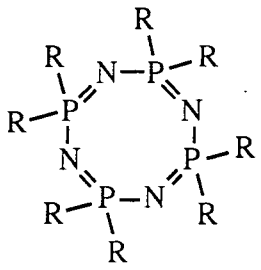
CHAPTER 2
PHOSPHAZENE CHEMISTRY.

2.A Introduction.

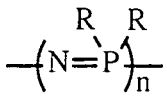
The borderline between organic and inorganic chemistry has been a fertile area for dramatic advances, particularly in the field of cyclic (44), (45) and open chain (46) phosphazenes (phosphonitriles).



(44)



(45)



(46)

[49]

Aspects of interest are, of course, the synthesis and mechanism, but, most importantly, their unusual structural characteristics and potential industrial applications, mainly in polymer chemistry.

2.A.1 Structure of phosphazenes.

There are some difficulties in explaining why the phosphorus-nitrogen bonds are shorter, slightly stronger, and more chemically stable than phosphorus-nitrogen bonds in other compounds (i.e.: phosphazanes, phosphinic amides), and how the electrons are distributed in the skeleton.

It is generally assumed that two of the electrons at each nitrogen occupy the sp^2 hybridised orbital oriented in the plane, and pointing outwards. The spare electron in the nitrogen p_z orbital (perpendicular to the ring plane) is thought to be involved in some type of π bonding with an electron from phosphorus. In addition the non bonded electron pair on nitrogen can be donated into the phosphorus 3d orbitals to form a second (in-plane) coordinate π' system. These two effects contribute to strengthening and shortening the phosphorus nitrogen bonds, and explain ring puckering[27-34].

From a theoretical point of view, though, it has to be pointed out that both phosphorus d_{yz} and d_{xz} orbitals may participate in the formation of a π bond with the nitrogen p_z orbital. The phosphorus d_{yz}-nitrogen p_z interaction produces a homomorphic type of π bond, perhaps comparable to the $p\pi$-$p\pi$ aromatic system, while the phosphorus d_{xz}-nitrogen p_z interaction would form a heteromorphic "pseudo aromatic" π orbital. Also, the π' type of bonding (phosphorus d_{x2-y2} and phosphorus d_{xy} with nitrogen p_z orbitals) occurs when highly electronegative substituents are attached to phosphorus. In fact, they bring about contraction of the phosphorus 3d orbitals, lowering the energy, and allowing π bond to take place.

2.A.2 Synthesis of phosphazene skeleton.

The synthesis of the cyclotriphosphazene skeleton, principally chloro and bromo derivatives, can be accomplished by a number of routes[35]. However, the reaction which provides the most convenient approach for their syntheses is [50].

$$n\ NH_4Cl + n\ PCl_5 \xrightarrow{i)} [NPCl_2]_{3to>10} + 4n\ HCl$$

i) solvent, heat

[50]

Ammonium chloride reacts with phosphorus pentachloride in a suitable solvent to afford a mixture of cyclic and linear phosphazenes, which are then separated. The reported mechanism (Scheme 4) suggests a sequence of steps for the formation of salt (47)[36] which then reacts with ammonium chloride inducing chain growth followed by cyclisation.

$$PCl_5 + NH_4Cl \longrightarrow Cl_4PNH_2 + 2HCl$$

$$Cl_4PNH_2 \longrightarrow Cl_3P{=}NH + HCl$$

$$Cl_3P{=}NH + PCl_5 \longrightarrow Cl_3P{=}N\text{-}PCl_4 + HCl$$

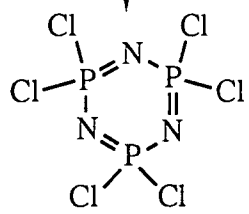
$$Cl_3P{=}N\text{-}PCl_4 + PCl_5 \longrightarrow [Cl_3P{=}N{=}PCl_3]^+\ PCl_6^-$$

(47)

$$[Cl_3P{=}N{=}PCl_3]^+\ PCl_6^- + NH_4Cl \longrightarrow [Cl_3P{=}N{=}P(Cl_2){=}N{=}PCl_3]^+\ Cl^-$$

(47)

NH_4Cl | Cyclisation



(48)

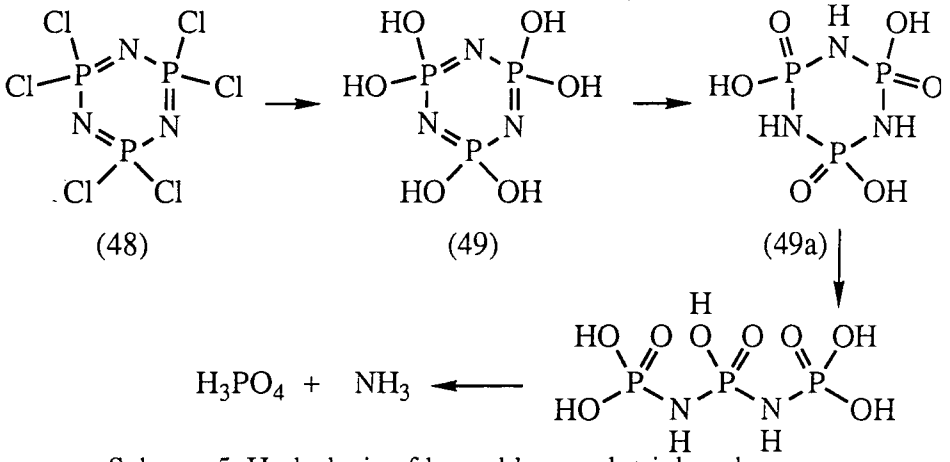
Scheme 4. Suggested mechanism for the formation of hexachlorocyclotriphosphazene.

Hexachlorocyclotriphosphazene (48) can be used as a precursor for nearly all organo-phosphazenes.

2.A.3 Hydrolytic stability

Although the hydrolytic behaviour of organo-phosphazenes is of considerable technological interest, little has been reported in this area. It is known that halocyclotriphosphazenes hydrolyse quite quickly in basic homogeneous media to yield hydroxyphosphazenes (49) and cyclophosphazanes (49a) and eventually phosphates and ammonia (Scheme 5).[37,38] The initial step involves the hydrolysis of the phosphorus

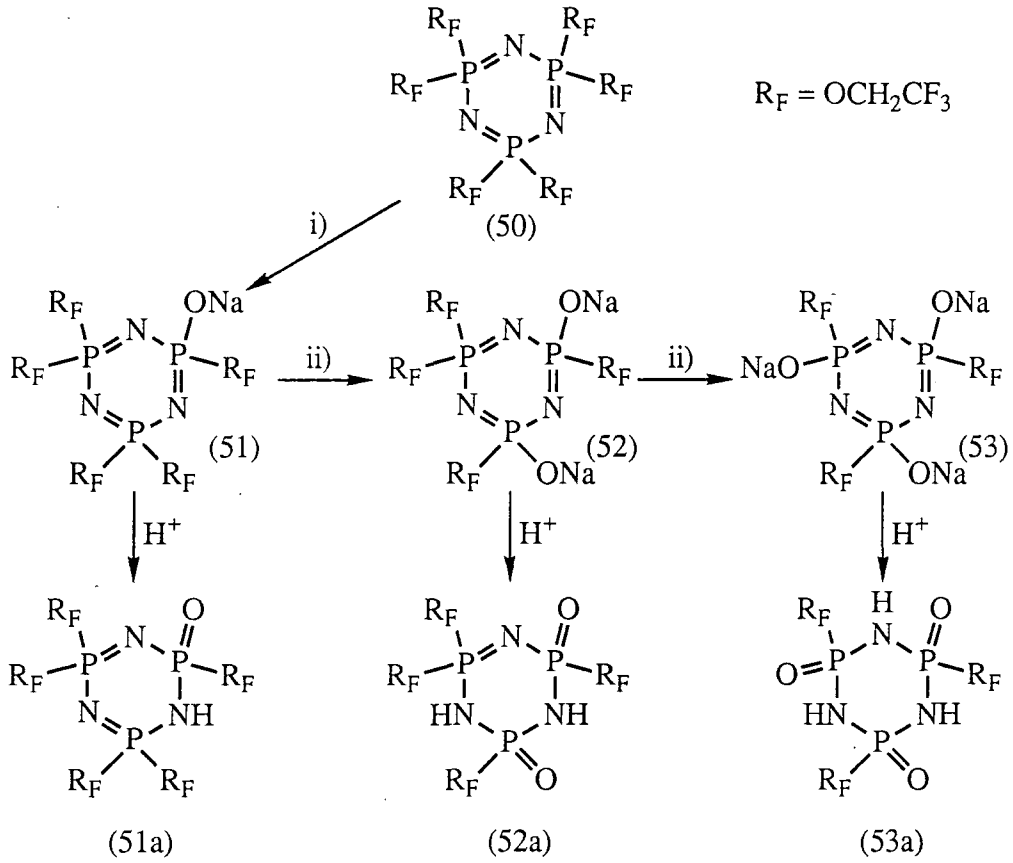
chlorine bonds, the second, proton migration from oxygen to nitrogen and the third, ring cleavage and skeletal degradation.



Scheme 5. Hydrolysis of hexachlorocyclotriphosphazene.

When both halogen and organo groups are present as ligands on the same ring, the halogen group is removed first in basic media. Completely organo-substituted phosphazenes (methoxy, ethoxy, isopropoxy, butoxy, and benzyloxy) are stable to water but decomposed in acid media at high temperature.[39,40]

The available information for fluoroalkoxycyclophospphazenes is restricted to the knowledge that hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50)[41-43] is hydrolysed by boiling 50% volume aqueous methanol containing 1M sodium hydroxide solution for 75 hours to give 1-hydroxy-1,3,3,5,5-pentakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (51) (Scheme 6), which, when treated with acids, gives the correspondent phosphazadiene (51a). Prolonged hydrolysis of (51) for 250 hours in the same medium and condition gives the di-sodium salt (52) and traces of the tri-sodium salt (53). Both derivatives (52) and (53) can be converted into the corresponding hydroxy cyclophosphazene (52a) and (53a) with acids.



i) NaOH 1M in 50% vol. aqueous methanol, 75 hours
ii)NaOH 1M in 50% vol. aqueous methanol, 250 hours

Scheme 6. Hydrolysis of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene.

It was also reported that hexakis(2,2,3,3,3-pentafluoropropoxy)-cyclotriphosphazene and hexakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotriphosphazene may be hydrolysed in 25% aqueous diglyme solution containing 2 x 10^{-2} M sodium hydroxide at 80° C decomposing to give a monohydroxypentakis-(fluoroalkoxy)cyclotriphosphazene sodium salt with structure comparable to (51). Some ^{18}O studies of the hydrolytic reaction mechanism in 2.13 x 10^{-2} M sodium hydroxide 25% vol. aqueous diglyme media containing 1% $H_2{}^{18}O$, showed that the displaced alcohol did not contain ^{18}O, thus suggesting a phosphorus-oxygen rather than carbon-oxygen bond cleavage. However, Ferrar[44] and co-workers recently reported that sodium trifluoroethoxide cleaves the side groups of poly[bis(2,2,2-trifluoroethoxy)phosphazene to give incorporation of hydroxy groups onto the polymer, thus suggesting that the nucleophile attacks on carbon rather than on phosphorus. This matter of controversy will be dealt with in more details later on in Section 2.B.6.g.ii..

2.A.4 Complex and adduct formation.

Phosphazenes form a wide range of coordination complexes, salt like adducts, and molecular inclusion adducts. This behaviour can be attributed to five characteristics of phosphazenes:

1) the fact that the skeletal nitrogen atoms can donate their lone pair electrons to acceptor molecules to form coordination complexes,

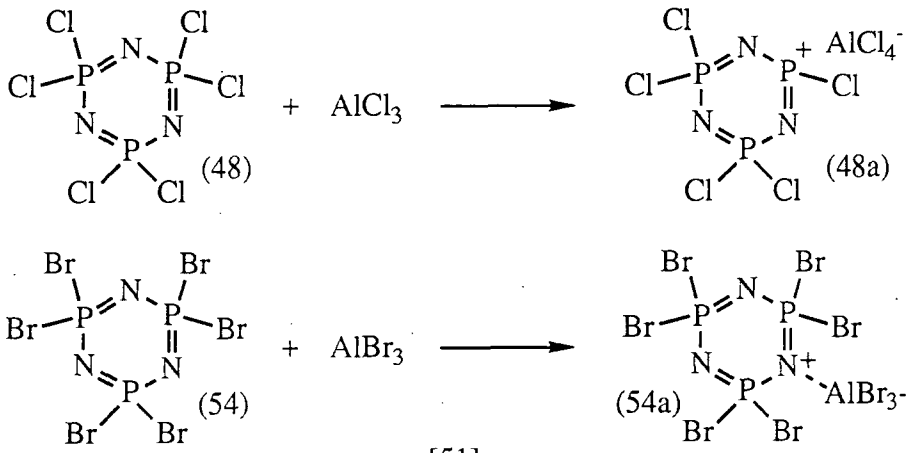
2) the ability of halophosphazene to release a halogen anion to form an anion-cation complex[45],

3) the ability of phosphazene to accept a cation to form "onium" type salts,

4) the availability of p electrons for coordination with metals, and

5) the rigidity of the cyclophosphazene ring, which facilitates the specific crystalline molecular-packing arrangements required for clathration[46].

Halophosphazenes could react with metal halides to give two kinds of coordination compounds. The first involves ion transfer at the phosphorus di-halide unit (48a), the second requires the coordination between the skeletal nitrogen and the metal of the Lewis acid (54a).



[51]

It is believed that complexes like (48a) are the intermediates formed during the Friedel-Craft arylation of phosphazenes.

Fluorophosphazenes react with antimony pentafluoride but the structure of these complexes seem to differ from (48a). Antimony pentafluoride normally reacts with ring systems to form complexes of formula $(NPF_2)_n \cdot 2\ SbF_5$ which are white crystalline compounds easy to sublime under vacuum below 110° C.[47]

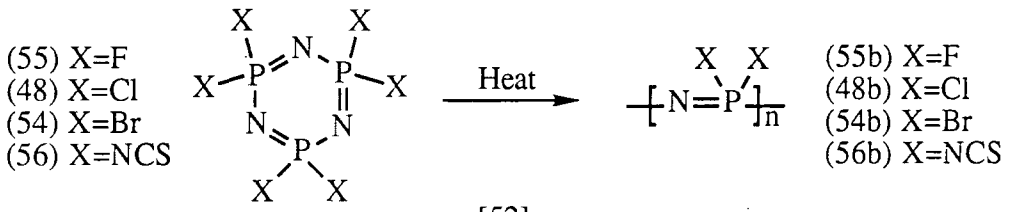
2.A.5 Thermal stability.

A number of phosphazenes are stable at elevated temperatures, for example hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50) can be heated at 320°-350°C from 10 to 30 hours without any appreciable decomposition.[48] Even attempted combustion in a stream of oxygen over copper oxide does not result in complete oxidation.[49] Organo-fluorophosphazenes are also inert to boiling nitric acid; however, they may undergo ring expansion when boiled at 340°C for 50 hours[49], but most remarkably, phenoxyphosphazenes are even more stable to pyrolysis, for instance, no degradation is observed after prolonged heating at 350°C.[50]

2.A.6 Polymerisation and de-polymerisation of halophosphazenes.

Molten hexachlorocyclotriphosphazenes (48) and octachlorocyclotetraphosphazene polymerise to a linear type high polymer when heated at 230° - 300°C[35]. At an early stage of polymerisation the polymer is soluble in benzene tetrahydrofuran (THF), but prolonged reaction times lead to the formation of a cross-linked material, which is swollen by organic solvent, but no longer taken into solution.

Cyclophosphazenes containing fluoro, bromo and isothiocyno groups also polymerise at elevated temperatures[35]

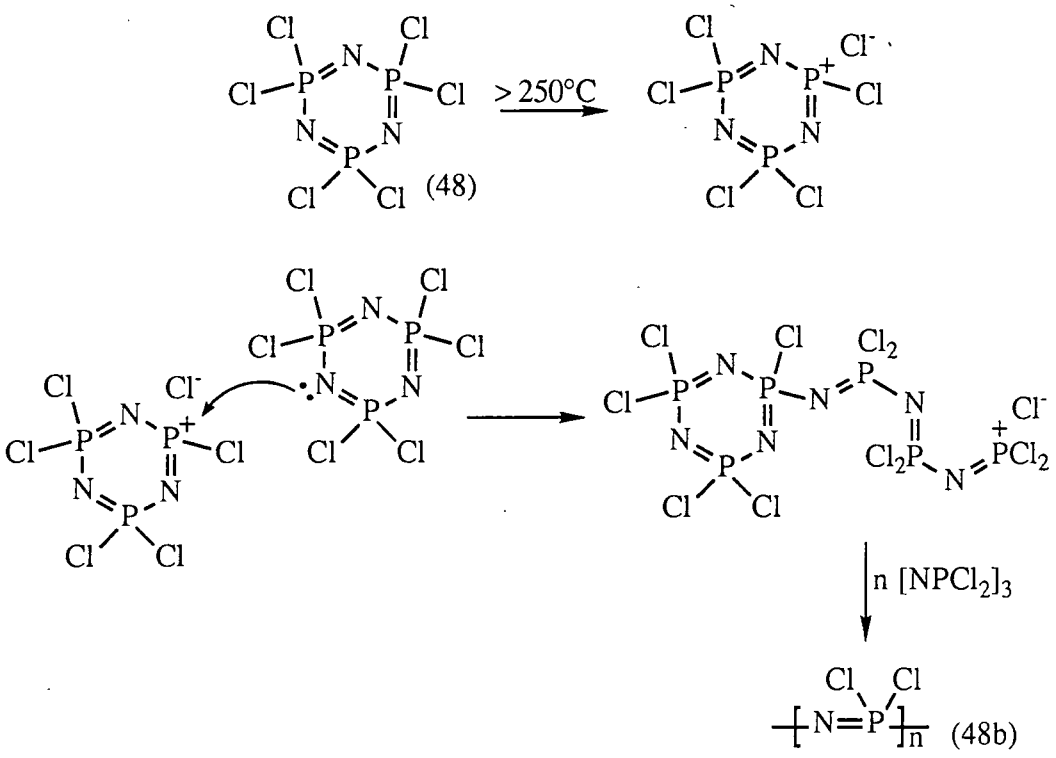


[52]

Although the experimental evidence pertaining to the polymerisation mechanism is still incomplete, some useful clues are available. In the first place, conventional free radical initiators have very little effect on the polymerisation rate,[51] secondly, for hexachlorocyclotriphosphazene, the conductance and capacitance rise sharply at the temperature of polymerisation,[50] and thirdly the reaction is catalysed by reagents which can induce removal of chlorine, promoting ionic cleavage of the phosphorus-chlorine bond.[52] All these facts would suggest an ionic mechanism of the type indicated in Scheme 7.

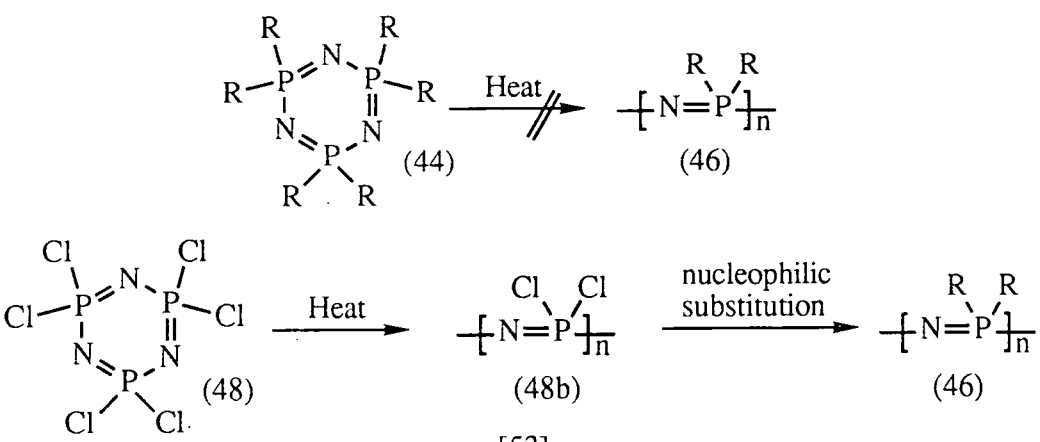
Nevertheless, poly(chloro)phosphazene (48b) has no practical value because of the intrinsic instability of the phosphorus chlorine bonds. Therefore, interest in the synthesis of poly(organo)phosphazenes (46) has developed to look for a new series of water stable polymers.

Unfortunately, high molecular weight organic derivatives cannot be obtained by a direct route because the polymerisation of a cyclophosphazene is usually inhibited when the halogens are replaced by organic units. The mechanistic explanation that has been formulated to explain this observation is to be found in thermodynamics[53,54]. Bulky organic substituents attached to phosphazene skeleton are believed to affect the position of the ring-polymer equilibrium. The conversion of a cyclic trimer to a linear polymer has the effect of shortening the intramolecular distances between the side groups on near-by phosphorus atoms and between side groups and near-by chain.



Scheme 7. Mechanism for ionic polymerisation of hexachlorocyclotriphosphazene.

If the substituents are small (chloro, fluoro) the intramolecular repulsions in the polymer are negligible and polymerisation will occur at relatively high temperatures. But, if bulky groups are present, the activation energy for ring opening will be so high (and so the temperature of polymerisation) that the polymer will be thermodynamically destabilised compared to the cyclic trimer. The consequence is that bulky substituted cyclic trimer (and tetramers) cannot be polymerised. Therefore, the only alternative route to poly(organo)phosphazenes (46) is the formation of uncross-linked poly(dichloro)phosphazene) (48b) followed by nucleophilic replacement of the chlorine atoms by the desired organic units.



[53]

2.B Reactions of halophosphazenes with nucleophiles.

2.B.1 Introduction.

The nature of the phosphorus-halogen bond is such that nucleophilic substitution on phosphorus provides one of the easiest routes to organo-phosphazenes (44), using hexachlorocyclotriphosphazene (48) as starting materials. This, in addition to the fact that certain phosphazene derivatives show excellent thermal and hydrolytic stability, has undoubtedly justified the flourishing number of publications in the literature. Most alkoxy and aryloxy phosphazenes, of structure $[NP(OR)_2]_3$, are stable, white crystalline solids, readily soluble in most organic solvents. They are among the most stable phosphorus-nitrogen derivatives known, and their thermal and hydrolytic stability depends on the nature of the substituent OR[35]. In particular, the presence of fluorinated groups makes fluoroalkoxyphosphazenes exceptionally stable to both heat and neutral hydrolysis. Studies[55-57] have shown that the substitution of the trimeric ring with fluoroalkoxy and aryloxy groups lowers the melting point to such a degree that the materials have useful properties as fire retardants, low temperature hydraulic fluids, or lubricants.

2.B.2 Synthetic approach.

Halocyclotriphosphazenes react with a wide variety of alkoxides, aryloxides, and mercaptides to give organo-substituted derivatives (57), (58).

$$6\ ROH + [NPX_2]_3 \longrightarrow [NP(OR)_2]_3 \quad (57)$$

$$6\ RSH + [NPX_2]_3 \longrightarrow [NP(SR)_2]_3 \quad (58)$$

[54]

In practice, the nucleophile ROH or RSH include almost any stable alcohol, phenol, mercaptan, or even diol or dithiol. The halogen atom, X, can be either fluorine, chlorine or bromine, and there appear to be no limits to the type of halophosphazenes $[NPX_2]_n$ (where *n* ranges from 3 to any degree of polymerization) involved in the reaction. A solvent medium is nearly always used. Most of the times the reactions are clean processes, and the products obtained are usually quite stable, easy to purify and characterise. Many reactions are carried out using sodium alkoxides, phenoxides, and thiolates instead of their free analogs. In such cases, sodium halide precipitates out of solution as a reaction product. The preparation of the sodium alkoxide or phenoxide is achieved by reacting the alcohol or phenol with either sodium or sodium hydride. Nevertheless, a number of modifications to this process are possible, for example, when the free alcohol, phenol, or thiol is used, bases such as tertiary amines, pyridine, sodium carbonate, or sodium bicarbonate can be used to remove the readily formed hydrogen

halides[58]. Sodium hydroxide has also proved to be successful as a base when phenol is used[59-67].

2.B.3 Fluoroalkoxy derivatives.

In particular, fluoroalkoxy groups can be substituted at phosphorus with ease, and the following are the substituents which have been used: CF_3CH_2O[49,68-71], $C_2F_5CH_2O$[49,68-71], $C_3F_7CH_2O$[49,68-71], $H(CF_2)_6CH_2O$[49,57], $H(CF_2)_{10}CH_2O$[49], $H(CF_2)_2CH_2O$[56,57,72,73], $H(CF_2)_4CH_2O$[56,57,72], $H(CF_2)_8CH_2O$[57,72], and $(CF_3)_2CHO$[72].

2.B.4 Aim of the work.

The aims of this work are:

- to investigate the reaction mechanism of the nucleophilic substitution at phosphorus in halocyclotriphosphazenes for a better understanding of the reactivity of the system;
- to synthesise some organo-phosphazenes as model compounds for gamma rays induced reactions, fluoroalkylation, fluorination, chlorination and bromination reactions;
- to synthesise fluoroalkoxyphosphazenes as potential additives for the thermal stabilisation of perfluoropolyether fluids operating at elevated temperatures.

More detailed information is available in the introduction to each subject in the course of the work.

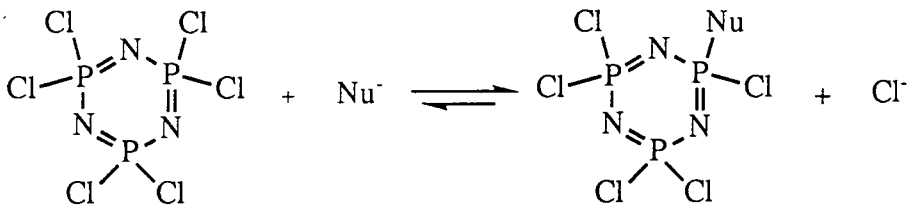
2.B.5 Results and discussion.

2.B.5.a Reactions of halocyclotriphosphazenes with selected nucleophiles to investigate the reaction mechanism.

The nature of the reaction of alcoholysis, phenolysis or thiolysis is strictly connected to the mechanistic problems of substitution in phosphazenes. However, the available information in literature is incomplete and fragmentary[35], therefore, we wanted to establish whether the reaction path proceeded via a S_N2-type, like-wise aliphatic systems, or via an addition-elimination-type mechanism like-wise aromatic systems, and, as a consequence, what was the influence of the halogen on the reactivity of the halophosphazenes. To this end, we investigated the reactivity of hexachlorocyclotriphosphazene (48) and hexafluorocyclotriphosphazene (55) in competition reactions with selected nucleophiles (sodium 2,2,2-trifluoroethoxide, sodium phenoxide, sodium thioethoxide), to produce mono-substituted phosphazenes and determine the rates of reaction. As far as we are concerned, this is a new approach for attempting rationalisation of the reaction mechanism.

Sodium 2,2,2-trifluoroethoxide, sodium phenoxide, sodium thioethoxide were prepared and then reacted individually with two molar equivalent of hexachlorocyclotriphosphazene (48) and hexafluorocyclotriphosphazene (55) in anhydrous diethylether at 0°C. The nucleophile-halocyclotriphosphazenes molar ratio was chosen as 1 to 2 so that the nucleophile / number of phosphorus-chlorine bonds molar ratio could be of 1 to 12, to reduce di-substitution to a minimum. The mixtures were sampled for analysis every ten minutes, and the process quenched in liquid air.

Results showed that the reactions between hexachlorocyclotriphosphazene (48) and sodium 2,2,2-trifluoroethoxide, sodium phenoxide, sodium thioethoxide, respectively, occurred extremely rapidly, but not quantitatively.

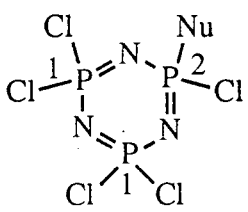


(48) (48c) $Nu^- = CF_3CH_2O^-$; (48d) $Nu^- = C_6H_5O^-$; (48e) $Nu^- = EtS^-$

[55]

The degree of nucleophilic replacement was monitored by ^{31}P n.m.r. spectroscopy. The formation of the mono adduct is proved by the presence of a doublet and a triplet with a relative intensity of 2 to 1 due to the phosphorus-phosphorus coupling in the AX_2 system (Table 4).

The doublet is due to the two n.m.r. equivalent phosphorus atoms P-1 where no chlorine has been displaced, and results from the coupling with the remaining phosphorus atom P-2. The triplet is attributed to the one phosphorus atom P-2 where one chlorine has been substituted and results from the coupling with the other two phosphorus atoms P-1 (Table 9).



(48c) $Nu^- = CF_3CH_2O^-$; (48d) $Nu^- = C_6H_5O^-$; (48e) $Nu^- = EtS^-$

[56]

Nu^-	δ P1 (ppm)	δ P2 (ppm)	J_{P1-P2} (Hz)
$CF_3CH_2O^-$	23.2	16.8	~66
PhO^-	24.6	8.7	~60
EtS^-	19.2	39.7	~34

Table 9. ^{31}P n.m.r. data for the AX_2 systems (48c)-(48e)

It is worthwhile pointing out that the coupling constants depend on the substituents attached to each phosphorus atom. The $J_{P1\text{-}P2}$ term shows a rough trend towards higher values as the electron-withdrawing capacity of the substituent increases.

Furthermore, the fact that the reactions are always very fast, that the conversion of the nucleophiles into the mono-substituted phosphazene derivatives is not quantitative, and that an excess of nucleophile is needed to achieve complete substitution may suggest the possibility that the reaction is an equilibrium!

Indicative calculations have therefore been carried out to determine an equilibrium constant for the reaction involving (48c).

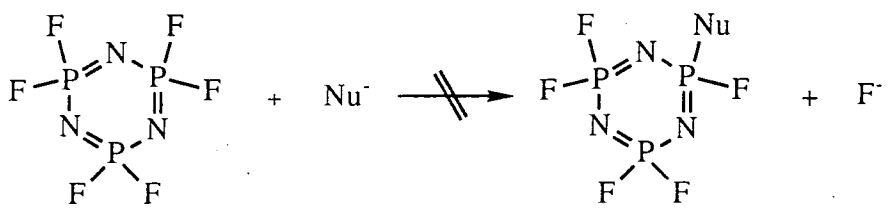
$$Keq = \frac{[N_3P_3Cl_5(OCH_2CF_3)]}{[(NPCl_2)_3][CF_3CH_2O^-]} = 2.37$$

[57]

The equilibrium constant has been calculated using the concentration values of the species at equilibrium. These values where derived as follows: if 0.8 M and 0.4 M were the concentration of hexachlorocyclotriphosphazene (48) and the 2,2,2-trifluoroethoxide respectively before reaction, then (0.8 - x) M and (0.4 - x) M would have been the concentration of hexachlorocyclotriphosphazene and 2,2,2-trifluoroethoxide at equilibrium; the value x was directly derived from the ^{31}P n.m.r. spectrum of the mixture at equilibrium.

Attempts to follow the kinetics of the reaction leading to (48c) in the n.m.r. probe have been carried out by timed acquisition of ^{31}P n.m.r. spectra. However, the reaction was too fast for kinetics to be studied by such a technique. Nevertheless n.m.r. data for the reaction at equilibrium were in good agreement with the ones obtained before. In this very case,though, poor quality spectra were obtained because of the system heterogeneity (precipitation of sodium chloride) .

Conversely, when sodium 2,2,2-trifluoroethoxide, sodium phenoxide, sodium thioethoxide, respectively, were reacted with hexafluorocyclotriphosphazene in anhydrous ether at 0°C, no sign of reaction was detected, even after prolonged stirring.



(55)

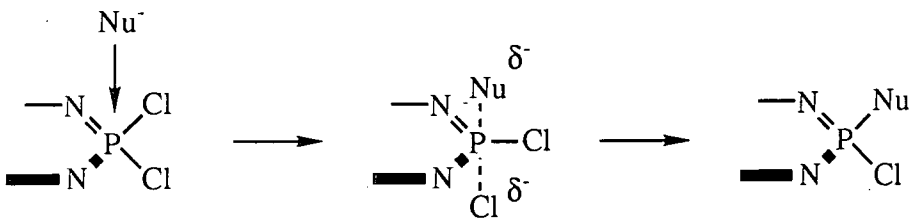
(55c) $Nu^- = CF_3CH_2O^-$
(55d) $Nu^- = C_6H_5O^-$
(55e) $Nu^- = EtS^-$

[58]

2.B.5.b Direct Substitution or Addition-Elimination Mechanism?

We showed that, under the same reaction conditions, hexachlorocyclotriphosphazene (48) reacted very rapidly with nucleophiles such as sodium 2,2,2-trifluoroethoxide, sodium phenoxide, sodium thioethoxide, and that conversely, hexafluorocyclotriphosphazene (55) does not react at all. This trend suggests that nucleophilic displacement at phosphorus is very likely to follow an S_N2 type-mechanism, where the rate determining step depends on the carbon-halogen bond strength. An addition-elimination type of mechanism seems rather unlikely, because it would have predicted hexafluorocyclotriphosphazene to be more reactive than hexachlorocyclotriphosphazene, as for the nucleophilic substitution in aromatic compounds where the rate determining step is not carbon-halogen bond cleavage.

All replacement reactions, can therefore be viewed to proceed from the attack of a nucleophile R^- at the skeletal phosphorus atom with the displacement of one of the original ligands. The most logical possibility for the approach of the nucleophile is via a backside attack and through a trigonal bipyramidal transition state (59).



(59)

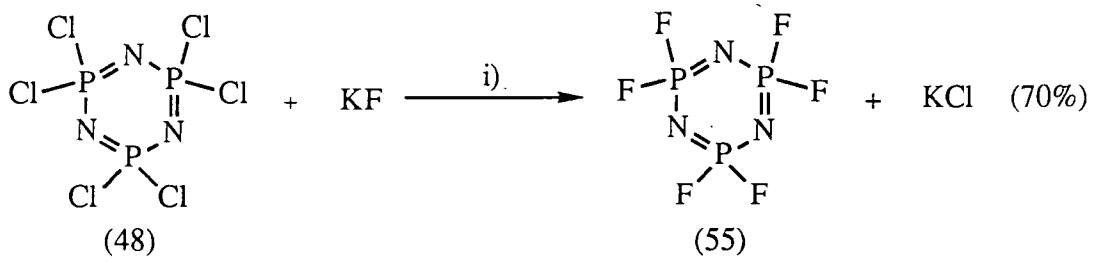
[59]

2.B.6 Reactions of hexachlorocyclophosphazenes with nucleophiles.

2.B.6.a Fluoride ion.

A variety of reagents have been reported to effect replacement of chlorine by fluorine in chlorophosphazenes. These include potassium fluorosulphite and potassium fluoride,[69,74,75] lead difluoride, silver monofluoride,[76,77] sodium fluoride[78,79] and antimony trifluoride.[80]

The method involving potassium fluoride was reported as the most effective, therefore we reacted hexachlorocyclotriphosphazene (48) with an excess of anhydrous potassium fluoride in acetonitrile at temperature of reflux, to give hexafluorocyclotriphosphazene (55). The yield of the reaction varied from 65 to 70%, however, when 18-crown-6 was added to the reaction mixture in a catalytic amount (ca. 5%), the yield increased up to 85 %, perhaps due to the ability of 18-crown-6 to solvate potassium ions, and thus making fluoride ions more ready available in solution.



(48) (55)

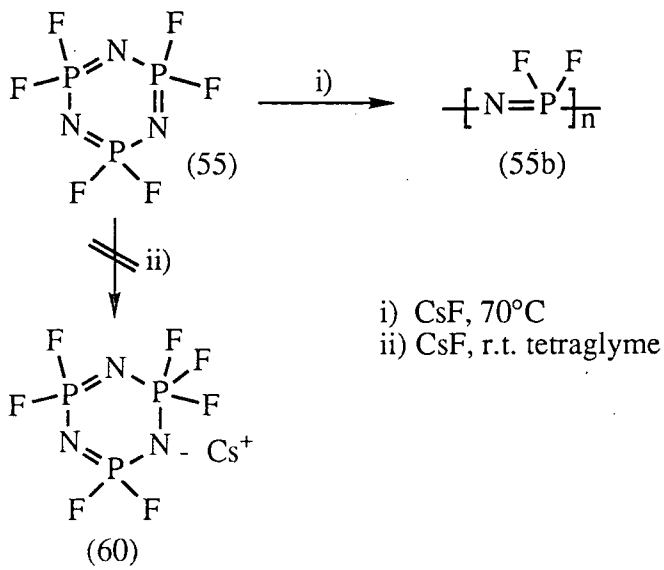
i) MeCN, reflux
[60]

Hexafluorocyclotriphosphazene (55) is a transparent colourless liquid (Bp.39°C) and shows a quite complicated second order ^{31}P and ^{19}F n.m.r. spectra ($ABCX_2$ system), mainly consisting of a triplet of multiplets at 13.9 ppm, and a doublet of multiplets at -70.5 ppm, respectively.

N.B. Work up is easily carried out by adding water to the mixture and separating the fluorinated layer which is purified by distillation. It is remarkable to note that hexafluorocyclotriphosphazene does not react with water as opposed to its organic analogue, trifluorotriazine $[CNF_2]_3$, which readily hydrolyses!.

2.B.6.b Formation of poly-fluorophosphazene.

We investigated the reaction between hexafluorocyclotriphosphazene and caesium fluoride in an attempt to produce a complex adduct $[(NPF_2)_3F]^- Cs^+$ (60). The reaction was monitored by means of ^{31}P and ^{19}F n.m.r. spectroscopy. At room temperature no evidence for the formation of adduct (60) was detected, but most surprisingly, when the mixture was heated up to 60 - 70°C polymerisation of hexafluorocyclotriphosphazene took place.



(55) (55b) (60)

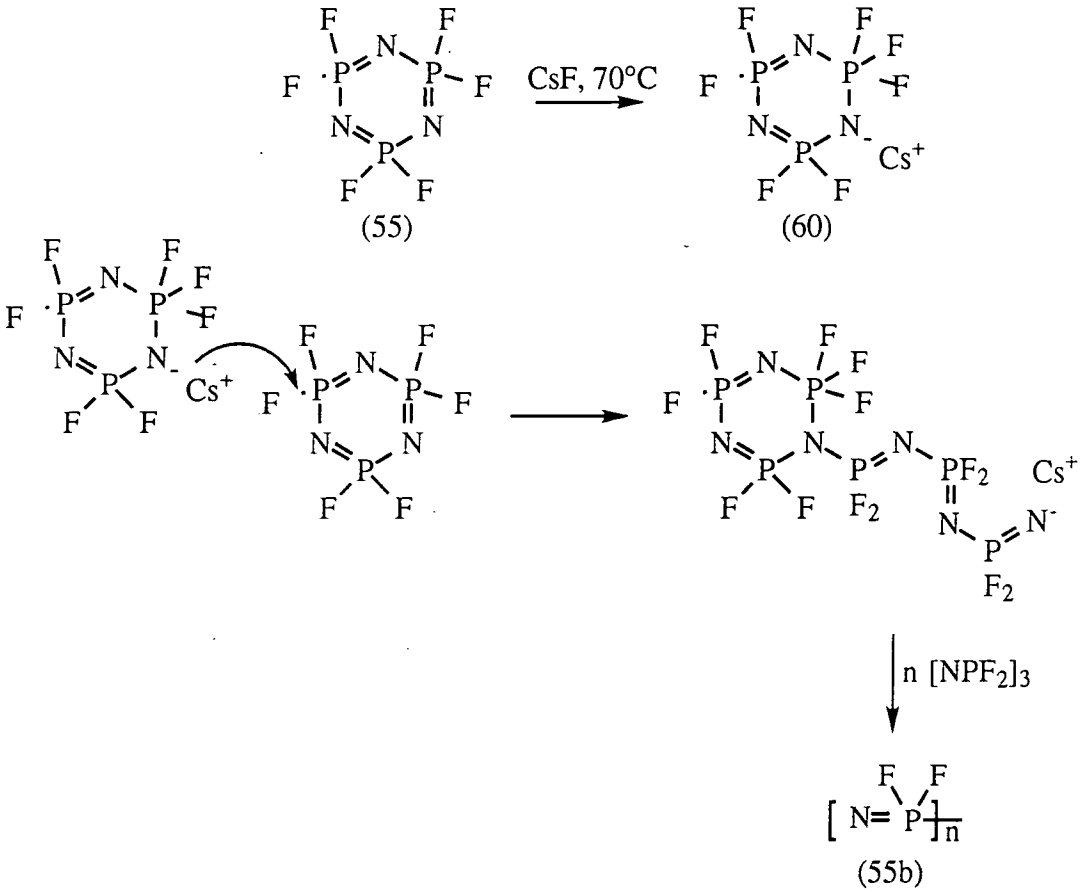
i) CsF, 70°C
ii) CsF, r.t. tetraglyme

[61]

This is a very interesting result because thermal polymerisation of hexafluorocyclotriphosphazene would normally occur at temperatures above 350°C under autogenous pressure[81]. Evidence for the formation of the polymer was obtained by elemental analysis and ^{31}P n.m.r. spectroscopy, which showed that the phosphorus

signals were shifted from +10 ppm.(starting material) to -4.5 ppm (polymer). This is also in agreement with what is found to be the general trend for the ^{31}P chemical shifts in going from the cyclic trimers to the linear polymers.[35]

The catalytic effect of fluoride ion suggested an ionic reaction mechanism: fluoride ion attacked the phosphorus atom to form the negative charged intermediate (60) (not isolated), which induced polymerisation through the nitrogen atom (Scheme 8).



Scheme 8. Suggested mechanism for fluoride ion induced polymerisation of hexafluorocyclotriphosphazene

2.B.6.c Attempted synthesis of hexabromocyclotriphosphazene and hexaiodocyclotriphosphazene form hexachlorocyclotriphosphazene.

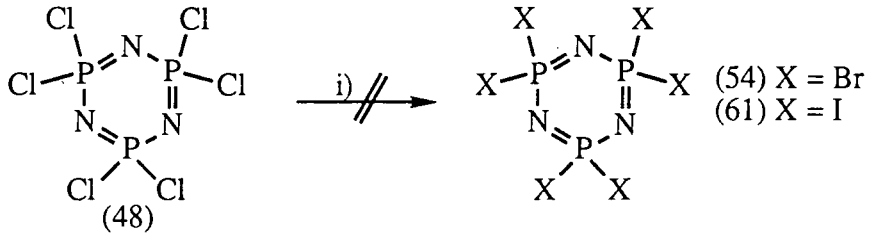
Phosphonitrilic bromides can be obtained by allowing phosphorus (III) bromide to react with ammonium bromide with yields comparable to the best reported for the chlorides.[82-84]

$$PBr_3 + NH_4Br \longrightarrow [NPBr_2]_3 \quad (54)$$

[62]

Nevertheless, no route using hexachlorocyclotriphosphazene (48) as starting material has ever been reported up to now. Also, we are not aware of any reported route

to hexaiodocyclotriphosphazene (61). This led us to investigate a Finkelstein-type reaction on hexachlorophosphazene to replace chlorine for either bromine or iodine. The reactions were carried out in acetone where potassium chloride should have come out of solution, but extensive decomposition of the ring occurred, instead.



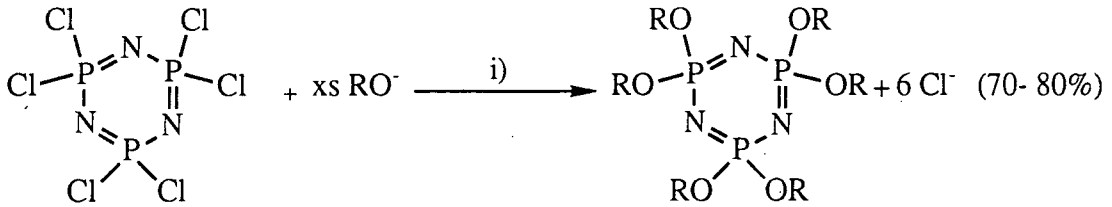
i) KX, acetone, r.t.
[63]

2.B.6.d Organo-cyclotriphosphazenes.

Alkoxyphosphazenes (57) and aminophosphazenes (62) are known compounds[35] and their synthetic route has already been established in the past. Indeed, they are very useful model compounds to study the effect of phosphorus on gamma rays induced perfluoroalkylation of methylene groups activated electron donating substituents (e.g.: P-O-CH_2-R, P-N(R)-CH_2-R).

2.B.6.d i Sodium alkoxides.

Both sodium methoxide and ethoxide reacted smoothly with hexachlorocyclotriphosphazene to give the corresponding hexasubstituted derivatives (63) and (64) in high yields.



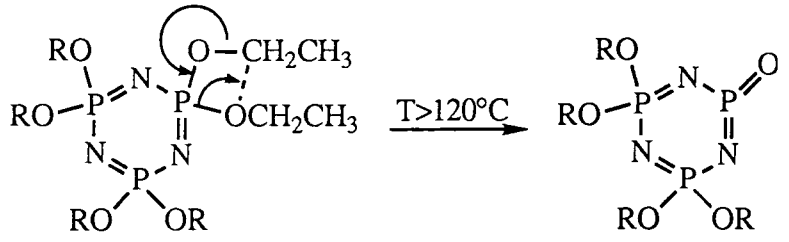
(48)

(63) R = $-CH_3$
(64) R = $-CH_2CH_3$

i) ROH, reflux

N.B. -Work up for most of these displacement reactions involved the use of water for quenching the alkoxide in excess. This precaution was avoided for hexakis(methoxy)cyclotriphosphazene (63) because it is surprisingly water soluble!!.

-When purification of hexakis(ethoxy)cyclotriphosphazene (64) was carried out by sublimation under reduced pressure, care had to be taken not to exceed ca.120°C because decomposition occurred with evolution of diethylether.



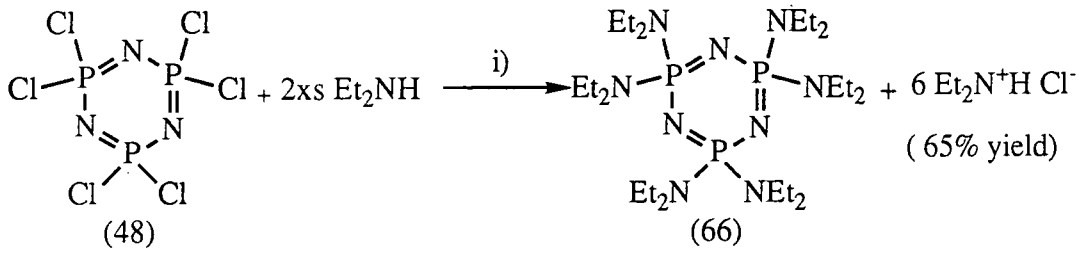
(64) (65)

[65]

An intermolecular pathway is also likely to be followed to give cross-linked material which is found as a solid by-product of the sublimation process.

2.b.6.d.ii Diethylamine.

Hexachlorocyclotriphosphazene (48) was reacted with two fold excess of diethylamine to give the hexakis(diethylamino)cyclotriphosphazene (66) in good yields. To achieve complete substitution the reaction had to be carried in an autoclave at 180°C.



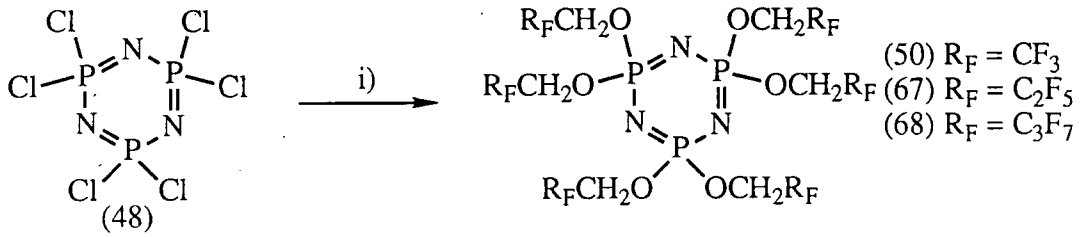
(48) (66)

i) 180°C, toluene

[66]

2.B.6.e Organo-fluorophosphazenes.

Fluoroalkoxide groups were able to replace the chlorine atoms in (48) with ease. We found that the most convenient preparative method was to generate the fluoroalkoxide by reaction of the fluoroalcohol with sodium hydride, followed by reaction with hexachlorocyclotriphosphazene (48), using either diethylether or tetrahydrofuran as solvents. The yields of the reactions were moderate (60%), but improved to 70-80% when the reaction was carried out at temperature of reflux for at least one hour.



(48)

i) $R_FCH_2O^-\ Na^+$, Ether, r.t -> reflux, (yield 70-80%)

[67]

Alternative synthetic routes were also attempted. For example, sodium could be used in place of sodium hydride successfully, conversely, sodium carbonate, sodium hydroxide, and triethylamine did not appear to be efficient when used as bases.

A very interesting analytical method was used to establish the achievement of complete substitution on the phosphazene ring. The method was based on the analysis of the splitting pattern in the ^{31}P n.m.r. spectrum, due to the phosphorus-phosphorus coupling. This feature was only observed when the phosphorus atoms in the ring, being differently substituted, were not n.m.r. equivalent, and thus resulting in an AX_2 type spectrum. Conversely, when complete substitution was achieved the three phosphorus atoms appeared as a singlet.

Particularly interesting was the successful preparation of phosphazenes fully substituted by perfluoroalkylpolyether-alkoxy groups. Typically, the perfluoroalkylpolyether-alcohols we used are known as hydroxy-terminated Fomblin Y fluids (manufactured by Ausimont S.p.A.- Italy) of formula R_FCH_2OH (69), having an equivalent weight of 457 a.m.u. (69a), or of 900 a.m.u. (69b) and a C_3/C_1 units ratio of 36.8.

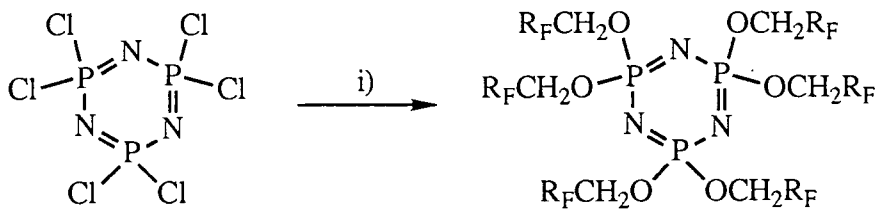
$$T\text{-}O\text{-}\ (CF(CF_3)CF_2O)_m(CFXO)_n\text{-}CFZ\text{-}CH_2OH$$

(69)

where: T = $-CF_3$, $-C_2F_5$, $-C_3F_7$; X = -F, $-CF_3$; Z = -F, $-CF_3$; m and n are numbers so that the n/m ratio ranges from 0.01 to 0.5 and the molecular weight is in the above mentioned range.

[68]

The perfluoroalkylpolyether-alcohols (69a) and (69b) were reacted with sodium hydride in tetrahydrofuran, to give the corresponding alkoxides, which were then reacted with hexachlorocyclotriphosphazene to give fully substituted derivatives (70a), (70b). These new materials were colourless, transparent , and very viscous liquids easy to purify by molecular distillation at temperatures above 200°C, 3 x 10^{-3} mbar, without undergoing decomposition. These liquids were not soluble in most organic solvents (ethers, chlorinated solvent), but they were perfectly soluble in trichlorotrifluoroethane (R-113) and and in its mixtures with other organic solvents (e.g.: R113-acetone).



(48)

(70a) R_F = Perfluoropolyether (69a)
(70b) R_F = Perfluoropolyether (69b)

i) $R_FCH_2O^-\ Na^+$, Ether, r.t -> reflux, (yield 70%)

[69]

2.B.6.f Degree and pattern of halogen replacement.

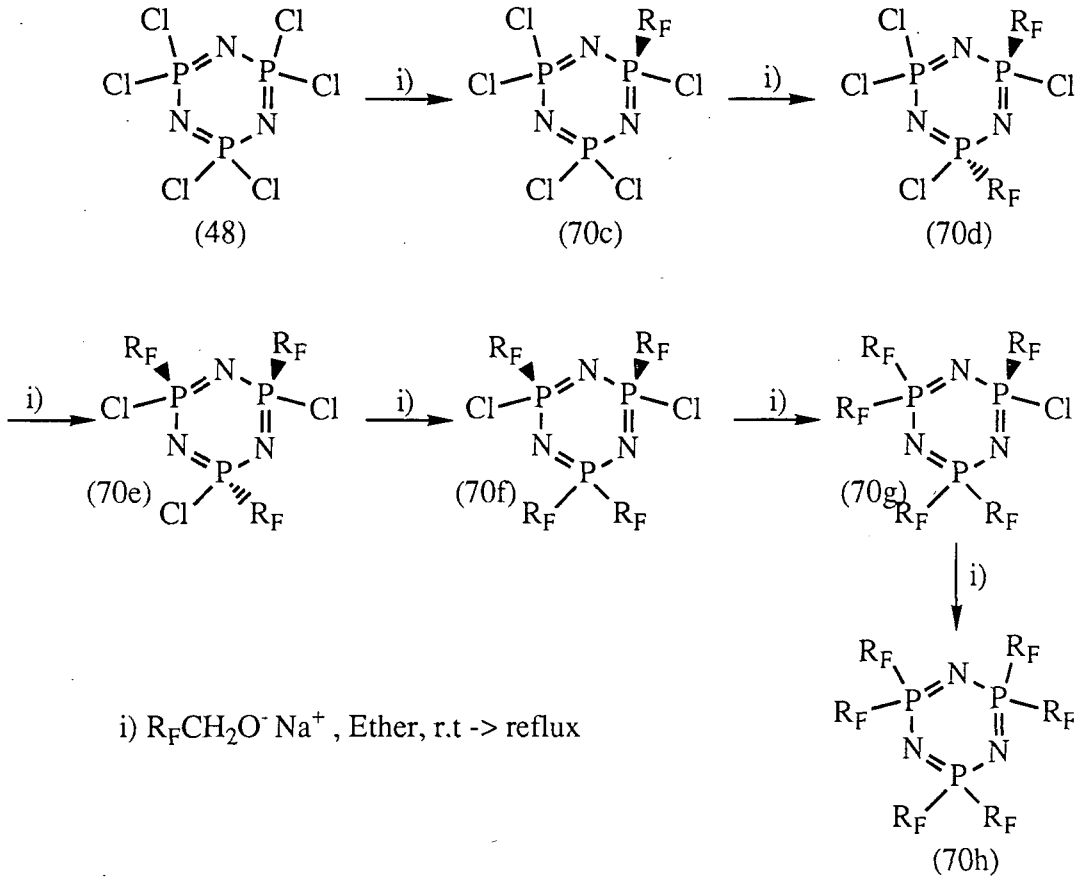
2.B.6.f.i Introduction.

Replacement of all chlorine atoms in hexachlorocyclotriphosphazene (48) occurs readily with low molecular weight substituents like methoxide, ethoxide, 2,2,2-trifluoroethoxide, but more drastic conditions are required to achieve complete substitution with isopropoxide or phenoxide ions.[35] However, partially substituted fluoroalkoxy derivatives such as $N_3P_3Cl_n(OCH_2CF_3)_{6-n}$ n = 1-5, can be prepared under very mild conditions using the correct reagent stoichiometry.[69,85] It has also been suggested[35] that the steric dimensions of the nucleophile influence the degree of halogen replacement with bulky side groups being the most difficult to introduce as substituents on the phosphazene ring. For example: replacement of chlorine in hexachlorocyclotriphosphazene by unbranched alkoxy groups takes place more rapidly than replacement by phenoxy or branched alkoxy groups.

Some patterns of successive replacement of chlorine atoms in hexachlorocyclotriphosphazene have been examined; thus dimethylamine reacts by non-geminal substitution[86-88], whereas ethylamine [89], potassium fluoride[90], and mercaptide[91], follow geminal patterns. The reaction between sodium 2,2,2-2,2,2-trifluoroethoxide and (48) has also been carefully studied[92]. Intrigued by the ease at which perfluoropolyether-alkoxy groups were able to displace the chlorine atoms in (48), we wanted to undertake a study in the effort to synthesise, separate, and identify the stereoisomers of the series $N_3P_3Cl_{6-n}(OCH_2R_F)_n$ where n = 1-6 and, if possible, to identify the pattern of chlorine replacement.

2.B.6.f.ii Discussion.

Reaction of hexachlorocyclotriphosphazene (48) with perfluoroalkylpolyether-alkoxide ($R_FCH_2O^-$) afforded the derivatives depicted in structures (70c)-(70h) (Scheme 9). Replacement of the first three chlorine atoms occurred at room temperature, giving (70e). However, heating at reflux for some hours was required to achieve fully substituted derivatives, and this immediately suggests a non-geminal pathway for the substitution.



Scheme 9. Suggested mechanism for replacement of chlorine by perfluoroalkylpolyether-alkoxy groups in (48).

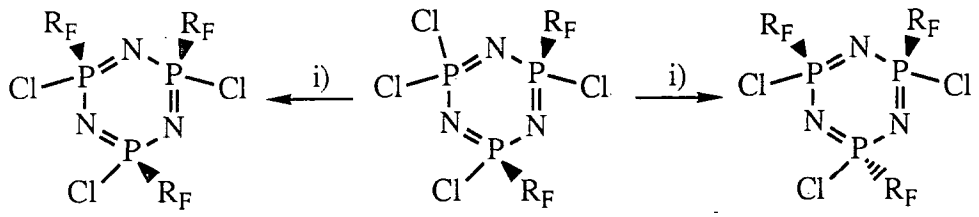
Structures (70c)-(70h) have been assigned on the basis of ^{31}P n.m.r. data. We find that all derivatives but (70e) show a first order spectrum typical of AX_2 systems (Table 10), where the chemical shifts difference values are larger than the spin-spin coupling constants. The A-type phosphorus atoms appear as triplets with relative integration 1, and the X-type phosphorus atoms as doublets with relative integration 2.

Compounds	Spectrum-type	δA (ppm)	δX (ppm)	J_{PA-PX} (Hz)
$[NPCl_2]_3$ (48)	A_3	20.5	-	-
$N_3P_3Cl_5(R_F)_1$ (70c)	AX_2	16.2	22.4	~67
$N_3P_3Cl_4(R_F)_2$ (70d)	AX_2	25.1	19.2	~69
$N_3P_3Cl_3(R_F)_3$ (70e)	AB_2	22.1	-	~7
$N_3P_3Cl_2(R_F)_4$ (70f)	AX_2	11.5	24.7	~85
$N_3P_3Cl_1(R_F)_5$ (70g)	AX_2	9.8	18.5	~70
$[NP(R_F)_2]_3$ (70b)	A_3	17.2	-	-

Table 10. N.m.r. data for structures (70b)-(70g)

The only exception is the tri-substituted compound (70e), which gave a signal that appears as a singlet. However, when the sweep-width of the acquisition is reduced

down to 20 ppm the phosphorus peak proves to be a doublet J = 7Hz, which may result from the incidental degenaration of an AB_2 system where $\Delta\delta<<J$. This important indication led us to conclude that (70e) is the trans-non geminal substituted derivative. Indeed, the cis-non geminal derivative(70j), would have appeared as a singlet, and the geminal trisubstituted derivative as an AMX system. It follows that if (70e) is the only tri-substituted derivative then bi-substituted derivative (70d) has to be its precursor. In fact, if we were in presence of isomer (70i), we would expect may be a mixture of the cis-tris (70j) and trans-tris (70e) non-geminal isomers[70]. At this point the reaction pathway probably proceeds with the nucleophile attacking the less hindered side of the ring in (70e) to give the cis-gem-tetrafluoroalkyl derivative (70f), however, so far, we have no experimental evidence to confirm this argument. Possibly, the ^1H coupling constants would have been of extreme utility in this case, but unfortunately, the effect of the different type of fluorinated chains caused line broadening and did not allow to show the fine phosphorus-proton coupling. To conclude, evidence suggests that the mechanism is consistent with a trans non-geminal S_N2 type substitution where the steric requirements, rather then electronic "cis-effect" are postulated to account for this pattern. Nevertheless we are unable to explain why compounds (70d) and (70f) show an AX_2 system type of spectrum rather than a AXY second order spectrum, as suggested elsewhere.[92]



(70j) (70i) (70e)

i) $R_FCH_2O^-Na^+$, Ether, r.t -> reflux

[70]

2.B.6.g Reactions and properties of fluoroalkoxyphosphazenes.

The previously obtained fluoroorgano-phosphazenes (50), (68), (70b), were tested under different conditions to evaluate their thermal stability, resistance to hydrolysis and interaction with Lewis acids.

2.B.6.g.i Thermal stability.

Compounds (50), (68), (70b) were heated at 320°C in an oxygen free atmosphere for three hours. Pyrolyses were carried out in quartz n.m.r. tubes to follow the course of the reaction by timed ^{31}P n.m.r. monitoring. Results reported in Table 11 indicate that the thermal stability of fluorinated phosphazene rings increase with the length of the perfluorinated chain.

Product	Starting material left (%)	Pyrolysis conditions	
		Temp (°C)	Time (Minutes)
$[NP(OCH_2CF_3)_2]_3$ (50)	84	320	180
$[NP(OCH_2C_3F_7)_2]_3$ (68)	90	320	180
$[NP(OCH_2(PfPE)_2]_3$ (70a)	100	320	180
$[NP(OCH_2CF_3)_2]_3$ (68)	35	420	20
$[NP(OCH_2(PfPE)_2]_3$ (70a)	49	420	20

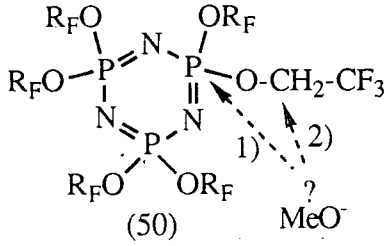
Table 11. Pyrolysis of organo-fluorophosphazenes

Pyrolysis under more severe conditions (420°C for 20 minutes) resulted in an extensive decomposition of the starting materials. N.m.r. data concerning the decomposition of $[NP(OCH_2(PfPE))_2]_3$ (70a) showed the presence of the typical AX_2-type system (two of the three phosphorus atoms are n.m.r. equivalent). This seems to suggest that decomposition would probably have its origin in the break-down of one of the substituents in a position near to the phosphorus atom, possibly with an analogy to what occurs to (64) when heated above 120°C (2.B.6.d.i). Detailed investigation of such a process was not carried out.

2.B.6.g.ii Hydrolytic stability.

The hydrolytic stability of derivatives (50), (68), (70a) was studied, and tests were carried out in basic 25% aqueous diglyme. Reactions at 70°C over 5 days did not show any sign of appreciable decomposition.

The alcoholysis of the P-O-C group in hexakis(2,2,2-trifluoroethoxy)cyclo-triphosphazene was also investigated to determine whether the attack of nucleophile would occur on the phosphorus or on the carbon atom. If the attack occurred on phosphorus, then 2,2,2-trifluoroethanol would have been produced, on the contrary, if the attack occurred on carbon, then ether (71) would have been generated.



1) CF_3CH_2OH

2) $CF_3CH_2OCH_3$

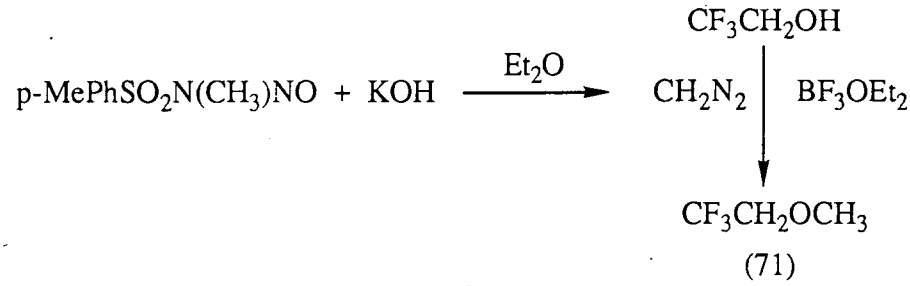
(71)

$R_F = -CH_2CF_3$

[71]

Thus, hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50) was reacted with sodium methoxide in methanol. The analysis of the volatiles showed the presence of the ether (71), only (GC/MS m/z^+ 114). The presence of ether (71) was confirmed by

comparison of the GC/MS data with those of an authentic sample of $CF_3CH_2OCH_3$ (71), obtained by reacting 2,2,2-trifluoroethanol and diazomethane in presence of BF_3OEt_2 as a catalyst.



[72]

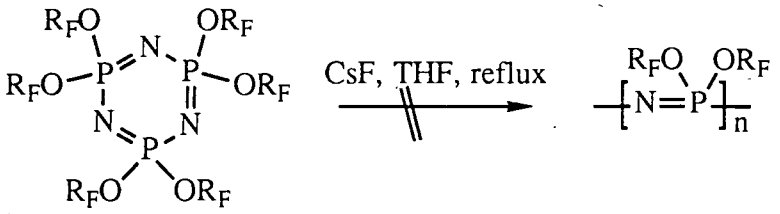
The ^{31}P n.m.r. of the residue was very complicated and its interpretation was not attempted. However, our results clearly demonstrate that at least part of the alcoholysis reaction occurs by nucleophilic attack on carbon, in agreement with Ferrar' s results[44]. Nevertheless, of course, we cannot exclude the possibility of some attack on phosphorus, consistent with other findings.[35]

2.B.6.g.iii Interaction with Lewis acids.

Perfluoroalkylpolyether-alkoxy substituted phosphazene (70a) was reacted with aluminium trichloride to study the possible formation of a π complex. Monitoring by ^{31}P n.m.r. showed no sign of interaction after one hour at room temperature. However, when the mixture was heated up to 100°C its colour changed into dark brown and the ^{31}P n.m.r. showed an up-field shift of 1 ppm for $[NP(OCH_2(PfPE))_2]_3$ (70a) and two small broad bands (15% integrated area) at +9 and -6 ppm. After prolonged heating, 4 hours, the bands took shape of a doublet (J = 81Hz) and a triplet (J = 74Hz) respectively in an approximately 1:1 ratio (30% integrated area). No change was noted in both ^{19}F and ^{1}H n.m.r. spectra. This result suggested that if a complex was formed the main effect was the up-field shift of the phosphorus atoms of the phosphazene ring (in agreement with the effect of electron-withdrawing groups interacting with the phosphazene ring). The interaction with the Lewis acid also afforded, to a lesser extent, decomposition to form species (corresponding to the doublet and the triplet) which have not been investigated further.

2.B.6.g.iv Attempted fluoride ion induced polymerisation.

We showed earlier in this work (2.B.6.b) that telomerisation of hexafluorocyclotriphosphazene was found to be induced by the presence of caesium fluoride. In a similar fashion, (50) and (70a) were reacted in presence of caesium fluoride using tetrahydrofuran as a solvent , and heated to temperature of reflux. Unfortunately, fluorinated phosphazenes (50) and (70a) do not undergo telomerisation.



RF = CH_2CF_3, CH_2PfPE

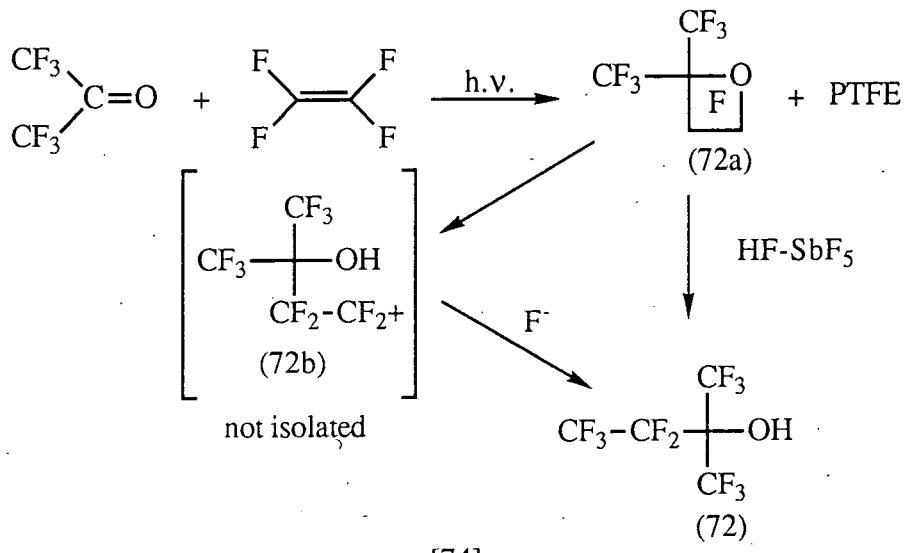
[72]

2.B.6.h Attempted syntheses of phosphazene substituted by tertiary fluorinated alcohols

We wanted to investigate the possibility of replacing the chlorine atoms in (48) by perfluorinated tertiary alcohols. To this end we synthesised the tertiary fluorinated alcohols following previously established routes.[93,94]

2.B.6.h.i Synthesis of the fluorinated tertiary alcohol $CF_3CF_2(CF_3)_2COH$ (72)

The alcohol (72) was synthesised in two steps. In the first hexafluoroacetone $(CF_3)_2CO$ and tetrafluoroethylene (TFE) were reacted under ultra-violet radiation in a Paterno-Buchi-type fashion to give oxetane (72a). In the second step oxetane (72a) underwent a super acid ($HF{\cdot}SbF_5$) catalysed ring-opening to give the corresponding alcohol (72). The oxetane ring-opening proceeds by protonation at oxygen followed by ring-opening and formation of the more stabilised carbocation (72b).

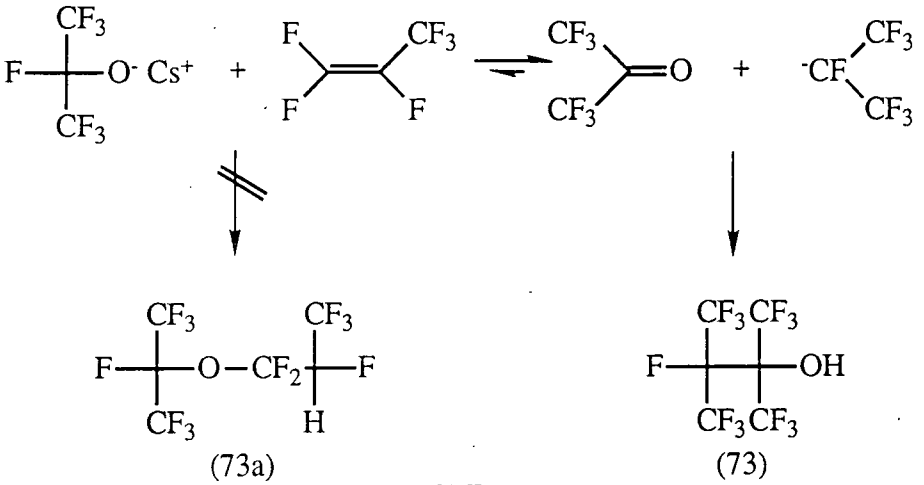


[74]

2.B.6.h.ii Synthesis of the fluorinated tertiary alcohol $(CF_3)_2CF(CF_3)_2COH$ (73).

Alcohol (73) was synthesised by reaction of hexafluoroacetone with an excess of caesium fluoride in sulpholane followed by addition of hexafluoropropene (HFP).

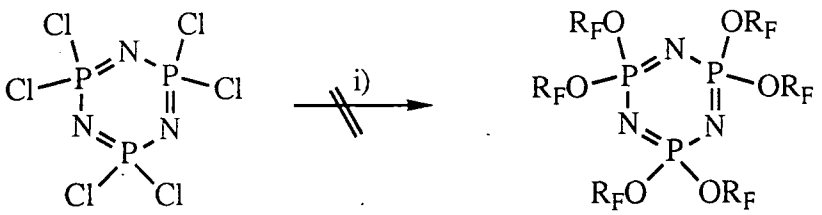
Initially, hexafluoroacetone formed a soluble complex with caesium fluoride, followed by addition of hexafluoropropene (HFP) to give alcohol (73). No evidence for the formation of ether (73a) was found, indicating that the complex was too weak a nucleophile to attack hexafluoropropene. The reaction pathway thus proceeded via formation of anion $(CF_3)CF^-$ (from HFP and caesium fluoride) followed by attack upon the hexafluoroacetone available at equilibrium.



(73a) (73)

[75]

Unfortunately the alkoxides obtained from alcohols (72) and (73) did not react with hexachlorocyclotriphosphazene (48) probably because they are very weak nucleophiles.



(48)

i) $R_FO^- Na^+$, Ether, r.t -> reflux,

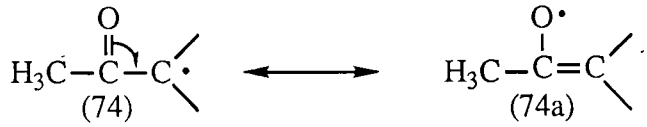
$R_F = (CF_3)_2CF(CF_3)_2C$, $CF_3CF_2(CF_3)_2C$,

[76]

2.C Gamma rays induced free radical reactions of hexafluoropropene and organo-phosphazenes.

2.C.1 Introduction.

Reactions involving free radicals have been the object of regular surveys of the literature[95] and reviews[96,97]. Particularly interesting is the use of high energy radiation for initiating the free-radical processes. They have the advantage of ease of handling, and operating in absence of a chemical initiator, and allow manipulation of the reaction conditions at will. Of course, the effect of various substituents on the carbon-hydrogen bond dissociation energy of has already been investigated[98]. The radical formation is favoured by α-substituents with π electrons (e.g.: ketones, esters, alkenes) or non bonded p electrons (e.g.: halogen, alkoxy) because of the possibility of radical delocalisation.



(74) (74a)

(75) (75a)

[77]

In particular, substituents such as alkoxy groups (75) make the radical very nucleophilic (75a) and more reactive towards fluorinated olefins, by donation of the non-bonded electron pairs on oxygen into the semi-vacant p_z orbital on carbon.

Conversely, radical formation is disfavoured by strongly electron-withdrawing α–substituents (e.g.: perfluoroalkyl groups).

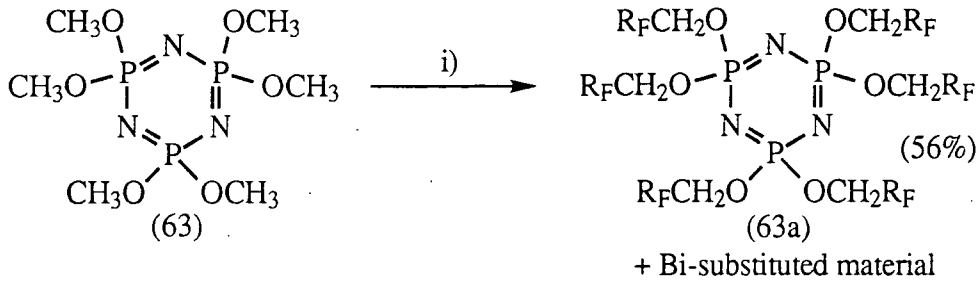
The aim of this work was to investigate the effect of phosphorus in the free radical perfluoroalkylation of methylene units activated by electron donating substituents. To this end, model compounds (63), (64), (66), (50), (48) were reacted with hexafluoropropene using gamma rays irradiation as initiator.

2.C.2 Results and discussion.

2.C.2.a Reaction of hexafluoropropene with $[NP(OCH_3)_2$.

Hexakis(methoxy)cyclotriphosphazene (63) $[NP(OCH_3)_2]_3$, was reacted with four fold excess of hexafluoropropene (HFP) under gamma rays irradiation for three weeks. The ^{31}P n.m.r. spectrum showed the presence of starting material at 20.9 ppm (20%), fully mono-substituted product at 17.2 ppm (56%) and of some not-identified species whose major peaks were at 12.4 and 11.9 ppm. These peaks were probably due to further addition of HFP to the fully mono-substituted derivative. This is also

consistent with the fact that an up-field shift of the signals is related to an increase in the electron-withdrawing capacity of the substituents attached to the phosphorus atom. The ^{19}F n.m.r. spectrum showed mainly the typical pattern for the $-CF_2-CFH-CF_3$ group (fluorines at the difluoromethylene (CF_2) group are diastereotopics and result in an AB system).



i) HFP, γ rays, r.t., 3weeks

$R_F = -CF_2-CFH-CF_3$

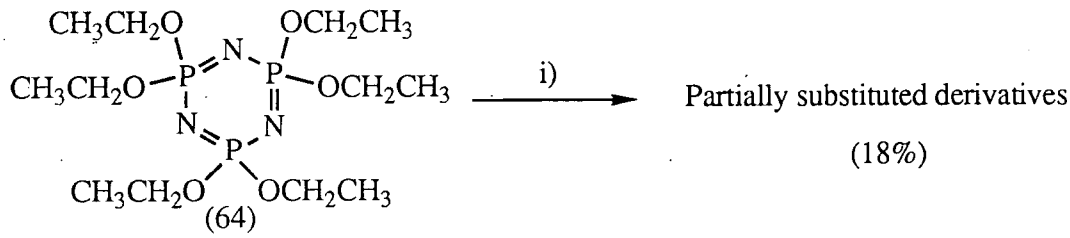
[78]

When the reaction was carried out in the same conditions, but with a 10 fold excess of hexafluoropropene, no starting material was left, and the peaks at 12.4 and 11.9 were the most relevant in the ^{31}P n.m.r. spectrum.

Though it was not possible to separate (column chromatography) and fully characterise the mixture of products, it is reasonable assume that the fluoroalkylation reaction proceeds to a certain extent of bi-substitution and may-be tri-substitution.

2.C.2.b Reaction of hexafluoropropene with $[NP(OCH_2CH_3)_2]_3$.

Hexakis(ethoxy)cyclotriphosphazene (64) $[NP(OCH_2CH_3)_2]_3$, was reacted with four fold excess of hexafluoropropene (HFP) under gamma rays irradiation for three weeks. ^{31}P n.m.r. analysis showed the presence of starting material (72%, 18 ppm) and some other peaks between -4 and +15 ppm which may be attributed to fluoroalkylated species. Attempts to separate the mixture were not carried out.



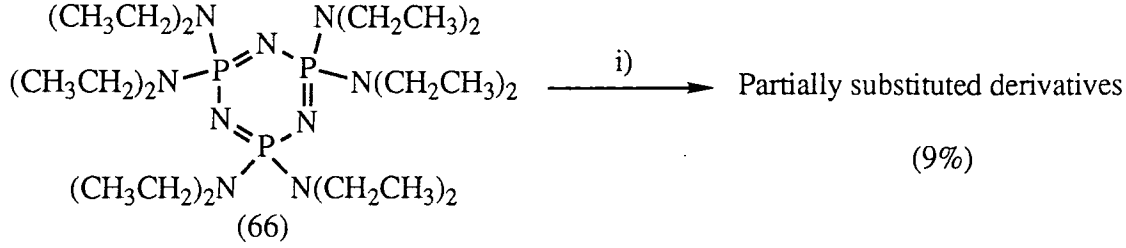
i) HFP, γ rays, r.t., 3weeks

[79]

2.C.2.c Reaction of haxafluoropropene with $[NP(N(CH_2CH_3)_2)_2]_3$.

Hexakis(diethylamino)cyclotriphosphazene (66) $[NP(N(CH_2CH_3)_2)_2]_3$, was reacted with 4 fold excess of hexafluoropropene (HFP) under gamma rays irradiation for three weeks. ^{31}P n.m.r. analysis showed the presence of starting material (91%, 22.3

ppm) and some other peaks between +7 and +16 ppm which may be attributed to fluoroalkylated species. Attempts to separate the mixture were not carried out.



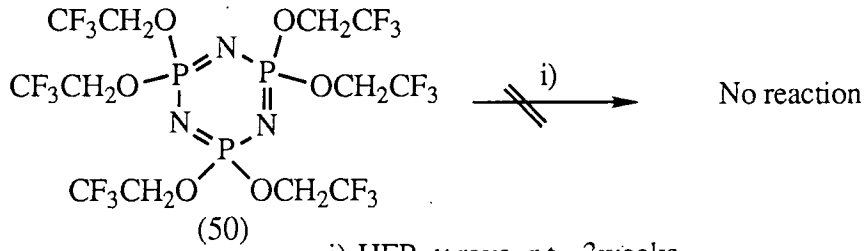
(66)

i) HFP, γ rays, r.t., 3weeks

[80]

2.C.2.d Reaction of hexafluoropropene with $[NP(OCH_2CF_3)_2]_3$.

Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50) $[NP(OCH_2CF_3)_2]_3$, was reacted with four fold excess of hexafluoropropene (HFP) under gamma rays irradiation for three weeks, but no sign of reaction could be detected by means of ^{31}P n.m.r. analysis.

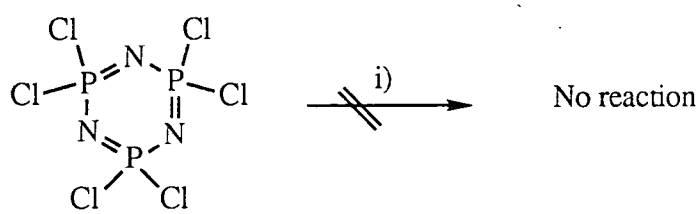


(50)

i) HFP, γ rays, r.t., 3weeks

[81]

The reactivity of hexachlorocyclotriphosphazene (48) $[NPCl_2]_3$ towards gamma ray initiated perfluoroalkylation was also investigated by reacting (48) with four fold excess of hexafluoropropene (HFP) for three weeks. However no sign of reaction could be detected by means of ^{31}P n.m.r. analysis.



(48)

i) HFP, γ rays, r.t., 3weeks

[82]

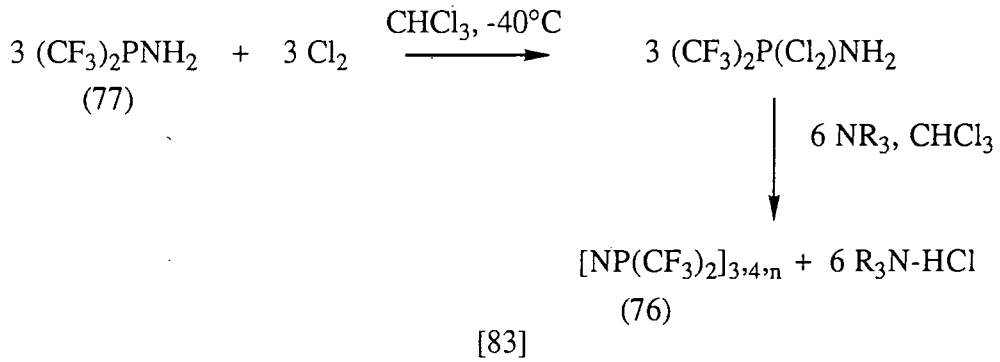
2.C.2.e Conclusions.

From the data obtained it seems that the reactivity towards free-radical addition is de-activated by electron-withdrawing substituents (perfluoroalkyl groups), but above all, it is strongly affected by the steric hindrance of the substituents on the phosphazenes: $[NP(N(CH_2CH_3)_2)_2]_3 < [NP(OCH_2CH_3)_2]_3 < [NP(OCH_3)_2]_3$.

2.D. Novel synthetic approaches to perfluoroalkylcyclotriphosphazenes.

2.D.1 Introduction.

The synthesis of trimeric bis(trifluoromethyl)phosphonitrile (76) $[NP(CF_3)_2]_3$ has already been object of investigation in the past[99], and its preparations was accomplished by chlorination of the corresponding bis-(perfluoromethyl)-dichlorophosphorus amides $(CF_3)_2PNH_2$ (77) followed by dehydrohalogenation with a tertiary amine [83].



[83]

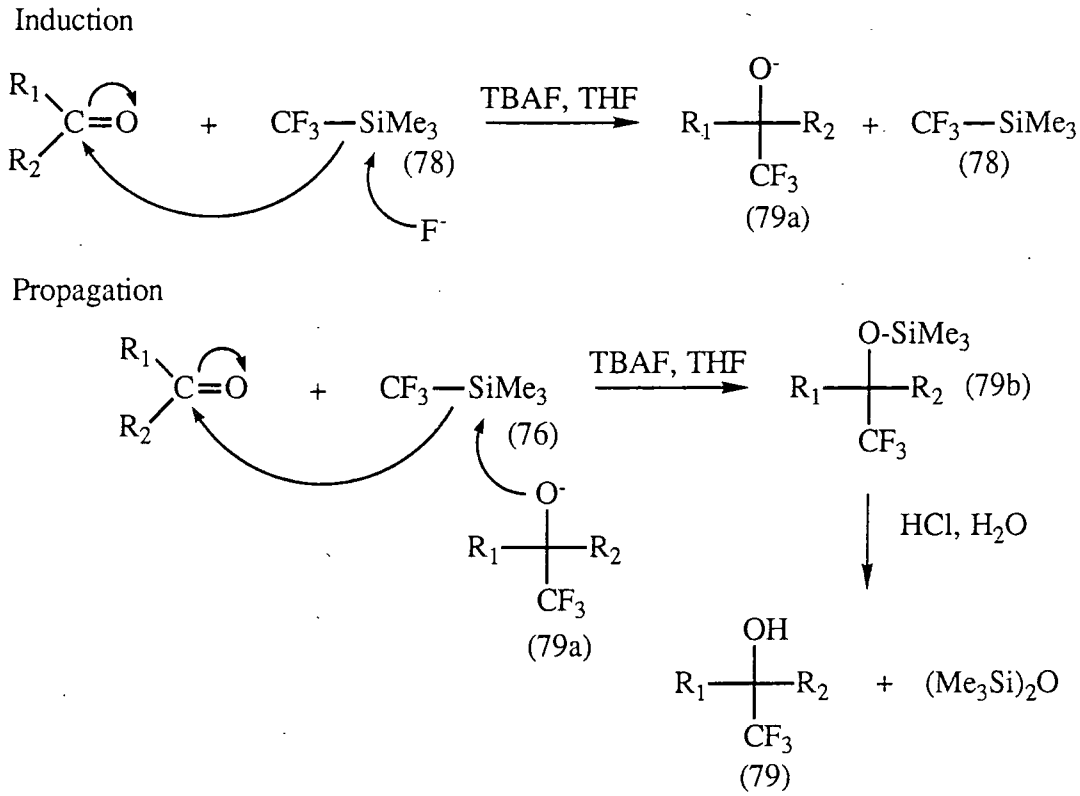
Unfortunately, though, this route is not very selective because it also allows the formation of other higher molecular weight bis(trifluoromethyl)phosphonitriles e. g.: $[NP(CF_3)_2]_{4,n}$.

Therefore, it was our intention to find a new selective synthetic approach to hexakis(trifluoromethyl)cyclotriphosphazene by direct trifluoromethylation. Although the literature abounds with examples for introducing perfluoroalkyl groups through organo-metallic reagents of zinc[100-102], calcium[103,104], manganese[105], magnesium[106], their application is very seldom effective, because of the great tendency for fluoride ion elimination and formation of trifluoromethane.

Recently Prakash and Olah reported [107] a very efficient nucleophilic trifluoromethylating agent: trifluoromethyltrimethylsilane (78) which reacts with carbonyl compounds to give the correspondent trifluoromethylcarbinol (79), in presence of catalytic amount of fluoride ion (Scheme 10).

2.D.2 Aim.

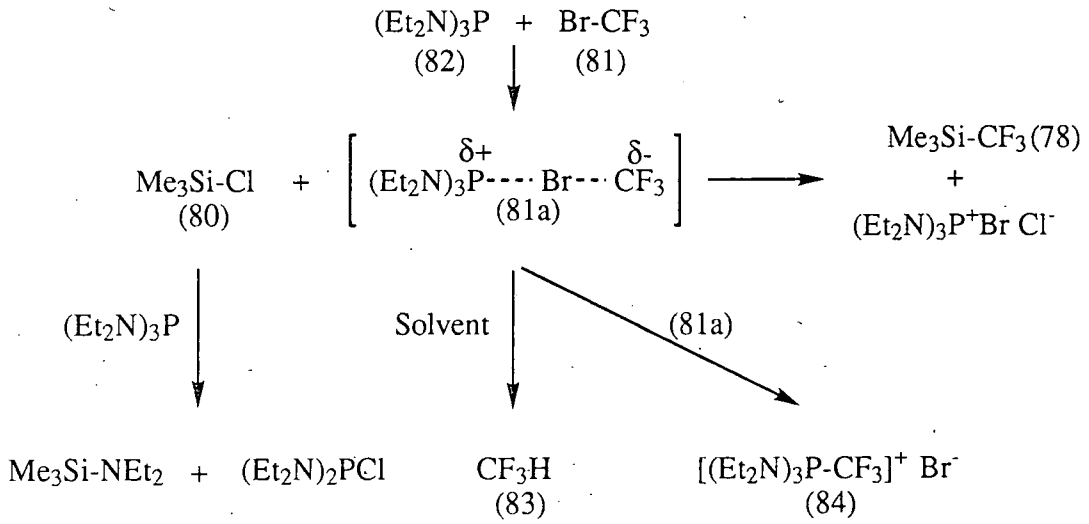
It was our aim to investigate the trifluoromethylation of the phosphorus-halogen bond in halophosphazene following a similar approach.



Scheme 10. CF_3SiMe_3: a new trifluoromethylating agent.

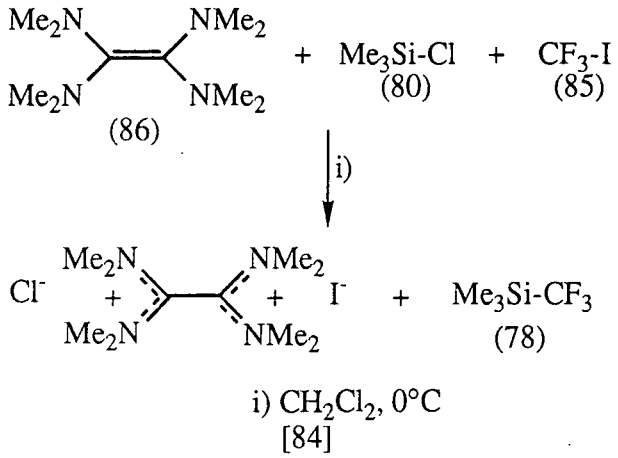
2.D.3 Synthesis of trifluoromethyltrimethylsilane.

Trifluoromethyltrimethylsilane (78) (Bp 45°C) was easily prepared[108] by reacting the electrophile trimethylsilylchloride (80) Me_3SiCl with the ready available bromotrifluoromethane (81), hexaethylphosphorustriamide (82) in benzonitrile (in about 80% yield). The reaction mechanism is described in Scheme 11. Note that intermediate (81a) may also react with the solvent to give trifluoromethane (83) and tris(diethylamino)trifluoromethylphosphonium bromide (84).



Scheme 11. Mechanism for the synthesis of Me_3SiCF_3

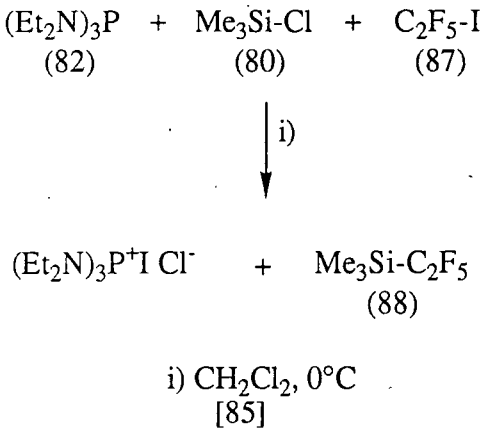
In addition, following the procedure reported in the literature,[109] trifluoromethyliodide (85) was reacted with trimethylsilylchloride (80) in presence of tetrakisdimethylaminoethylene (TDAE) (86) in dichloromethane to give (78) in comparable yields (78%).



i) CH_2Cl_2, 0°C
[84]

2.D.4 Synthesis of pentafluoroethyltrimethylsilane (88).

We found that the preparation of silyl derivatives can also be carried out reacting fluoroalkyl iodides with trimethylsilylchloride (Me_3SiCl) (80) in presence of tris(diethylamino)phosphine (82). Thus reacting pentafluoroethyl iodide (CF_3CF_2I) (87) with trimethylsilylchloride, pentafluoroethyltrimethylsilane (88) is obtained in a 78% yield.

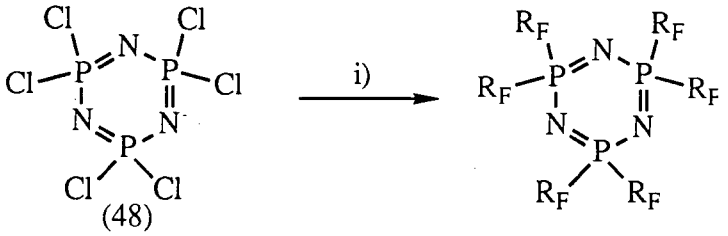


i) CH_2Cl_2, 0°C
[85]

2.D.5 Trifluoromethylation of halophosphazenes.

The original intention was to carry out trifluoromethylation on the most reactive system: hexachlorocyclotriphosphazene (48). To this end we reacted (48) with trifluoromethyltrimethylsilane and a catalytic amount of tetrabuthylammonium fluoride (TBAF). The reaction was monitored by means of ^{19}F n.m.r. which showed that very little replacement of the chlorines by the trifluoromethyl groups occurred. This suggested that chloride ion was not able to catalyse the reaction further. Addition of a stoichiometric amount of TBAF also proved to be ineffective because of the competing reaction which led to the replacement of chlorine by fluorine. The ^{19}F n.m.r. spectra of these mixtures

of products are of difficult interpretation due to the complex pattern of the phosphorus-fluorine coupling constants.



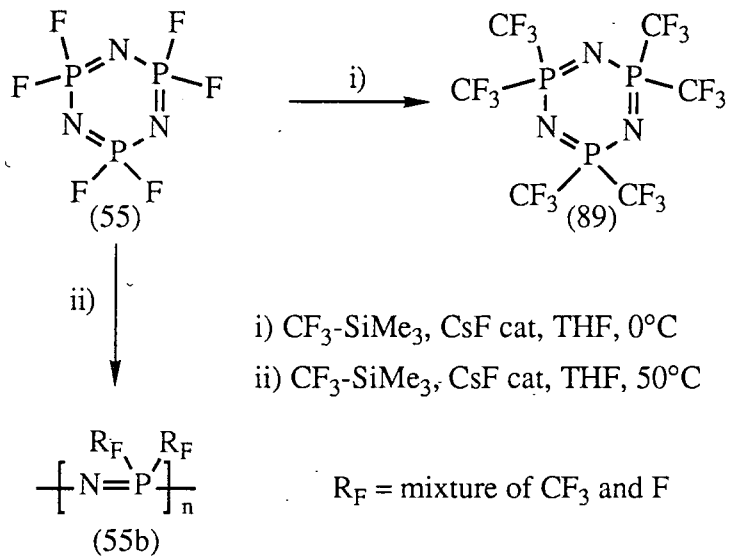
i) CF_3-$SiMe_3$, TBAF, THF

R_F = CF_3 and F

[86]

We then turned to trifluoromethylation of hexafluorocyclotriphosphazene (50) because this system offered the ease of working with a catalytic amount of fluoride ion, even though it had the disadvantage of being less reactive than (48).

Hexafluorocyclotriphosphazene (55) was reacted with an equimolar excess of trifluoromethyltrimethylsilane (78) in presence of catalytic amount of caesium fluoride under a different range of conditions.



i) CF_3-$SiMe_3$, CsF cat, THF, 0°C

ii) CF_3-$SiMe_3$, CsF cat, THF, 50°C

R_F = mixture of CF_3 and F

[87]

Replacement of fluorines by trifluoromethyl groups was carried out at 0°C to give hexakis(trifluoromethyl)cyclotriphosphazene in a mixture with high molecular weight fluorinated impurities. The ^{31}P n.m.r. spectrum of hexakis(trifluoromethyl)cyclotriphosphazene showed a septuplet at 3.9 ppm (J = 109 Hz) and its ^{19}F n.m.r spectrum showed a doublet at -74.7 ppm. It was found that the rate of trifluoromethylation at low temperatures (-10°C) was slow because it took almost 36 hours to achieve complete substitution. Of course, the rate of the reaction increased with the temperature, but above ca. 20°C fluoride ion was also able to induce oligomerisation of hexafluorocyclotriphosphazene to give (55b). Nevertheless, the oligomerisation process seemed to occur more readily when the phosphazene ring was very little substituted.

In fact, allowing the temperature to raise slowly from -10°C to room temperature, when the trifluoromethylation process was on its half way through, did not affect the course of the reaction. Whereas, when a suspension of caesium fluoride in tetrahydrofuran was heated up to 50°C before adding a mixture of trifluoromethyltrimethylsilane and hexafluorophosphazene, then oligomerisation and trifluoromethylation occurred simultaneously to give a very complicated mixture (the ^{31}P n.m.r. spectrum showed numerous peaks in the region between 10 and -20 ppm, and this is in agreement with the up-field shift of the signals, found when the molecular weight of the phosphazenes increases)

Tetrabutylammonium fluoride (TBAF) could also be used in place of caesium fluoride to achieve the same results.

2.D.6 Attempted direct perfluoroalkylation of hexachlorocyclotriphosphazene.

It has been shown that perfluoroalkyl iodides reacted with aroylchlorides in presence of tris(diethylamino)phosphine (82) in refluxing dichloromethane to give arylperfluoroalkylketones (90).[110]

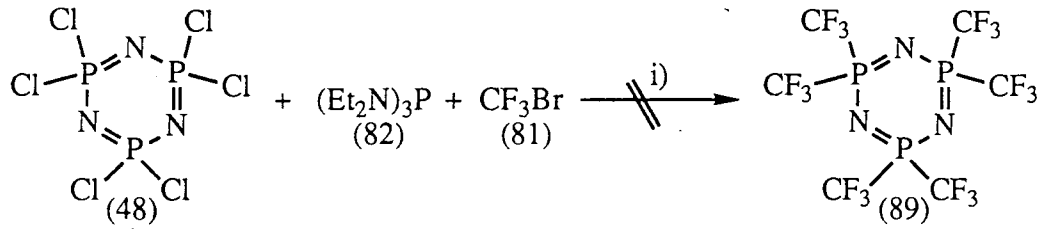
$$R_FI + ArCOCl + \underset{(82)}{P(NEt_2)_3} \xrightarrow{i)} \underset{(90)}{ArCOR_F}$$

i) CH_2CCl_2, reflux
[88]

Thus we investigated the reactions of hexachlorophosphazene (48) with trifluoromethyl-bromide (81) and -iodide (85), in presence of a base such as tris(diethylamino)phosphine (82) or tetrakisdimethylaminoethylene (86) to establish whether it was possible to carry out direct perfluoroalkylation of halophosphazenes.

2.D.6.a Trifluoromethylation using bromotrifluoromethane and tris(diethylamino)phosphine.

Hexachlorocyclotriphosphazene (48) was reacted with bromotrifluoromethane (81) in presence of tris(diethylamino)phosphine (82) in benzonitrile, but, to our surprise, we obtained mainly tris(diethylamino)trifluoromethylphosphonium bromide (84), trifluoromethane (83) and very little substitution onto the phosphazene ring.



i) PhCN, -30°C, r.t.

i)

$[(Et_2N)_3P\text{-}CF_3]^+ Br^-$ (84)

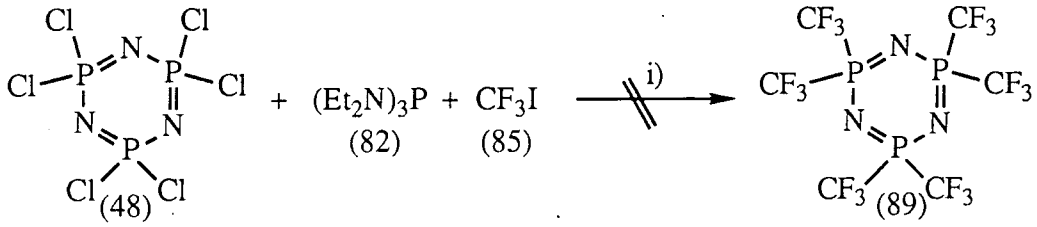
+

CF_3H (83)

[89]

2.D.6.b Trifluoromethylation using iodotrifluoromethane and tris(diethylamino)phosphine.

Hexachlorophosphazene (48) was then reacted with iodotrifluoromethane (85) in presence of tris(diethylamino)phosphine (82), but mainly highly involatile fluorinated by-products were obtained as the main product. Very little trifluoromethylation took place, and no evidence was found for the formation of trifluoromethyltris-(diethylamino)phosphonium iodide (84a).



i)

i) PhCN, -30°C, r.t.

High molecular weight material containing fluorine

[90]

2.D.6.c Study of the trifluoromethylhalides-tris(diethylamino)phosphine interactions.

For a better understanding of the results mention above, we investigated the nature of the interaction of both trifluoromethyl-bromide (81) and -iodide (85) with tris(diethylamino)phosphine (82) in various solvents (e.g.: benzonitrile, acetonitrile, dichloromethane, tetrahydrofuran, diglyme).

Reaction of bromotrifluoromethane (81) and tris(diethylamino)phosphine (82) in dipolar aprotic solvent with no acidic protons (e.g.: benzonitrile and diglyme) gave trifluoromethyltris(diethylamino)phosphonium bromide (84) and trifluoromethane (83) in a 9/1 ratio. The ratio was determined from the integration values of the respective

trifluoromethyl groups in the ^{19}F spectrum. However, when the reaction was carried out in aprotic dipolar solvents with acidic protons, only trifluoromethane (83) was obtained.

Reaction of trifluoromethyliodide (85) and tris(diethylamino)phosphine (82) in dipolar aprotic solvents always gave a complex mixture whose composition was not investigated further.

This seemed to be in contradiction with some previous work on a similar topic where trifluoromethyl iodide was reported to react with tris(dimethylamino)phosphine (82a) to give the trifluoromethylbis(dimethylamino)phosphine (84c) and tetrakis(dimethylamino)phosphonium iodide (84d).

$$\underset{(82)}{2\ P(NMe_2)_3} + \underset{(85)}{CF_3I} \xrightarrow{60°C} \underset{(84c)}{CF_3\text{-}P(NMe_2)_2} + \underset{(84d)}{I^{-}\ ^{+}P(NMe_2)_4}$$

[91]

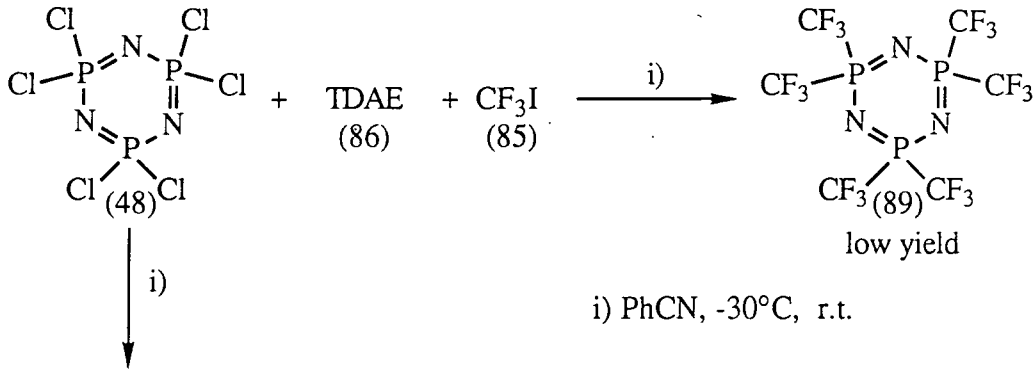
The ability of tris(diethylamino)trifluoromethylphosphonium bromide (84) as a trifluoromethylating agent was also investigated. To this end tris-(diethylamino)trifluoromethylphosphonium bromide (84) was separately heated in presence of methyl iodide and trimethylchlorosilane, but no reaction occurred, thus suggesting that the trifluoromethylation of (82) is an irreversible process.

2.D.6.d Conclusions.

Since trifluoromethyl bromide reacts with trimethylchlorosilane to give the trifluoromethyltrimethylsilane in presence tris(dimethylamino)phosphine, and reacts faster with tris(dimethylamino)phosphine than with hexachlorocyclotriphosphazene, it is reasonable to assume that the trifluoromethylating agent: trifluoromethyl bromide-tris(diethylamino)ethylene is a hard nucleophile which reacts preferentially with hard electrophiles, in agreement with the order of reactivity: trimethylsilylchloride > bromotris(diethylamino)phosphonium chloride > hexachlorophosphazene.

2.D.6.e Trifluoromethylation using iodotrifluoromethane and tetrakis(dimethylamino)ethylene (TDAE).

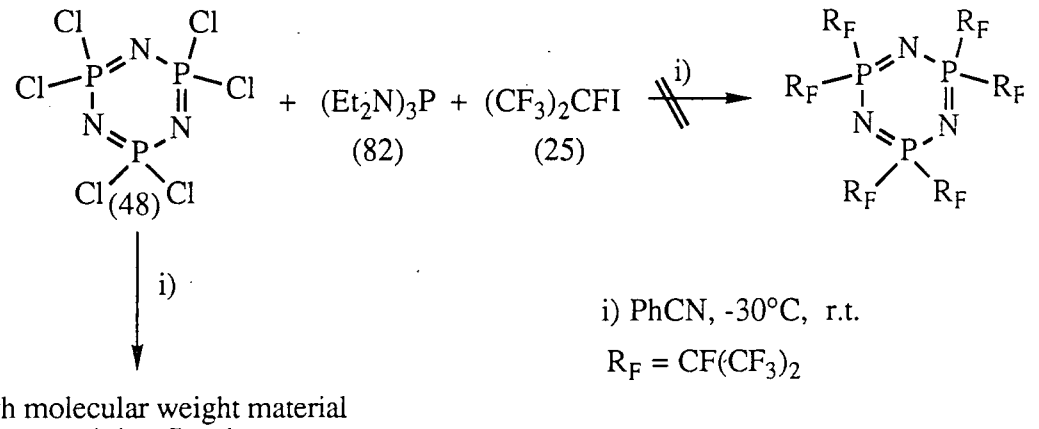
Reaction of hexachlorocyclotriphosphazenes (48) with trifluoromethyliodide (85) in presence of tetrakis(dimethylamino)ethylene led to partially trifluoromethylated phosphazene which could be detected by GC/MS analysis. However, most trifluoromethyliodide was converted in some high molecular weight fluorinated species.



[92]

2.D.6.f Perfluoroalkylation using heptafluoroisopropyl iodide and tris(diethylamino)phosphine.

Reaction of hexachlorocyclotriphosphazene (48) with heptafluoroisopropyl iodide (25) in presence of tris(diethylamino)phosphine (82) led to formation of involatile fluorinated derivatives and very little substitution on the phosphazene.

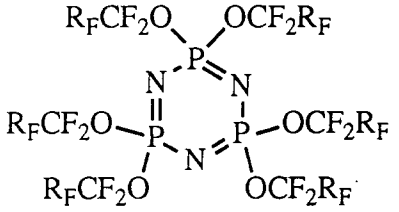


[93]

2.E Routes to per haloalkoxy phosphazenes.

2.E.1 Introduction.

As far as we know the synthesis of perfluoroalkoxy substituted phosphazenes of type (91) has never been reported. We are not quite sure whether this may be due to the instability of the P-O-CF_2-R_F group, which may easily decompose to form the phosphorus-fluorine bond and the corresponding fluorinated acyl fluoride R_F-C(O)F, or , may be, because of the difficulty in finding an appropriate synthetic equivalent for the fluoroalcohol.

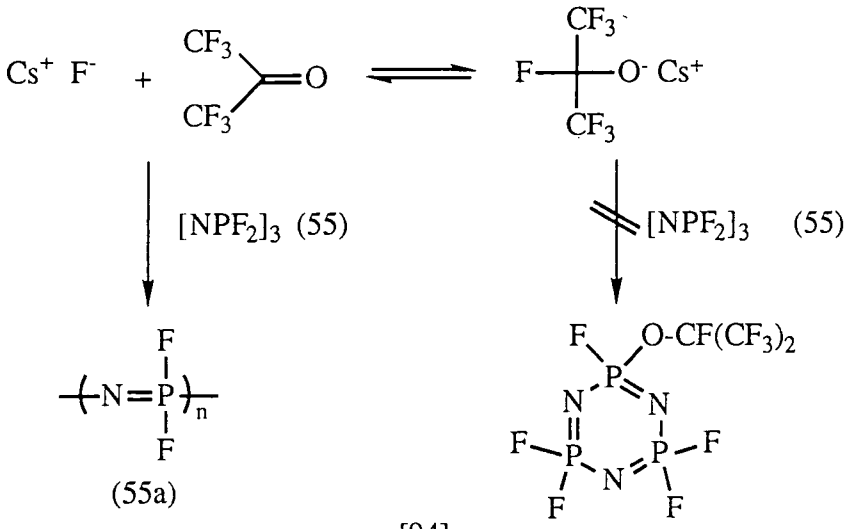


(91)

2.E.2 Reactions with hexafluoroacetone-cesium fluoride complexes.

We first tried to replace the chlorine atoms in the hexachlorocyclotriphosphazene (48) with perfluoroalkoxy groups (R_FCF_2O-). As opposed to what is known for hydrogenated systems, the synthetic equivalents for these groups are not the corresponding perfluorinated alcohols of type R_FCF_2OH, because of their inherent instability to lose hydrogen fluoride and give the corresponding acyl fluoride ($R_FC(O)F$). Alkali metal fluorides which complex with fluorinated ketones, such as hexafluoroacetone, are used instead. These complexes tend to behave like fluorinated alkoxides, but their application in the syntheses is often difficult because they are weak nucleophiles and, at temperatures necessary for reactions to occur, they tend to give back the fluoro-ketone and fluoride ion, which, in its turn, may act as a nucleophile in a competing reaction [94]. To avoid fluorination of hexachlorophosphazene (48) taking place, we preferred to react the hexafluoroacetone-cesium fluoride complex with hexafluorophosphazene, in spite of the lower reactivity of the latter towards nucleophilic displacement of fluorines, as it was shown before (2.B.5.a).

Thus, hexafluorocyclotriphosphazene (55) was reacted with a twelve fold excess of hexafluoroacetone and a catalytic amount of caesium fluoride in a range of temperatures varying from 0°C to 70°C. At temperatures below 20°C, the ^{31}P and ^{19}F n.m.r. monitoring did not show any sign of reaction, but when the temperature was raised up to 70°C fluoride ion catalysed oligomerisation of hexafluorocyclotriphosphazene took place, and indeed, this proves that fluoride ion becomes available as a nucleophile at relatively high temperatures despite the excess of hexafluoroacetone.



[94]

2.E.3 Reactions with elemental fluorine.

Having been thwarted in this first direct attempt to introduce perfluoroalkoxy groups on the phosphazenes, we turned to fluorination of hexakis(2,2,2-trifluoroethoxy)-cyclotriphosphazene (50) with elemental fluorine. We considered the potential inertness of the starting material towards direct fluorination due to the poor electron density on the protons, resulting from the electron withdrawing effect of the fluorine atoms and which prevents fluorine electrophilic radicals from reacting according to the mechanism firstly proposed by Miller.[111-113]

$$RH + F_2 \longrightarrow R\bullet + HF + F\bullet \qquad \Delta H = 4.1 \text{ Kcal/mol}$$

[95]

This problem could be easily overcome by increasing the concentration of fluorine radicals by using UV irradiation which promote the alternative initiation step[96].[9]

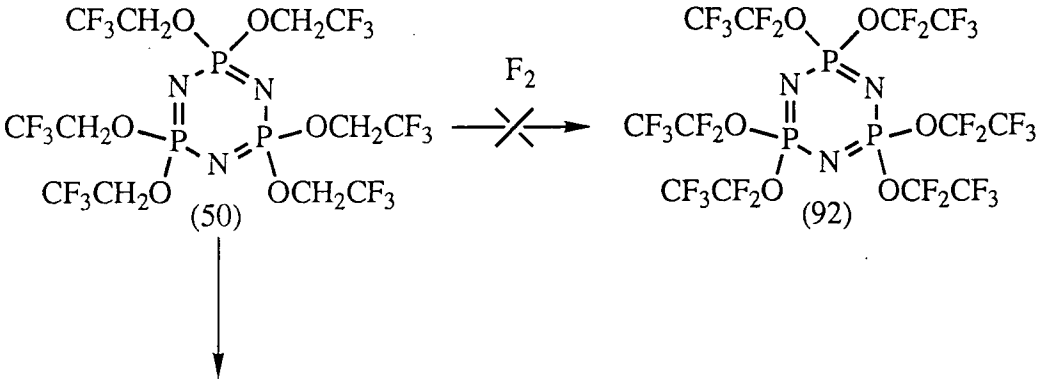
$$F_2 \longrightarrow 2\,F\bullet \qquad \Delta H = 37 \text{ Kcal/mol}$$

$$RH + F\bullet \longrightarrow R\bullet + HF$$

[96]

However, before doing the the reaction we also looked up in the literature some information about the U.V. spectrum of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50),[71] which indicated an absorption maxima in the near ultra-violet region below 200 mμ. Nonetheless, inertness of (50) to ultra-violet radiation was investigated in presence of acetone as a sensitiser (10%) and carbon tetrachloride, but analysis by ^{31}P n.m.r. spectrum of (50) did not show any sign of reaction after two days of exposure to U.V. light.

Direct fluorination was carried out by bubbling fluorine (diluted with nitrogen in 50% mixture) down a FEP (tetrafluoroethylene-propylene copolymer) capillary tube into a quartz tube containing the substrate. The mixture was then stirred thoroughly to disperse the bubbles of gas while the tube was being irradiated with an ultra-violet lamp.



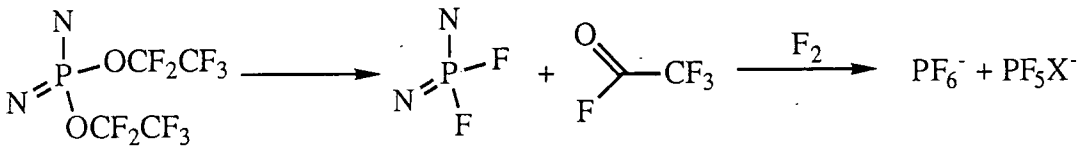
PF_6^- + PF_5X^- X = substituent

[97]

To our surprise, the major product of the reaction was PF_6^- (ca. 60%) δ_P -144 , sept, J_{PF} = 705 Hz, δ_F -72.9, d, J_{FP} = 705 Hz together with a species of the type PF_5X^- where X is a substituent δ_P -144, sex, J_{PF} = 760 Hz, δ_F -58.63, d, J_{FP} = 760 Hz, and some other degradation products whose signals appeared in the region between 1 and -29 ppm in the ^{31}P n.m.r spectrum. The nature of these degradation products was not investigated further.

The reaction was then repeated in less drastic conditions, using fluorine in a 10% mixture with nitrogen, without exposing the reaction mixture to ultra-violet radiation. Nevertheless, similar results were obtained.

Up to this stage a definite mechanism for the reaction could not be ascertained. However, on the assumption that fluorine was able to replace the two protons of the trifluoromethoxy group, to give the perfluoroalkoxy intermediate (92), we think that the degradation may proceed via a 1,3-fluorine shift, to form the P-F bond and the corresponding acyl fluoride. The fluorophosphazene obtained reacts further with fluorine to afford highly coordinated phosphorus fluoride anions.



(92)

[98]

This idea is based on the fact that this process is energetically favoured by the formation of the phosphorus fluorine bond (117 Kcal mol^{-1}) and on the precedent that analogous degradation pattern is typical of perfluoroalkoxy derivatives of silicon().

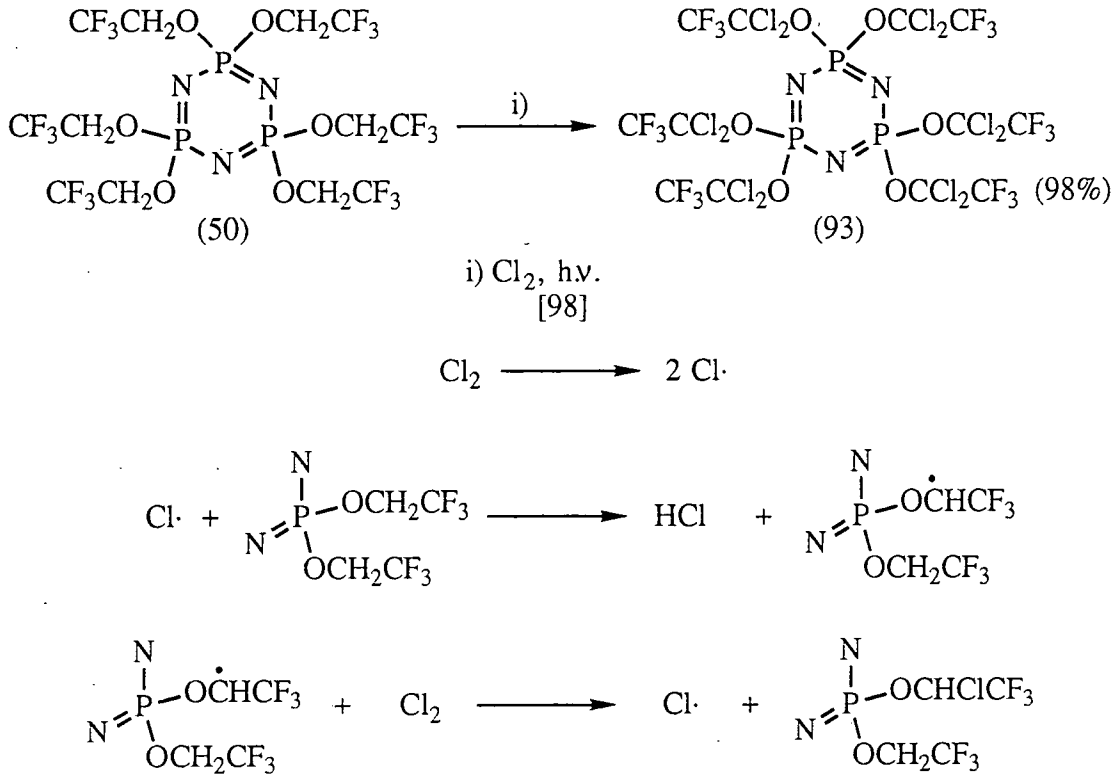
2.E.4 Reactions with elemental chlorine.

2.E.4.a Synthesis of hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)-cyclotriphosphazene.

We showed that direct fluorination of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene did not work because of the high reactivity of

fluorine towards the substrate. Thus, in order to obtain the perfluoroalkoxy derivatives (91), we thought of converting perfluoroalkoxyphosphazenes (50) into the chloro derivative (93), followed by replacement of chlorine by fluorine.

Chlorination of partially fluorinated phosphazenes is known[114]. Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50) was reacted with chlorine in carbon tetrachloride into a Pyrex Rotaflo tube under ultra-violet radiation to give hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)cyclotriphosphazene (93) in excellent yields. The mechanism for the chain reaction is reported in Scheme 12.



Scheme 12. Mechanism of the chlorination

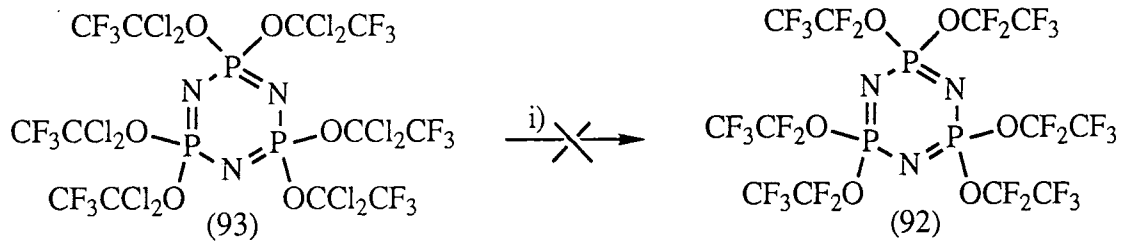
2.E.4.b Thermal stability of hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)-cyclotriphosphazene.

The thermal stability of (93) was investigated. A small sample of (93) was heated for 24 hours at 200°C in a non oxidising atmosphere. Analysis by ^{19}F and ^{31}P n.m.r. did not show any sign of decomposition. The thermal stability of (93) was remarkable, because (93) had a chlorine atom in the α-position with respect to oxygen, which, in theory, could have favoured the formation of the phosphorus-chlorine bond and the corresponding acyl chloride.

2.E.4.c Replacement of chlorine for fluorine.

A variety of methods were investigated to bring about replacement of chlorine for fluorine in hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)-cyclotriphosphazene (93). They

included acidic fluorinating agent (antimony trifluoride, antimony pentafluoride), which were expected to assist the removal of chlorine as chloride ion, and basic fluorinating agents (caesium fluoride), under various conditions. However, so far, they all proved to be unsuccessful.



(93) (92)

i) Fluorinating agents = SbF_3, SbF_5, CsF

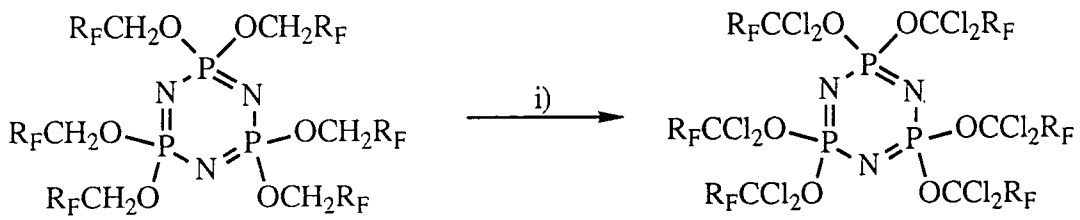
[100]

The difficulty in effecting the replacement using acidic fluorinating agents is probably due to the poor ability of chlorine as an electron-donor associated with the destabilisation of the carbocationic transition state induced by the trifluoromethyl group.

Reaction of (93) with antimony pentafluoride in refluxing perfluoropolyether (Galden 70 fluid, Bp. 80°C) led instead to extensive decomposition of both starting material and solvent. This seemed to indicate that when fluorination takes place intermediate (92) immediately undergoes decomposition.

2.E.4.d Synthesis of hexakis(dichloroperfluoroalkylpolyether-)-cyclotriphosphazene

Considering the ease of chlorination of (50), we concentrated on the synthesis of other chlorinated derivatives. In particular, we were intrigued by the effect of a long perfluorinated chain on the chlorination of the methylene unit.



(70b) (94)

R_F = Perfluoropolyether (69b)

i) Cl_2, R-113, hν.

[101]

Thus we reacted hexakis(dihydroperfluoroalkylpolyether-alkoxy)cyclotriphosphazene (70b) and chlorine in 1,1,2-trichloro-2,2,1-trifluoroethane (R-113) were irradiated for 48 hours to give hexakis(dichloroperfluoroalkylpolyether-alkoxy)cyclotriphosphazene (94) in quantitative yields, and this proves that the hindrance of the perfluorinated chain has no effect on the reaction. To achieve complete replacement of

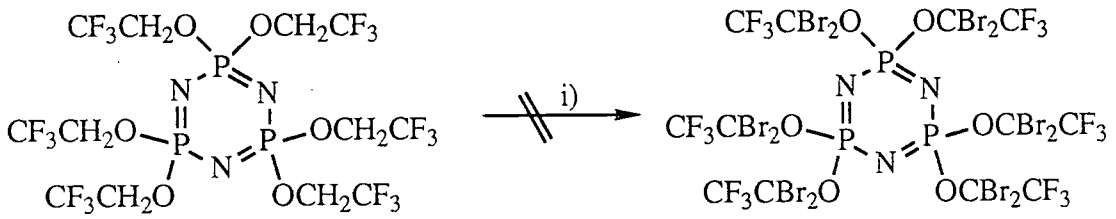
protons by chlorines, though, the reaction mixture had to be homogeneous and, therefore, the use of R-113 as a solvent was crucial, in fact when the reaction was carried out using carbon tetrachloride as a solvent the chlorination was very little effective.

2.E.4.e Thermal stability of hexakis(dichloroperfluoroalkylpolyether-alkoxy)cyclotriphosphazene.

As for (93) we investigated the thermal stability of (94) to establish the role of the long perfluorinated chain on the degradation. Prolonged heating of a small sample of material at 200°C in a non oxidising atmosphere did not appear to effect phosphazene (94).

2.E.5 Reactions with elemental bromine.

Having failed in our attempts to displace chlorine for fluorine efficiently we wanted to attempt the synthesis of perfluoroalkoxy phosphazenes by bromination of precursor (50) followed by replacement of bromine for fluorine,bromine being a better leaving group than chlorine. To this end hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50) was reacted with bromine in carbon tetrachloride.



(50)

i) Br_2, CCl_4, hν.
[102]

A variety of different reaction conditions were investigated, including simple irradiation with a tungsten lamp and ultra-violet irradiation at relatively high temperatures (80°C); however they all turned out to be quite ineffective affording nothing more than a mixture of partially brominated derivatives of (50).

2.F Fluorinated phosphazenes as potential additives for perfluoropolyether based fluids.

2.F.1 Introduction.

With the development of advanced high performance aerospace systems, designed to operate at consistently elevated temperatures to improve both efficiency and power new fluids and lubricants are needed. The strict requirements that they have to meet require withstanding severe thermal and oxidative stress at temperatures higher than 260°C without appreciable degradation. High temperature thermal and oxidative stability must be accompanied by good temperature flow characteristics and satisfactory lubricating properties. State of the art materials such as super refined mineral oils, diesters, and polyphenylethers lack at least one of the important properties required for the use in a high temperature lubricant system which is open to atmosphere. For example, the super refined mineral oils have good low temperature flow properties, excellent lubricating ability, and are thermally stable at 370°C, but they have poor oxidative resistance at high temperatures. The esters which meet current gas turbine engine oil requirements, cannot be expected to survive oxidatively at the 250°C level. The polyphenylether based fluids have shown good oxidative and thermal stability, but have high pour points and relatively poor lubricating ability. Nevertheless, and most important of all, none of the aforementioned fluids is non flammable. This property is fundamental in the hydraulic fluid area, because aircraft are vulnerable to any open fires resulting from leaks in the hydraulic lines or components within the aircraft themselves as it may happen when involved in combat or during both take off and landing. Hence, primarily because of their thermal stability, chemical inertness and non flammability, it has been recognised that perfluoroalkylpolyether fluids have great potential use as lubricants for gas turbine engines, non flammable hydraulic fluids, greases compatible with liquid oxygen, liquid coolants and general purpose lubricants in both military and civil aircraft [115].

In particular, the perfluoroalkylpolyether fluids which we are interested in have the general formula (95):

$$A\,O\,(\,CF_2\,CF_2\,O\,)_m\,(\,CF_2\,O\,)_n\,B \qquad (95)$$

where A and B may be the same or different and each may be CF_3- or C_2F_5-, m and n are integers whose sum is between 2 and 200 and the ratio n/m is between 0.1 and 10. The ($CF_2\,CF_2\,O$) and ($CF_2\,O$) units are randomly distributed in the polyether chains. These fluorinated polyethers are obtained with a wide molecular-weight distribution and it is usual practise to fractionate the mixture to obtain a product having a desired average molecular weight and kinematic viscosity (in particular 130 cS at 38°C).

These types of fluorinated-polyethers are made commercially available by Ausimont S.p.A., Milan, Italy, under the designation of Fomblin Z.

However, although such fluids have been found to possess superior lubricating characteristics for a short period of time , a serious drawback in their use results from the fact that certain metals, i.e. those present in aircraft engine components, are corroded by these fluorinated fluids at elevated temperatures in an oxidative environment. For example, when the fluids are used as lubricants for mechanical components composed of mild steel, serious corrosion occurs at temperatures of about 287° to 315°C. Stainless steel, titanium and titanium alloys are attacked by the fluorinated fluids at a temperature of about 315°C. Moreover, at elevated temperatures, particularly in an oxidising atmosphere the perfluorinated fluids themselves undergo degradation to the detriment of continued lubricating capacity.

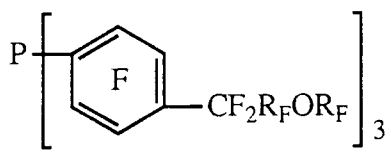
An ideal lubricant composition would be one having a relatively constant viscosity so that it is flowable and pumpable over a wide temperature range (-45° to 315°C), therefore in operating conditions perfluoropolyether fluids are formulated with thickeners such as perfluoroethylene-propylene copolymer (FEP) or polytetrafluoroethylene (PTFE), and corrosion and degradation inhibitors.

2.F.2 Degradation inhibitors.

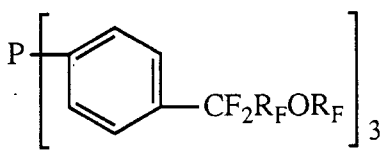
A wide range of phosphorus containing compounds including perfluoroarylphosphines and perfluorinated phenoxyphenylphosphines have been shown to be anti-corrosion, anti-oxidising and thermally stabilising additives [116].

Nevertheless, their activity has not been entirely satisfactory because they are generally poorly soluble in perfluorinated fluids at low temperature and possess high volatility characteristics for long term, high temperature applications.

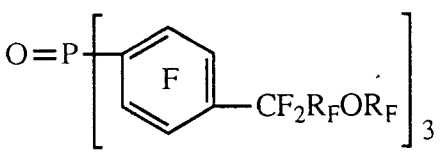
More recently, aromatic phosphines with perfluorinated alkylether substituents (96a)-(96c) have been reported in the patent literature[117,118].



(96a)



(96b)



(96c)

R_F = Perfluoroalkylether group

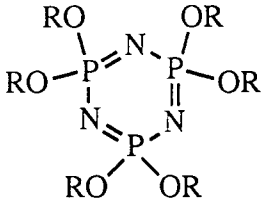
[103]

They provide a better temporary solution achieving little corrosive effect upon titanium, ferrous and titanium alloys, and virtually no reduction of lubricant properties at the elevated temperatures, even though the base fluid itself was severely degraded.

The current challenge is to provide another type of phosphorus based additive for a lubricant composition which at high temperature and in oxidising conditions, has little, if any, corrosive effect upon ferrous and titanium alloys and which undergoes substantially no degradation (possibly including the lubricating fluid itself) when exposed to those metals, yet with a relatively constant viscosity over a wide temperature range.

2.F.3 New potential additives.

The ideal candidates for this purpose seem to be the cyclotriphosphazene systems. In general, phosphazenes of structure $[NP(OR)_2]_3$ are among the most stable phosphorus-nitrogen derivatives known, the extent of their stability to heat and hydrolysis depending on the nature of the substituents OR. Moreover, the fact that the six chlorine atoms are potentially replaceable by a mixture of nucleophiles indicates how versatile the cyclotriphosphazene ring may be. In fact, in principle, it is possible to combine in a suitable ratio both substituents with stabilising activity and substituents which can make the phopshorus based additives soluble in perfluorinated fluids, such as perfluoroalkylpolyethers.



OR = perfluoroalkylethers and aromatics in a suitable ratio
[104]

We synthesised a number of potential additives (Table 10) to investigate the role of the phosphazene ring and of the substituents in the stabilisation of lubricating compositions in the presence of metals. The perfluoroalkylpolyether-alcohols we used were hydroxy-terminated Fomblin Y fluids of formula R_FCH_2OH (69), having an equivalent weight of 457 a.m.u. (69a), or of 900 a.m.u. (69b) and a C_3/C_1 units ratio of 36.8.

$$T\text{-}O\text{-}\ (CF(CF_3)CF_2O)_m(CFXO)_n\text{-}CFZ\text{-}CH_2OH$$

(69)

where: T = $-CF_3$, $-C_2F_5$, $-C_3F_7$; X = -F, $-CF_3$; Z = -F, $-CF_3$; m and n are numbers so that the n/m ratio ranges from 0.01 to 0.5 and the molecular weight is in the above mentioned range.

(70a) R = PfPE (69a)

(70b) R = PfPE (69b)

(96a) R = PfPE (69a) and phenol in a ca. 3.2 to 2.8 ratio.

(96b) R = PfPE (69b) and phenol in a ca. 2.2 to 3.8 ratio.

(96c) R = PfPE (69b) and phenol in a ca. 3.7 to 2.3 ratio.

(96d) R = PfPE (69b) and phenol in a ca. 5.4 to 0.6 ratio.

(97) R = PfPE (69b) and cyclohexanol in a ca. 3.4 to 2.6 ratio.

(98) R = PfPE (69b) and 2,2,2-trifluoroethanol in a ca. 2.8 to 3.2 ratio.

(99) R = PfPE (69b) and chlorine in a ca. 3.2 to 2.8 ratio.

(100) R = PfPE (69b) and 4-methoxyphenol in a ca. 3.6 to 2.4 ratio.

(101) R = PfPE (69b) and 3-nitrophenol in a ca. 3.9 to 2.1 ratio.

(102) R = PfPE (69b) and 2-methoxy-5-nitrophenol in a ca. 3.5 to 2.5 ratio.

(103) R = PfPE (69b) and 3-(N,N-dimethylamino)phenol in a ca. 3.3 to 2.7 ratio.

(104) R = PfPE (69b) and α-naphthol in a ca. 5.4 to 0.6 ratio.

(105) R = PfPE (69b) and catechol in a ca. 5.8 to 0.2 ratio.

(106) R = PfPE (69b) and aniline in a ca. 5.3 to 0.7 ratio.

(107) R = PfPE (69b) and α-naphthylamine in a ca. 5.2 to 0.8 ratio.

Table 10. Potential additives for perfluorinated fluids.

2.F.4 Experimental considerations.

The synthesis of the potenitial additives can be illustrated as follows:
An excess of the two nucleophiles was singularly treated with a base in a dipolar aprotic solvent (in particular diethylether and glymes). The bases which proved to work best were sodium hydride or sodium. The so obtained mixtures were then reacted with hexachlorocyclotriphosphazene (48) in any order, so far we have not found any evidence to suggest that the step sequence was critical. Furthermore, as an alternative, the reaction could also be carried out in a single step by reacting the hexachlorocyclotriphosphazene (48) with a previously obtained mixture of the two alkoxides. The reaction temperature was crucial, thus heating to temperature of reflux was necessary to achieve complete substitution on the phosphazene ring. The mixture of products was extracted in trichlorotrifluoroethane (R-113) and then both solvent and perfluoroalcohol in excess removed under reduced pressure. The mixture was distilled under vacuum by means of a molecular distillation apparatus and the coloured by-products formed during the course of the reaction were removed by passing the mixture through a column containing a high quality grade silica with a particle size of 40-63 mm. Silica was previously treated with trichlorotrifluoroethane to removed the plasticiser contained. Nevertheless, a small amount of plasticiser was found in the purified product, but this was easily removed by extraction in dichloromethane where the perfluoropolyether derivatives were not soluble.

Characterisation was carried out by C, H, N, P, and Cl elemental analysis, by IR, by ^{1}H, ^{19}F, and ^{31}P n.m.r.. In particular ^{1}H NMR was essential to establish the ratio perfluoropolyetheralkoxy/other substituent on the phosphazene ring. Calculations were carried out comparing the area of the peak corresponding to the methylene group of R_F-CH_2 -O divided by 2 (the number of protons) and the area of the peak corresponding to a known group of the other substituent divided by the number of protons in it. The ratio was then normalised and expressed as a fraction of 6 (which is the number of substituents in the phosphazene ring). For example if we take mixture (96b), the area of the signal corresponding to the R_F-CH_2 -O is 45.6, and therefore 45.6/2 = 22.8 is proportional to the amount of perfluoropolyether chains in the mixture, similarly, the total area for the signals corresponding to the protons of the phenoxy group is 274, and so 274/5 = 54.8 is proportional to amount of the phenoxy groups. At this point we know that for each phosphazene ring the normalised ratio perfluoropolyether-alkoxy/phenoxy groups is 1 to 1.58 and their sum is 6, thus resulting results in an average of 2.3 perfluoroalkoxy groups and 3.7 phenoxy groups.

Mass spectrometry does not add any valuable information as the spectrum in (Figure 4) proves and was carried out just for a few samples.

Most potential additives are transparent, viscous fluids, miscible in all proportions with Fomblin Z fluids and show an excellent thermal stability when heated to above 300°C.

2.F.5 Tests for the evaluation of the stabilisation activity.

A series of test-runs was conducted in the Ausimont S.p.A. company - Italy, for the purpose of determining the effectiveness of these potential additives for perfluorinated fluids operating at elevated temperatures. The tests were run in an apparatus consisting of a glass test-tube equipped with a gas inlet pipe, a vent pipe and a housing for a disc made of a titanium, vanadium, aluminium alloy. The perfluoropolyether fluid in study (Fomblin Z 25 (95), where A = B = CF_3 (CF_3O-$(C_2F_4O)_m(CF_2O)_n$-CF_3), kinematic viscosity 25 cSt at 20°C) was placed into the test-tube and mixed with the phosphazene derivatives in the amounts indicated in Table 11. The test-tube was heated to 316°C in an aluminium furnace while moisture free air was bubbled through for 72 hours, at a flow-rate of 1 liter/hour. Comparative tests were also run on the perfluoropolyether fluid in absence of stabilizers. The effectiveness of the stabilisers was evaluated by examination percentage difference in weight (Δw^L) and percentage difference in viscosity ($\Delta \eta^L$) of the lubricant, and the variation in the weight per surface unit of the metal alloy (Δw^M).

The weight percentage difference (Δw^L) values reported in Table 11 for the mixtures (70a)-(107) show that only the phosphazenes containing aromatic substituents (96b), (96c), (100), (101), (104) have stabilising activity. In particular, if we compare (96b), (96c), (96d) which contain both phenoxy and perfluoropolyether-alkoxy groups,

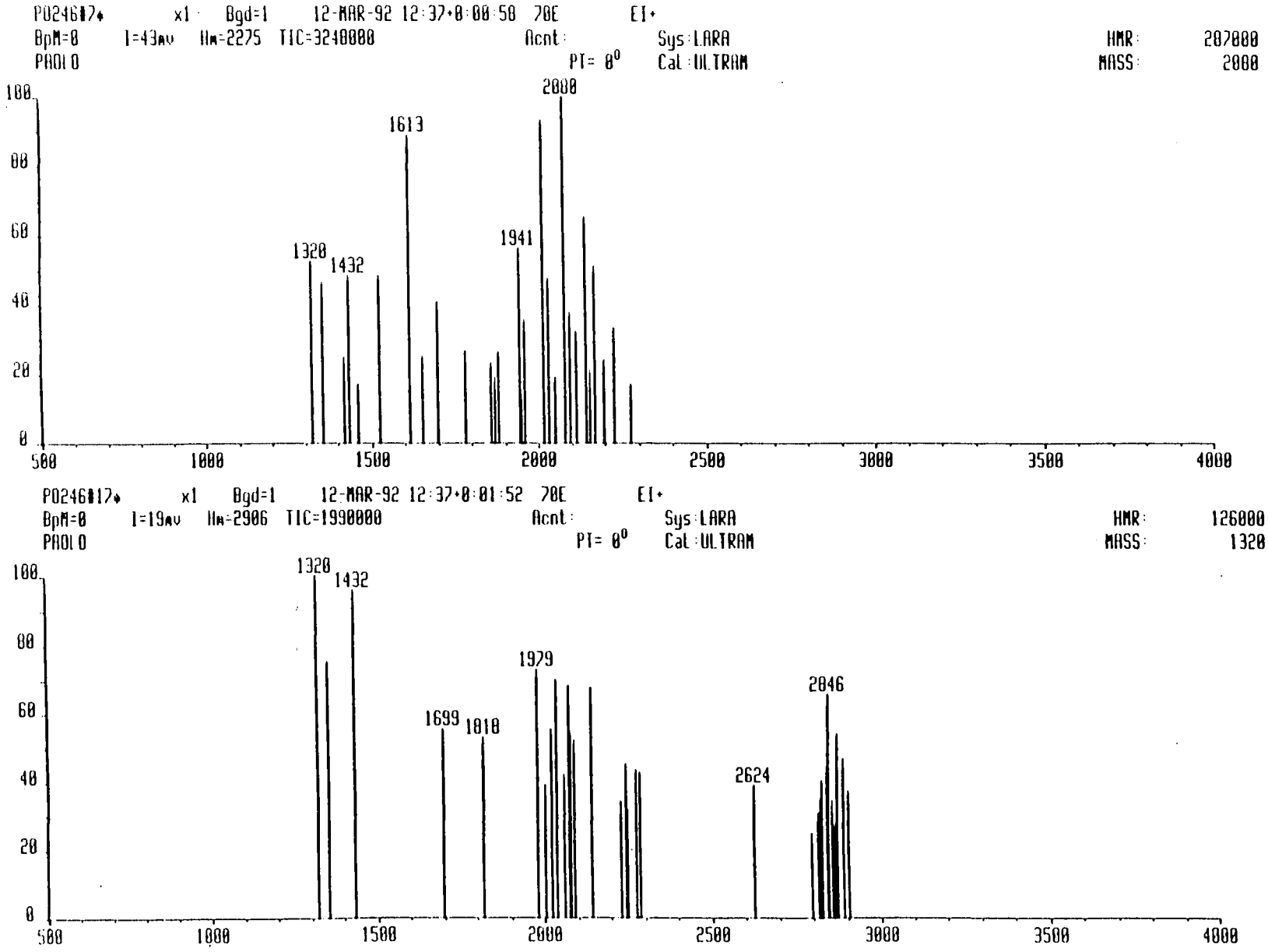


Figure 4. Typical mass spectra of cyclophosphazenes.

but in a decreasing ratio, we can see that the amount of phenoxy groups necessary to induce a stabilising effect is crucial. Indeed the presence of an aromatic group is essential because all mixtures (70a), (70b), (97), (99), which do not contain aromatic substituents, do not show any stabilising activity. The effect of electron-withdrawing groups (101), electron-donating groups (100), (103), or both (102) on the aromatic ring, has also been studied, and data seem to indicate that aromatics with electron-withdrawing substituents (101) work better. So far we have not been able to produce an explanation of why mixtures (104)-(107) do not have any stabilising activity, in spite of the presence of aromatic substituents, but we think, on the basis of previous results (96b)-(96d), that may be, the amount of aromatic substituents on the phosphazene ring was not enough to induce stabilisation as for (96d).

Stabiliser	conc (% b.wg.)	Δw^L (%)	$\Delta \eta^L$ (%)	Δw^M (mg/cm^2)
--	--	-100	n.d.	--
(70a)				
(70b)	0.65	-100	-6.8	-5.4
(96a)				
(96b)	0.80	-0.9	+5.7	0
(96c)	0.90	-3.3	-16.1	0
(96d)	1	-100	n.d.	+0.06
(97)	0.80	-100	n.d.	0
(98)	0.80	-100	n.d.	+0.08
(99)	0.80	-100	+2.5	+3.8
(100)	0.85	-15.1	-0.2	0
(101)	0.85	-0.7	+1.8	+0.13
(102)	n.d.	n.d.	n.d.	n.d.
(103)	0.80	-100	n.d.	0
(104)	0.85	-8.5	-32.4	0
(105)	0.60	-100	n.d.	0
(106)	0.85	-100	n.d.	n.d.
(107)	0.85	-100	n.d.	0

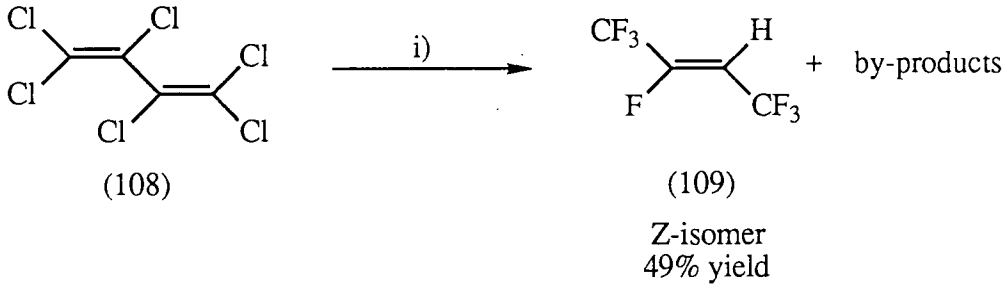
(*) comparative, n.d.: not determined.

Table 11. Stabilisation activity of the potential additives based on phosphazenes.

CHAPTER 3
PERICYCLIC REACTIONS OF FLUORINATED OLEFINS.

3.A Synthesis of (Z)-2-hydroheptafluorobut-2-ene.

(Z)-2-Hydroheptafluorobut-2-ene (109) was prepared in a one step reaction from hexachlorobutadiene, in moderate yields (49% yield)[119]. Quite interestingly, the reaction also afforded telomers of 2-hydroheptafluorobut-2-ene as by-products.



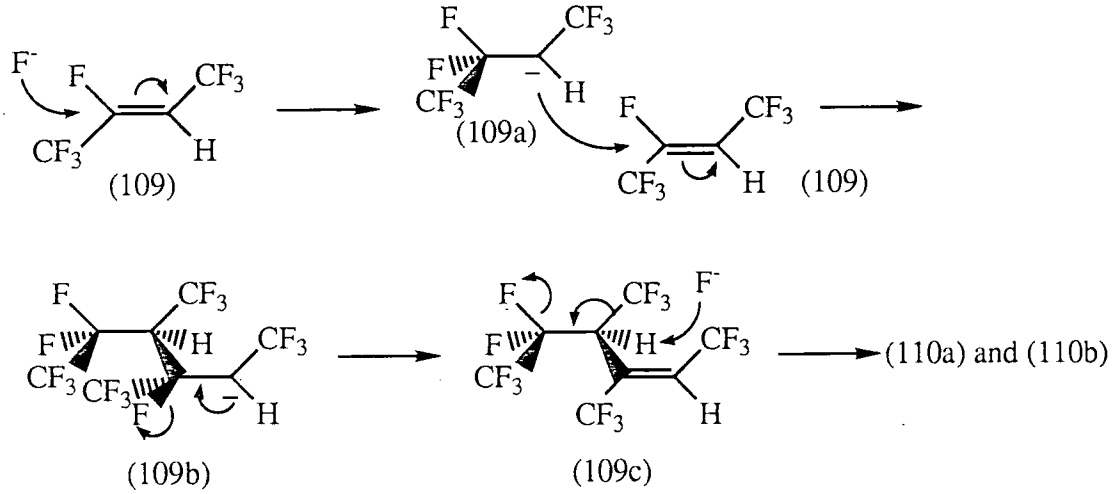
(108) (109)

Z-isomer
49% yield

i) KF, sulpholane, 180°C
[105]

3.A.1 Dimer: 5-hydro-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene.

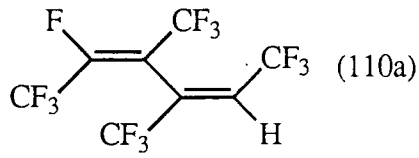
Among these telomers, dimer (110) was particularly interesting because of the presence of two differently substituted double bonds: the first, characterised by the presence of a vinylic fluorine and the second, by a vinylic hydrogen. The reaction probably occurs following the path reported in Scheme 13: fluoride ion attacks a molecule of 2-hydroheptafluorobut-2-ene (109) to form the more stable carbanion (109a) which then attacks another molecule of (109) to form once more the more stable carbanion (109b). Carbanion (109b) readily undergoes fluoride ion elimination to give mono-ene (109c), and at this point caesium fluoride, acting as a base, promotes dehydrofluorination to give the mixtures of dienes (110a) and (110b).



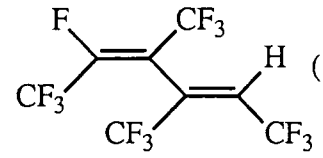
Scheme 13. Suggested mechanism for the formation of dimers (110).

Dimers (110), obtained in a mixture together with other telomers of higher

molecular weight, were purified by distillation (Bp 78 - 81°C) and characterised. Careful analysis of the coupling constants in the ^{19}F n.m.r. spectrum, indicated that the two stereoisomers were most probably the Z,E isomer (110a) and the Z,Z-isomer (110b) in ca. 7 to 3 ratio.



(110a)



(110b)

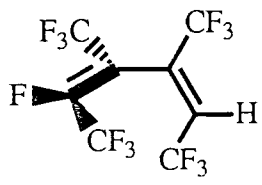
Z,E-isomer
70%

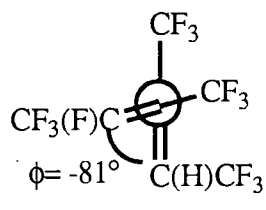
Z,Z-isomer
30%

[106]

The mixture of isomers (110a) and (110b) was reacted with caesium fluoride in sulpholane at room temperature with the intention of determining which isomer was thermodynamically more stable. The reaction was followed by ^{19}F n.m.r. which showed that the Z,Z isomer (110b) was very slowly converted into the Z,E isomer (110a) (ca.8 to 2 ratio after six days) confirming that (110a) was the most thermodynamically stable of the two.

The ultra-violet extinction coefficient (εmax.) of the of the mixture of dienes was measured as 1148 (λmax = 295 nm) and the relatively small value obtained, suggests that in dienes (110a) and (110b) the double bonds are not conjugated. The trifluoromethyl groups impose steric demand and repulsion, due to the non-bonded electron pairs on the fluorine atoms, resulting in a deviation of the geometry of the system from the planar conformation. Out of curiosity, structure (110a) has been studied by molecular modelling using the COSMIC package (MOPAC) on microVAX2 minicomputer. In spite of the intrinsic limits of the software (which does not take into account the electron density within the molecule nor all possible bonding arrangements) diene (110a) has been modelled and the resulting dihedral angle between the two double bonds has been given as ca -81°





[107]

The HOMO and the LUMO orbitals are reported in Figure 5 and 6 together with their respective calculated energies. The electron density on the carbon atoms involved in the double bonds is reported in Table 12.

carbon atom 1	carbon atom 2	carbon atom 3	carbon atom 4
0.105	-0.181	-0.087	-0127

Table 12. Electron density of the carbon atoms involved in the double bonds.

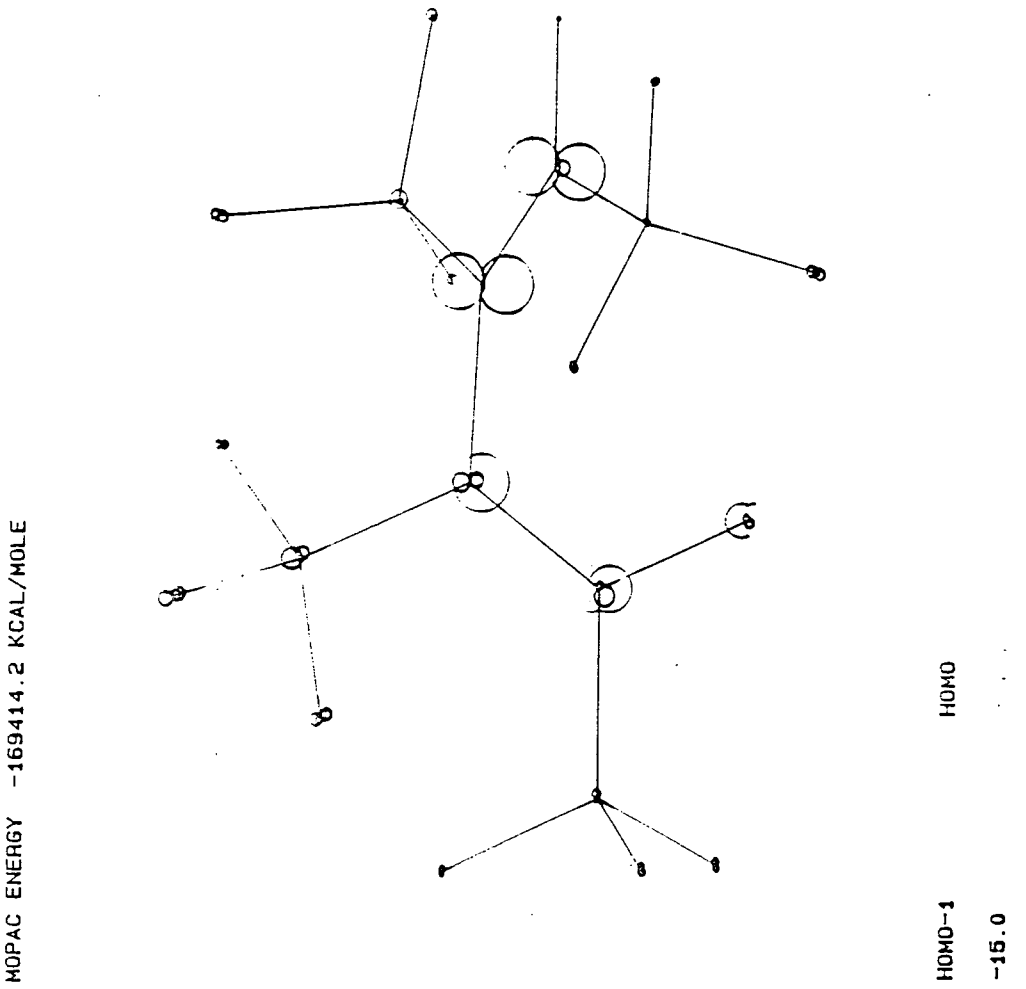


Figure 5. HOMO orbitals and respective energies for di-ene (110a)

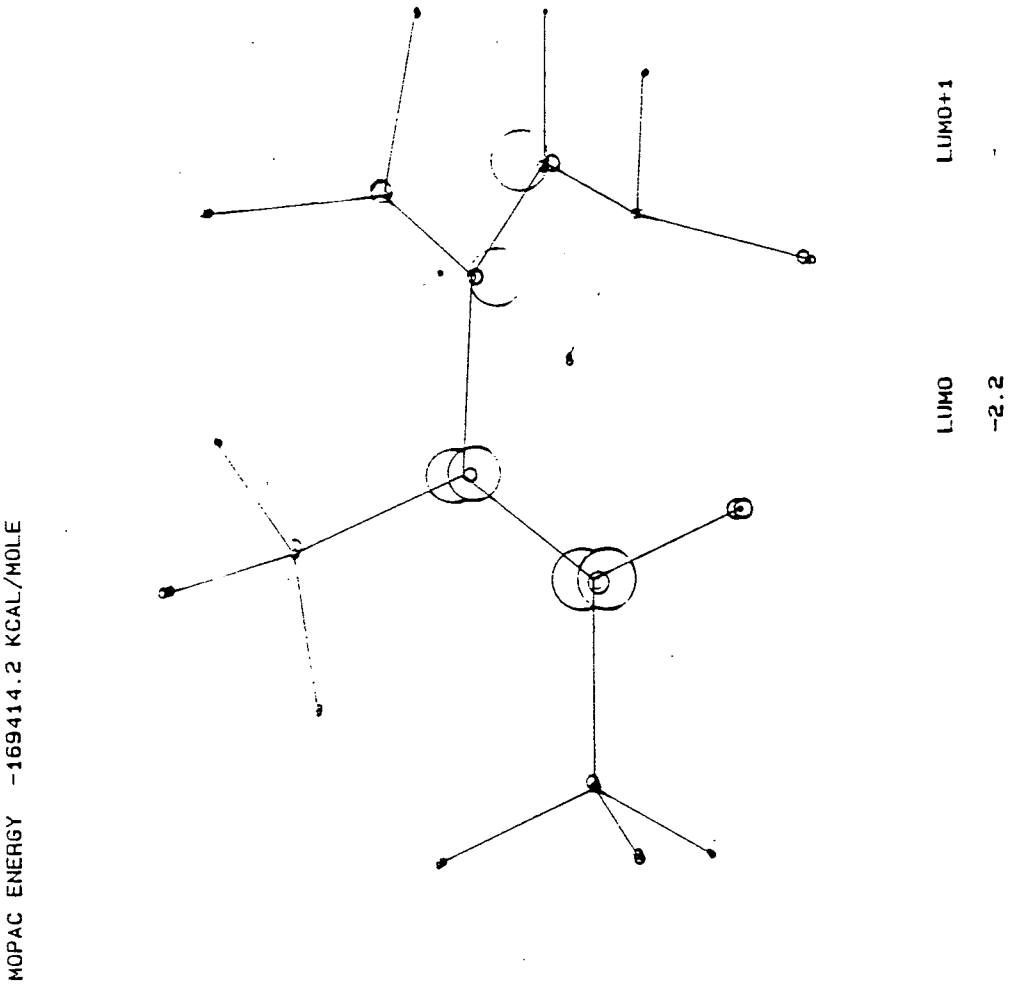


Figure 6. LUMO orbitals and respective energies for di-ene (110a)

Data obtained from these calculation indicate that the most reactive double bond towards nucleophilic attack is the one containing the vinylic fluorine whose LUMO energy is lower, although, a knowledge of the chemistry of fluorinated alkenes would also lead to this conclusion.

3.A.2 Higher telomers.

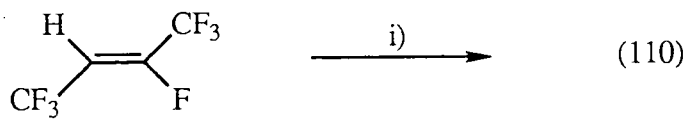
Trimers of 2-hydroheptafluorobut-2-ene were also investigated. Analysis by GC/MS clearly showed a series of compounds characterised by ions m/z^+ 505 (M-1) corresponding to a mixture of isomers of the trimer. In addition, the ^{19}F n.m.r. data showed numerous signals in the region between -53 and -70 ppm, which are consistent with the presence of trifluoromethyl group attached to double bonds, but so far, no definite attribution of the peaks has been made.

3.A.3 Residue.

We also made an attempt to investigate the nature of the residue left in the reaction flask, for a better understanding of why our yields were just 49% against the much higher values reported in previous works.[119] Analysis by means of ^{19}F n.m.r. spectrum showed a broad peak at about -50 ppm, but up to now, we have no definite evidence to support a consistent argument.

3.A.4 Attempted synthesis of 5-hydro-perfluoro-3,4-bis(trifluoro-methyl)hexa-2,4-diene.

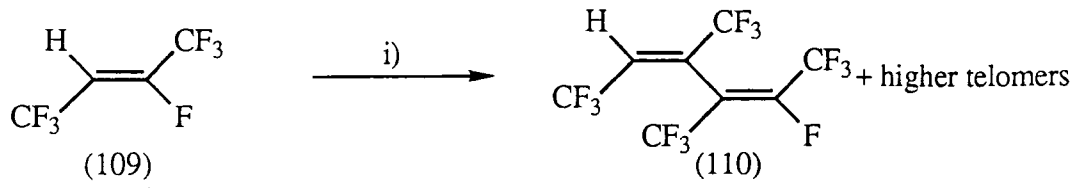
The synthesis of 5-hydro-perfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene using 2-hydroheptafluorobut-2-ene (109) as a starting was also investigated. 2-Hydroheptafluorobut-2-ene (109) was reacted with caesium fluoride in sulpholane under different conditions. When the reaction was carried out at room temperature no reaction occurred, and at 70°C only a little amount of dimer (110) was obtained.



(110)

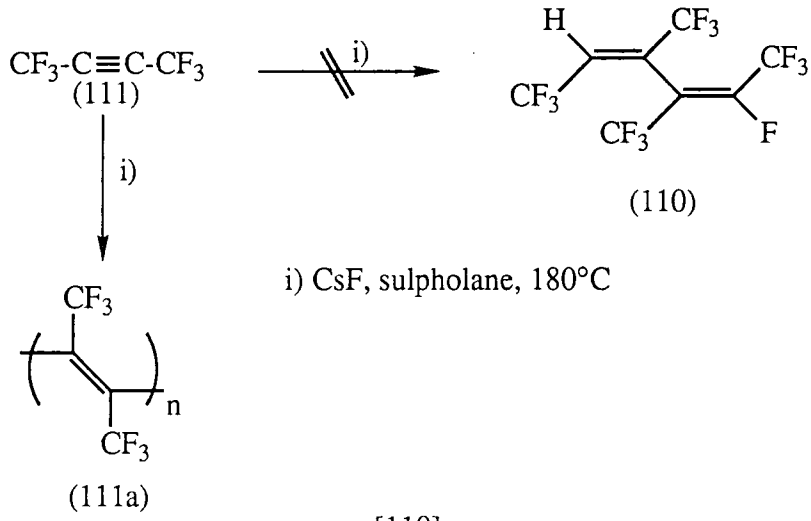
i) CsF, sulpholane, r.t.to 70°C
[108]

However, when reaction was carried out at 180°C, analysis showed the presence of the starting material (109), the dimer (110) and some higher telomers of 2-hydroheptafluorobut-2-ene, which appeared as a white volatile solid whose nature was not investigated in detail.



i) CsF, sulpholane, 180°C
[109]

In parallel a caesium fluoride catalysed telomerisation of hexafluorobut-2-yne was carried out at 180°C in sulpholane. In this case no volatile material was recovered and thus we assumed that all starting material had been converted into poly-hexafluorobut-2-ene, but no investigation was carried out on the residue.



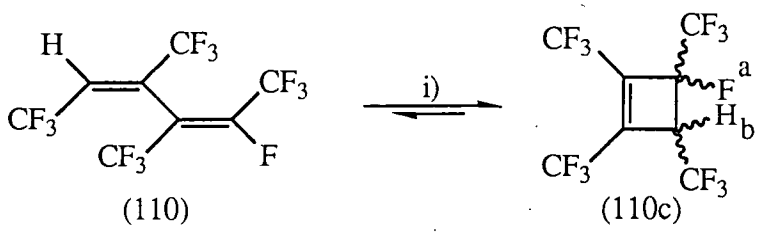
i) CsF, sulpholane, 180°C

[110]

3.A.5 Reactions of 5-hydro-3,4-bis(trifluoromethyl)perfluorohexa-2,4-diene

Isomers (110a) and (110b) were heated to 100°C to promote thermal cyclisation. The reaction mixture has been analysed but, so far, the results have been difficult to interpret. The ^{19}F n.m.r. clearly indicates the presence of the starting material (vinylic fluorine at -110 p.p.m.) and the presence of a signal at ca. -170 p.p.m. which may be attributed to fluorine (a) in cyclo-adduct (110c), similarly the ^{1}H n.m.r. spectrum showed the signal for the starting material (6.7 p.p.m.) and a signal at 3.4 which may be attributed to proton (b) in (110c). The mixture was also analysed by GC/MS and the results indicates the presence of several peaks with m/z^+ 343 which may be attributed to either the starting material or the cyclised products.

In another experiment the mixture of isomers (110) was irradiated by ultra-violet radiation (high pressure mercury lamp). Interestingly, analysis showed that the cyclisation reaction seemed to proceed even further. In this case no signal corresponding to the starting material was found in the ^{1}H n.m.r. spectrum. However, information gathered from ^{19}F n.m.r. and GC/MS was similar to the one obtained for the thermal cyclisation.



(110) (110c)

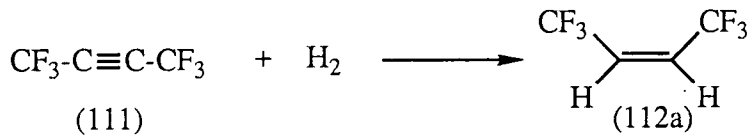
i) Δ or h.ν.

[111]

3.B Synthesis of (E)-2,3-dihydrohexafluorobut-2-ene.

3.B.1 Introduction.

Some synthetic routes to (Z)-2,3-dihydrohexafluorobut-2-ene (112a) have been reported in the literature, and they are based on hydrogenation of hexafluorobut-2-yne (111)[119a].

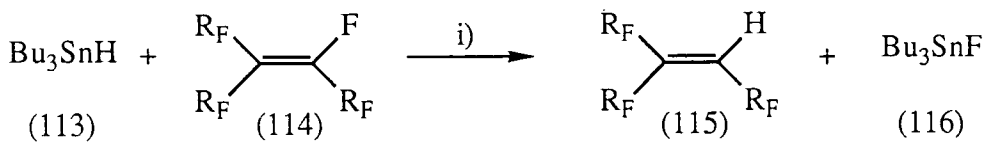


(111) (112a)

Z, isomer

[112]

In the early 1960's a number of studies involving the formation of tin-fluorocarbon bonds were produced[120]. Tin compounds such as organo-tin hydrides, dihydrides, and organo-ditins were reported to react under free radical condiditions with fluoroolefins (114) to give addition products followed by elimination of tin fluoride and the production of the corresponding reduced olefin (115)[120].



(113) (114) (115) (116)

i) free radical initiation

[113]

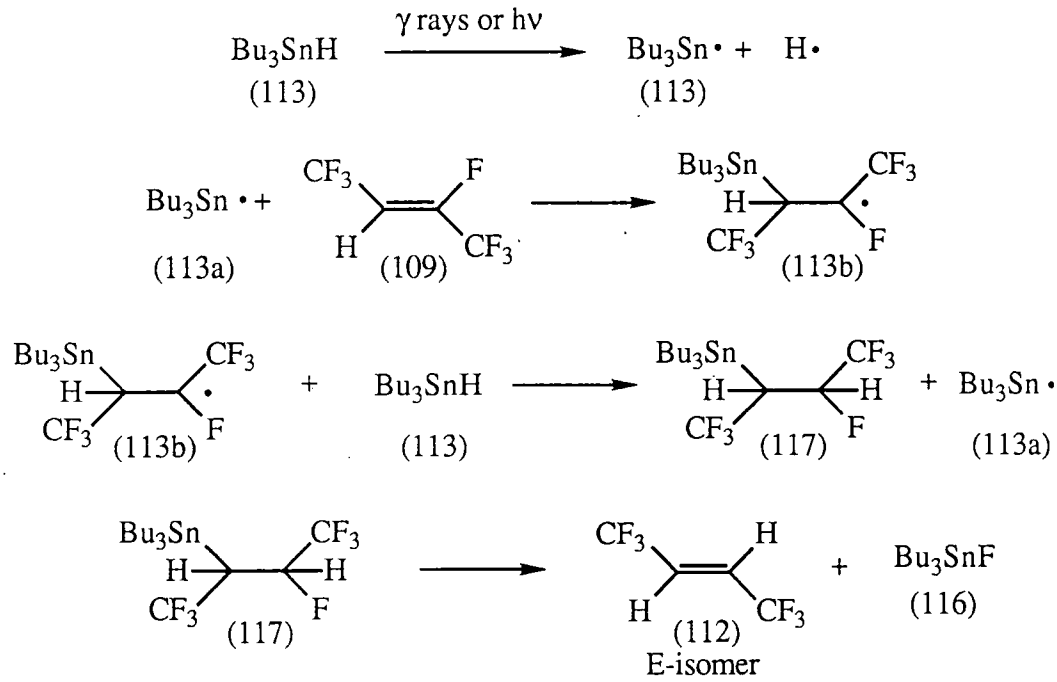
Thus, we wanted to explore this chemistry in an attempt to a new synthetic route to 2,3-dihydrohexafluorobut-2-ene, using 2-hydroheptafluorobut-2-ene as a starting material. The radical reaction could, in principle, be initiated by γ rays, ultraviolet radiation or any free radical initiator such as AIBN or peroxides. So far we have used γ rays and ultra-violet radiation for initiation and used ^{19}F n.m.r. spectroscopy to monitor the course of the reaction.

3.B.2 Gamma ray initiation.

The use of γ rays for initiating a free radical process at room temperature affords the great advantage of operating under very mild conditions so that heat sensitive products may be obtained. Thus, reacting tributyltin hydride (113) with 2-hydroheptafluorobut-2-

ene (112), adduct (117) was first obtained in good yields (according to ^{19}F n.m.r. integration 100% conversion,76% yield). Little elimination of tin fluoride occurred at this stage, but when adduct (117) was heated to 70°C under autogenous pressure, elimination of tributyltin fluoride proceeded readily to form 2,3-dihydrohexafluorobut-2-ene. Adduct (117) was identified using ^{19}F n.m.r. spectroscopy (e.g.: -59.9 p.p.m.CF_3 C(H)), -81 p.p.m.CF_3 C(F)), -171 p.p.m. $CF_3C(F)$).

The mechanism of the reaction is outlined in Scheme 14. Homolytic cleavage of the tin-hydrogen bond produces the tin radical $Bu_3Sn\cdot$ (113a) (initiator) which then adds to the double bond of 2-hydroheptafluorobut-2-ene (109). The direction of the addition is thermodynamically controlled to give the most stable radical (113b), which then abstracts a proton from Bu_3SnH to regenerate $Bu_3Sn\cdot$ (113a). Adduct (117) undergoes elimination of tributyltin fluoride under mild heating (70°C) to give (E)-2,3-dihydrohexafluorobut-2-ene (112).



Scheme 14. Suggested mechanism for the synthesis of 2,3-dihydrohexafluorobut-2-ene.

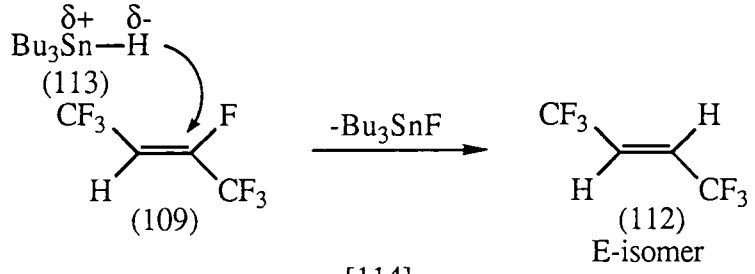
3.B.3 Ultra-violet initiation.

The radical reaction outlined in Scheme 14 proceeds much faster and is accompanied by elimination directly to 2,3-dihydrohexafluorobut-2-ene when the reactants are irradiated for one day by a high pressure mercury lamp. This is understandable in that excess energy is introduced in the photolytic process.

3.B.4 Anionic mechanism.

Tributyltin hydride is also known to react with some species as a nucleophile (H^-)[120a]. To investigate the contribution of the anionic pathway to the process outlined in

Scheme 14, the addition of tributyltin hydride to 2-hydroheptafluorobut-2-ene (109) was also carried out in the absence of light. Under these conditions the reaction proceeded very slowly (^{19}F n.m.r. showed less than 10% conversion after 3 days) and therefore, the anionic mechanism plays just a very minor part in the course of the reaction.



[114]

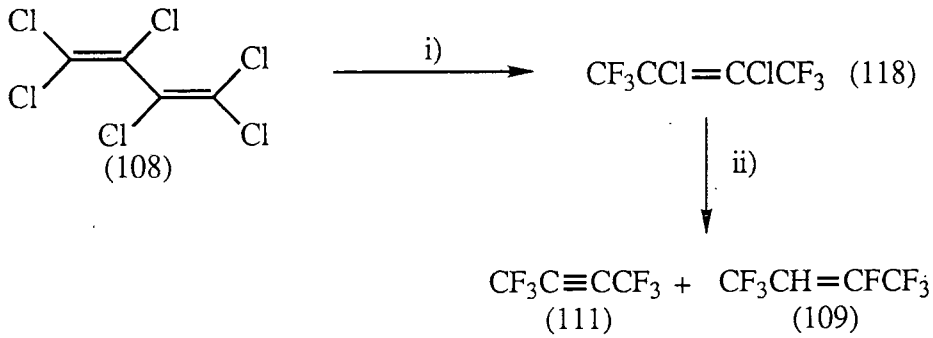
3.B.5 Attempted photolytic and thermal cyclisations of 2,3-dihydrohexafluorobut-2-ene.

2,3-Dihydrohexafluorobut-2-ene (112) was irradiated for seven days by a high pressure mercury lamp both by itself and in presence of acetone, used as sensitiser. In both cases ^{19}F n.m.r. monitoring did not show any sign of reaction.

Similarly, no reaction occurred when 2,3-dihydrohexafluorobut-2-ene (112) is heated at 100°C in an attempted thermal cyclisation.

3.C Attempted new route to hexafluorobut-2-yne.

Hexafluorobut-2-yne (111) is normally prepared in a two steps process from hexachloro-1,3-butadiene (108), and in the second step reduction of precursor (118) may also take place to give 2-hydroheptafluorobut-2-ene (109).



i) SbF_3, SbF_3Cl_2, 150°C
ii) Zn, Ac_2O, reflux temp.

[115]

Nowadays alkyne (111) is only produced on a small commercial scale because of its limited industrial demand and relatively high cost.

Surprisingly, we found that 2-hydroheptafluorobut-2-ene (109) stored on molecular sieves over 20 days decomposed to give uniquely hexafluorobut-2-yne (111). This remarkable observation induced us to investigate in detail molecular sieves as a new potential dehydrofluorinating agent. The outcome of the research, of course, might have

been useful for supplying a novel convenient method to convert 2-hydroheptafluorobut-2-ene into hexafluorobut-2-yne.

Thus, the investigation of the dehydrofluorination process was carried out by reacting 2-hydroheptafluorobut-2-ene with both molecular sieves and alumina, under a variety of conditions. The collected results are reported in Table 13. From the data it is clear that the activity of molecular sieves increases when the solid-liquid (dehydrofluorinating agent-2-hydroheptafluorobut-2-ene) interface is maximum. For grams scale quantities this was achieved using small vessels, while for little quantities cooling the vessels to temperatures around 0°C was necessary to have 2-hydroheptafluorobut-2-ene in the liquid phase.

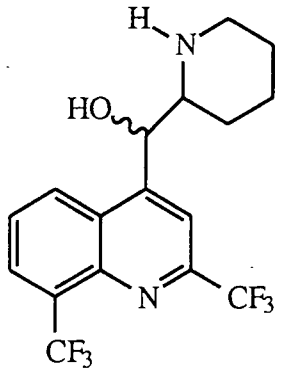
Good conversions were also obtained pyrolysing 2-hydroheptafluorobut-2-ene (109) over either molecular sieves or alumina. Both dehydrofluorinating agents were activated at 400°C before use under a stream of nitrogen. However, the yields of the reactions were only moderate, and this is probably due to the engineering of the apparatus, in particular, the amount of dehydrofluorinating agent used in the experiments. Nevertheless, so far, we have not been able to optimise the pyrolysis conditions.

dehydrofluorinating agent	temperature - time (°C) - (as indicated)	conversion (%)	yield (%)	liquid-solid contact
molecular sieves	r.t. - 25 days	53	-	good
molecular sieves	0°C - 2 days	61	-	good
molecular sieves	80°C - 3 days	40	-	poor
molecular sieves	250°C - ~1 minute	52	48	good
molecular sieves	300°C - ~1 minute	78	40	good
alumina	r.t. - 10 days	38	-	poor
alumina	260°C - ~1 minute	27	53	good
alumina	300°C - ~1 minute	46	42	good
alumina	360°C - ~1 minute	73	36	good

Table 13. Dehydrofluorination of 2-hydroheptafluorobut-2-ene.

3.D The importance of trifluoromethylation.

The introduction of trifluoromethyl groups into biologically active compounds may induce enhancement of therapeutic activities and uniquely increase absorption and transport rates of drugs in vivo [121-124]. Many examples of drugs containing this very lipophilic group are known, and some are available commercially [121,123], one being Mefloquine[125] (119) used throughout South East Asia to treat chloroquine resistant strains of malaria.



(119)

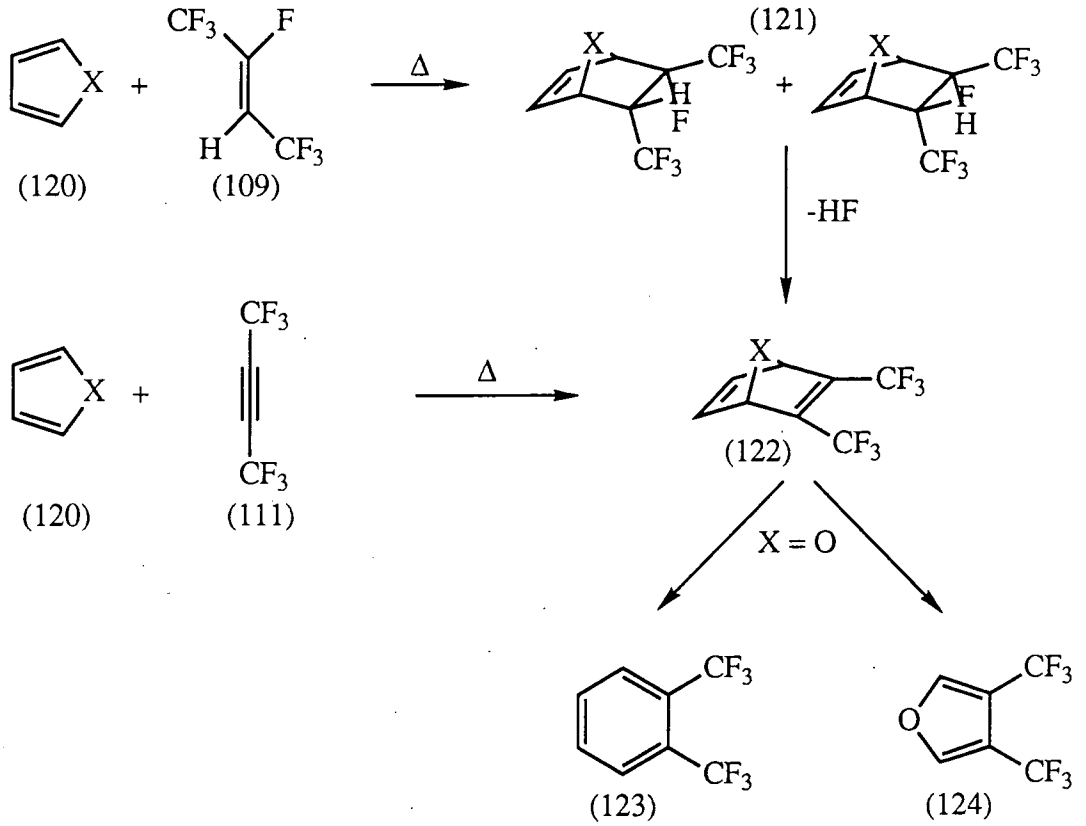
Methodologies for the introduction of the trifluoromethyl group into an aromatic system are numerous. They include halogen exchange of chlorine in trichloromethyl groups, using hydrogen fluoride,[126] which is probably the most important route commercially, but less useful in the laboratory; fluorination of carbonyl derivatives with SF_4 [127] and direct trifluoromethylation.[128] However many of these synthetic routes present disadvantages for a variety of reasons.

An alternative approach to obtaining trifluoromethylated aromatics is the use of appropriate fluorinated building blocks to use in pericyclic reactions (Diels-Alder reactions, 1,3-dipolar additions).[119] Derivatives containing one trifluoromethyl group are easily obtained from dienophiles such as 3,3,3-trifluoropropyne, 3,3,3-trifluoropropene.

Indeed, the opportunity to synthesise a range of systems containing two vicinal trifluoromethyl groups makes hexafluorobut-2-yne (111) an important candidate for investigation (Scheme 15).

However, there are two interesting fluorinated olefins which could be used as alternative synthons for the introduction of two trifluoromethyl groups in aromatic compounds. They are 2-hydroheptafluorobut-2-ene (109) and 2,3-dihydrohexafluorobut-2-ene (112). What is interesting about them is that 2-hydroheptafluorobut-2-ene (109) can be synthesised directly from ready available hexachlorobutadiene and potassium fluoride and that 2,3-dihydrohexafluorobut-2-ene (112) can be synthesised by reduction of (109) as described earlier in this work.

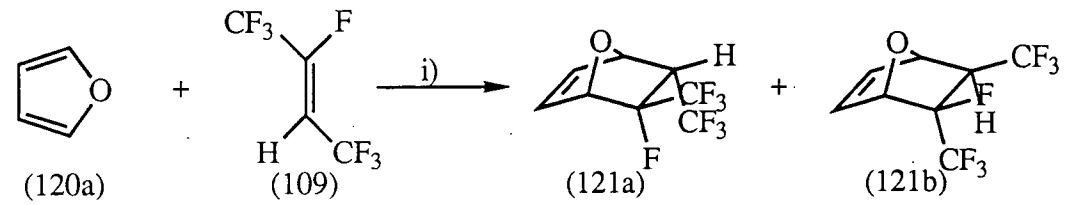
It was shown[119] (Scheme 15) that 2-hydroheptafluorobut-2-ene undergoes Diels-Alder reactions to suitable dienes (120) to give adducts of type (121) which on dehydrofluorination give (122), which is the same as compound obtained by reacting (120) and hexafluorobut-2-yne, although dehydrofluorination of (121) where X= O, is not easily effected and ring opening occurs instead. Furthermore, compound (122) where X = O, can be reduced to give (123) or pyrolysed to give (124).



Scheme 15. 2-Hydroheptafluorobut-2-ene as a synthon for hexafluorobut-2-yne.

3.D.1 Reaction of 2-hydroheptafluorobut-2-ene with furan.

2-Hydroheptafluorobut-2-ene undergoes cyclo-addittion with furan to give two enantiomers: the first one with the fluorine in the endo position (121a) and the other with the fluorine in the exo position (121b) in a 6 / 4 ratio, 49% overall yield.



i) THF, 130°C
[116]

The two isomers have been separated by means of preparative gas chromatography and the exact configurations assigned by careful investigation of the ^1H n.m.r.set of data. Coupling between protons on vicinal carbons in rigid systems depends primarily on the dihedral angle ϕ between the H-C-C' and the C-C'-H' planes (Karplus's rule). Therefore, it is possible to anticipate that the coupling constant for the protons H and H' in (121a) (exo hydrogen) is around 4 Hz, and in (121b) (endo hydrogen) is approximately 0 Hz.

(121a) (121b)

[117]

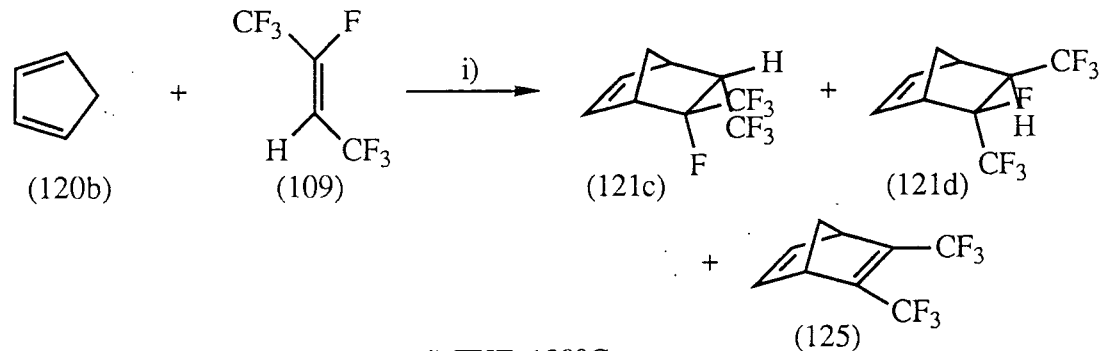
Analysis by ^1H n.m.r. resolved the C*H* CF_3 signals and allowed all the coupling constant for this protons to be determined.

The chemical shift value at 3.62 ppm (doublet of quartet of doublet, J_{HF} 12.6 Hz, J_{HCF_3} 8.9 Hz, J_{HH} 4.3 Hz) is consistent with the proton at the exo position (121a) which couples with its vicinal proton, and the chemical shift value at 3.17 ppm (doublet of quartet, J_{HF} 12.2 Hz, J_{HCF_3} 9 Hz) is consistent with the proton at endo position (121b) whose coupling constant with its vicinal proton in almost 0 Hz. The determined 6 / 4 ratio for the endo and exo isomers (with respect to fluorine) implies that the reaction carried out at 120°C is not particularly stereoselective. This suggests that trifluoromethyl substituents (which are trans to each other in the starting material) control the stereochemical outcome of the reaction, hydrogen and fluorine playing just a minor part.

It was reported[119] that adducts (121a) and (121b) in presence of a base did not eliminate hydrogen fluoride, but preferred to undergo ring-opening, may be, to relieve ring strain. We mentioned earlier the remarkable use of molecular sieves and alumina as potential mild dehydrofluorinating agents, and thus we reacted adducts (121a) and (121b) with both molecular sieves and alumina at room temperature in an attempt to induce dehydrofluorination without ring opening. Nevertheless, we were not successful because analysis by ^{19}F n.m.r. did not show any change in the spectra of the starting materials.

3.D.2 Reaction of 2-hydroheptafluorobut-2-ene with cyclopentadiene.

2-Hydroheptafluorobut-2-ene reacted very rapidly with cyclopentadiene at room temperature to give a mixture of isomers (121c) (121d) and di-ene (125) in a 4.2 / 3.2 / 2.6 ratio. The products have been identified by comparison of the ^{19}F n.m.r. data with those of an authentic samples and we were able to give correct attribution of the signals by careful analysis of the coupling constants in the ^1H n.m.r.



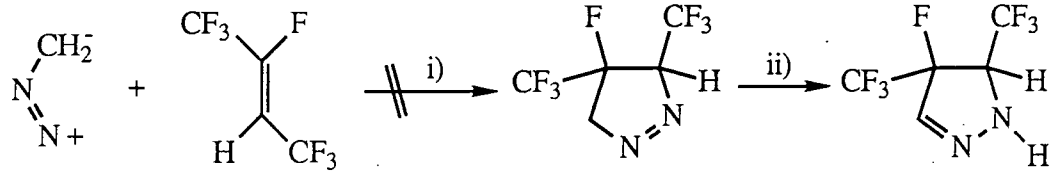
(120b) (109) (121c) (121d) (125)

i) THF, 130°C

[118]

3.D.3 Attempted reaction of 2-hydroheptafluorobut-2-ene with diazomethane.

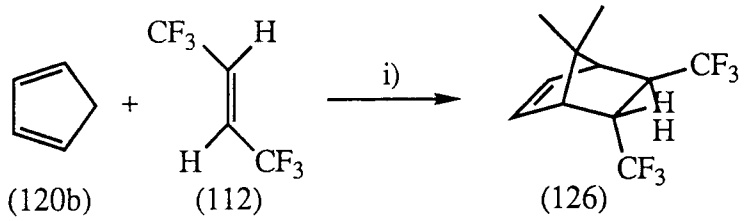
We wanted to study the feasibility of 1,3-dipolar addition to 2-hydroheptafluorobut-2-ene. Thus, we generated some diazomethane and reacted it with (109) in diethylether at 0°C. The reaction was monitored by ^{19}F n.m.r. which showed that after 24 hours very little reaction had taken place. It was not possible to fully characterise the addition products.



i) Ether, 0°C
ii) rearrangement
[119]

3.D.4 Reaction of 2,3-dihydrohexafluorobut-2-ene with cyclopentadiene.

2,3-Dihydrohexafluorobut-2-ene reacted readily with cyclopentadiene at 80°C to give adduct (126) whose ^1H n.m.r. spectrum is characterised by the AB system attributed to the methylene group at the bridge position (va = 1.53 ppm, vb = 1.68 ppm, J = 9.68Hz).

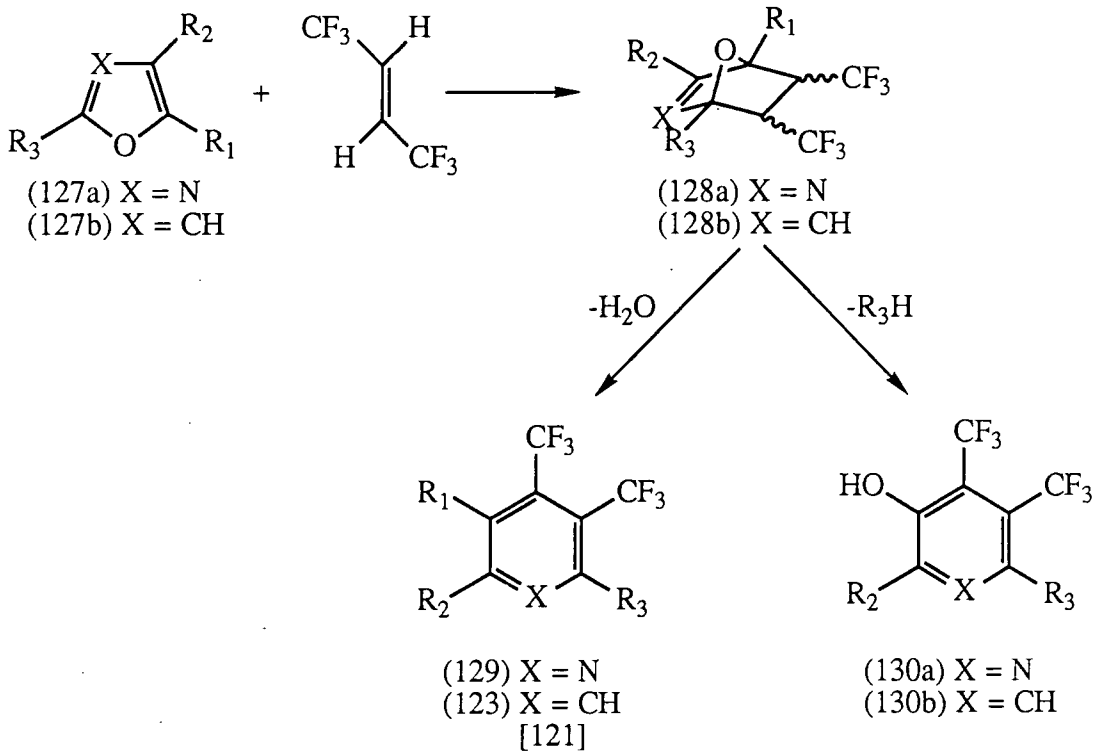


(120b) (112) (126)

i) THF, 130°C
[120]

3.D.5 Attempted direct synthesis to trifluoromethyl substituted aromatic compounds.

A potential alternative approach to trifluoromethyl substituted aromatics is provided by reacting 2,3-dihydrohexafluorobut-2-ene with substituted furans or oxazoles to give bis-trifluoromethylsubstituted benzenes or pyridines. Of course, the type of products that may derive from the fragmentation and subsequent aromatisation of the initial [4+2] adduct (128a) and (128b), very much depend on the substituents originally present on both oxazole (127a) and furan (127b). Simple dehydration of (128a) and (128b) should provide (129) and (123), while derivatives of type (130a) and (130b) should be formed when R_1 is a good leaving group (e.g.: OMe, OEt).



(127a) X = N
(127b) X = CH

(128a) X = N
(128b) X = CH

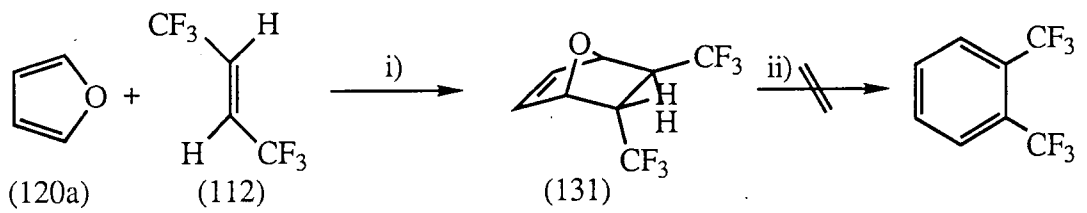
(129) X = N
(123) X = CH

(130a) X = N
(130b) X = CH

[121]

3.D.5.a Reaction of 2,3-dihydrohexafluorobut-2-ene with furan.

2,3-Dihydrohexafluorobut-2-ene was reacted with furan (120a) with the purpose of obtaining 1,2-bistrifluoromethylbenzene. However, at 70°C the reaction did not to proceed at all, and heating to 130°C was required to obtain adduct (131). Further rearrangement to 1,2-bistrifluoromethylbenzene did not occur, not even when the mixture was heated (130°C) in presence of p-toluensulphonic acid.



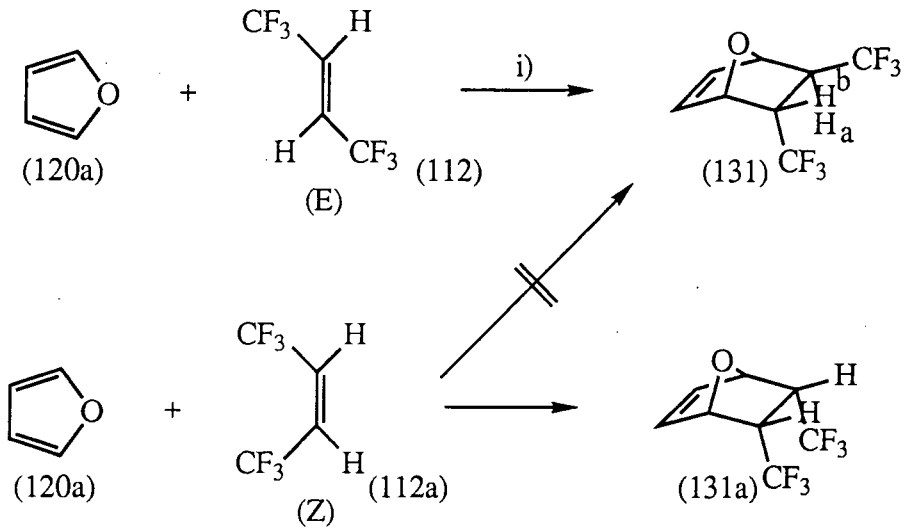
(120a) (112) (131)

i) THF, 130°C
ii) THF, p-toluensulphonic acid, 130°C

[122]

Despite the fact that reaction [122] did not give the desired product, we could derive very useful information concerning the stereochemical configuration of 2,3-dihydrohexafluorobut-2-ene (112). Up to now, we have always assumed that 2,3-dihydrohexafluorobut-2-ene (112) is present largely as the (E) isomer, but we have not been able to prove it, for instance, by means of n.m.r. spectroscopy. In fact, the symmetry of the system did not allow any coupling constant to be shown because of accidental degenerations in both proton and fluorine spectra. However, indirect confirmation that we had the (E) isomer was derived by examination of the ^{19}F and ^{1}H n.m.r. spectra of (131). The ^{19}F n.m.r. spectrum shows two separate peaks at -65.8 and -68.9 ppm attributed to the trifluoromethyl groups which are respectively at the endo and the exo position, furthermore, the splitting pattern and the magnitude of the spin-spin

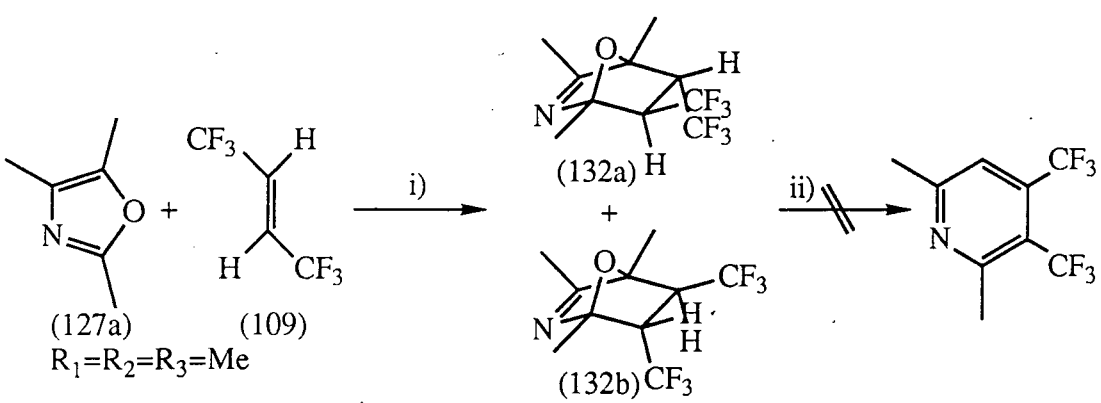
coupling constants (Karplus's rule) in the ^1H n.m.r spectrum of adduct (131) (Figure 7), clearly indicate that proton (a) is at endo position and proton (b) at the exo position. Therefore, according to the "cis principle", which is widely followed, the only possible way for obtaining (131) requires the dienophile to be in the (E) configuration so that the relative stereochemistry of the trifluoromethyl groups in the dienophile is retained in the adduct. Of course, isomer (Z) (121a) would have led to the formation of (131a), instead.



i) THF, 130°C
[123]

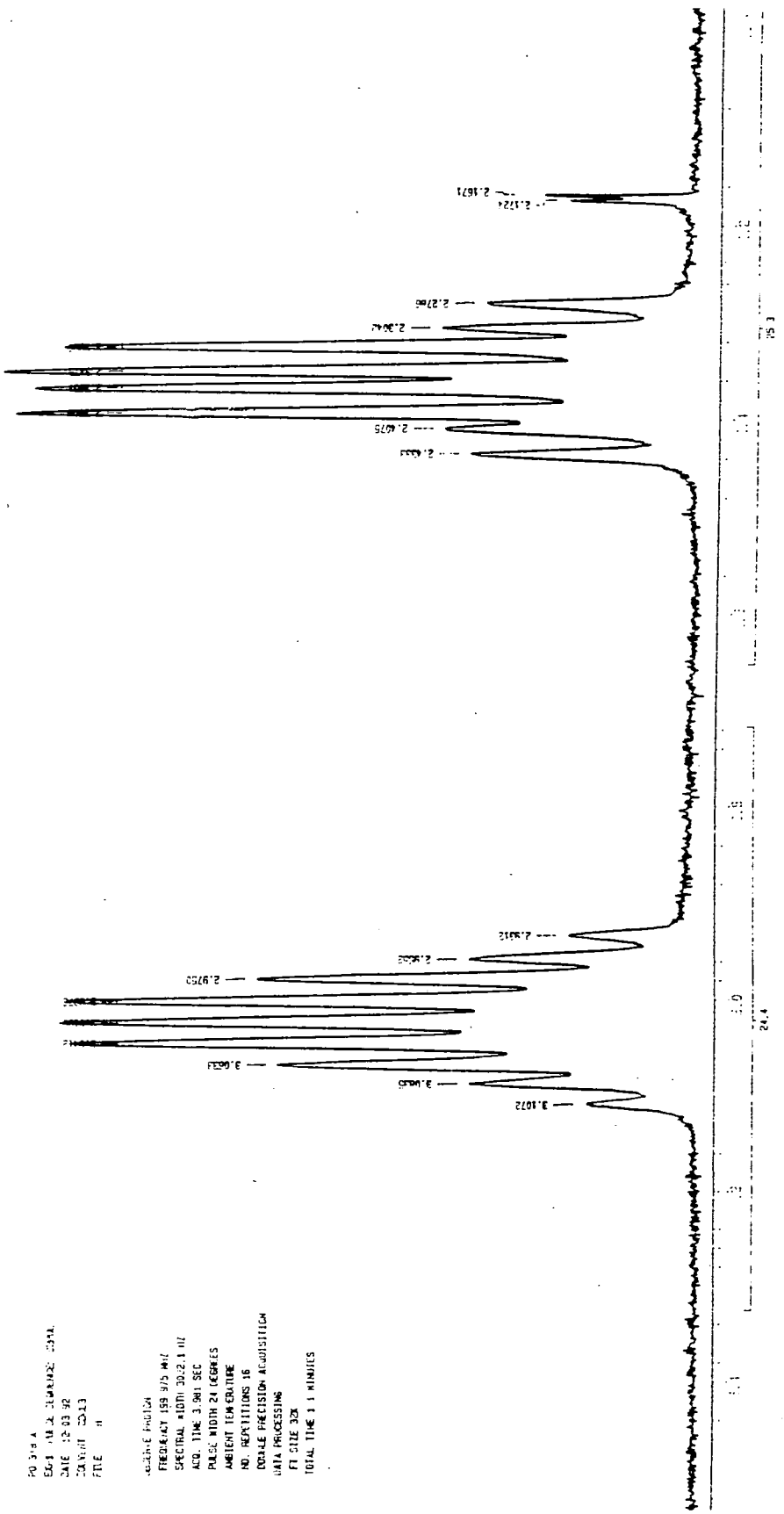
3.D.5.b Reaction of 2,3-dihydrohexafluorobut-2-ene with 2,3,5-trimethyloxazole.

So far we have used 2,3,5-trimethyloxazole as a precursor to fluorinated pyridines. Heating (127a) $R_1 = R_2 = R_3 = CH_3$ in presence of 2,3-dihydrohexafluorobut-2-ene in tetrahydrofuran at 130°C led to the formation of isomers (132a) and (132b) which did not undergo spontaneous rearrangement to 4,5-bistrifluoromethyl-2,3,6-trimethylpyridine. Furthermore, rearrangement did not occur even when the mixture was heated (130°C) in presence of p-toluensulphonic acid.



i) THF, 130°C
ii) THF, p-toluensulphonic acid, 130°C
[124]

Figure 7. Expansion of the ^{1}H n.m.r spectrum of (131).



REFERENCES

1. G. A. Olah, C. A. Cupas and M. G. Comisarow, *J. Am. Chem. Soc.,* 1966, **88**, 362.
2. G. A. Olah and Y. K. Mo, in *Advances in Fluorine Chemistry,* ed. J. C. Tatlow, R. D. Peacock and H. H. Hyman, Butterworths, London, 1973, vol. 7, p. 69.
3. R. D. Chambers, A. Parkin and R. S. Matthews, *J. Chem. Soc., Chem. Commun.,* 1973, 509.
4. R. D. Chambers, A. Perkin and R. S. Matthews, *J. Chem. Soc., Perkin Trans. I,* 1976, 2108.
5. M. K. Galakhov, V. A. Petrov, V. I. Bakhmutov, G. G. Belen'kii, B. A. Kvasov and L. S. German, *Izv. Akad. Nauk SSSR, Ser, Khim.,* 1985, 306.
6. M. V. Galakhov, V. A. Petrov, G. G. Belen'kii, L. S. German, E. I. Fedin, V. F. Snegirev and V. I. Bakhmutov, *Izv. Akad. Nauk SSSr, Ser. Khim.,* 1986, 967.
7. R. D. Chambers, M. Salisbury, G. Apsey and G. Moggi, *J. Chem. Soc., Chem. Commun.,* 1988, 680.
8. G. Apsey, Ph.D. Thesis, University of University of Durham, 1988.
9. R. D. Chambers, *Fluorine in Organic Chemistry,* John Wiely & Sons, 1973.
10. R. J. Gillespie and J. Liang, *J. Am. Chem. Soc.,* 1988, **110**, 6053.
11. C. G. Krespan, *J. Org. Chem.,* 1962, **27**, 1813.
12. P. Schleyer, P. Mison, G. K. S. Prakash and G. A. Olah, *J. Am. Chem. Soc.,* 1980, **102**, 683.
13. J. B. Stothers, *Carbon 13 NMR Spectroscopy,* Academic Press, New York, 1972.
14. R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *Tet. Lett.,* 1963, **10**, 619.
15. R. D. Chambers, J. Hutchinson, R. H. Mobbs and W. K. R. Musgrave,*Tet.* , 1964, **20**, 497.
16. K. L. Paciorek, B. A. Merkl and C. T. Lenk, *J. Org. Chem.,* 1962, **27**, 1015.
17. M. Hauptschein, M. Braid and F. E. Lawlor, *J. Am. Chem. Soc.,* 1957, **79**, 2549.
18. R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.,* 1955, 3005.
19. M. Hauptschein and R. E. Oesterling, *J. Am. Chem. Soc.,* 1960, **82**, 2868.
20. R. D. Chambers, W. K. R. Musgrave and J. Savory, *J. Org. Chem.,* 1961, 3779.
21. A. L. Henne and W. Postelneck, *J. Am. Chem. Soc.,* 1955, **77**, 4019.
22. M. Salisbury, Ph.D. Thesis, University of University of Durham, 1986.
23. R. N. Haszeldine and B. R. Steele, *J. Org. Chem.,* 1953, 1592.
24. J. Hutchinson, Ph.D. Thesis, University of University of durham, 1961.

25. G. Kojima and Y. Tabata, *J. Macromol. Sci. Chem.,* 1971, **A5**, 1087.
26. U.S. Pat. 4,235,804.
27. D. P. Craig, *Chem. Ind.,* 1958, 4.
28. D. P. Craig, *Theoret. Org. Chem.,Pap Kekule Symp.,* 1959, 20.
29. D. P. Craig, *J. Chem. Soc.,* 1959, 997.
30. D. P. Craig and N. L. Paddock, *J. Chem. Soc.,* 1962, 4118.
31. D. P. Craig and K. A. R. Mitchell, *J. Chem. Soc.,* 1965, 4682.
32. K. A. R. Mitchell, *J. Chem. Soc.,A,* 1968, 2683.
33. K. A. R. Mitchell, *Chem. Rev.,* 1969, **69**, 157.
34. D. A. Brown and C. G. McCormack, *J. Chem. Soc.,* 1964, 5386.
35. H. R. Allcock, *Phosphorus-Nitrogen Compounds,* Academic Press, New York and London, 1972.
36. J. Emsley and P. B. Udy, *J. Chem. Soc. A,,* 1970, 3025.
37. M. Becke-Goehring and K. Koch, *Chem. Ber.,* 1959, **92**, 1188.
38. F. Seel and J. Langer, *Z. Anorg. Allg. Chem.,* 1958, **295**, 316.
39. C. D. Schmulbach and V. R. Miller, *Inorg. Chem.,* 1966, **5**, 162.
40. D. L. Herring and C. M. Douglas, *Inorg. Chem.,* 1965, 1012.
41. H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.,* 1969, **91**, 3102.
42. H. R. Allcock and E. J. Walsh, 1970, *J.Chem.Soc., Chem. Commun.,* 580.
43. H. R. Allcock and E. J. Walsh, *J. Amer. Chem. Soc.,* 1972, **94**, 4538.
44. W. Ferrar, W. Lenhart, J. Lippert, T. Molaire, R. Guistina and D. Brown, *Phosphorus, Sulphur and Silicon,* 1989, **41**, 147.
45. H.Bode and H. Bach, *Chem. Ber.,* 1942, **75**, 215.
46. H. R. Allcock and J. H. Siegel, *J. Amer. Chem. Soc.,* 1964, **86**, 5140.
47. T. Chivers and N. L. Paddock, *J. Chem. Soc.,A,* 1969, 1687.
48. E. T. Mc Bee, H. R. Allcock, R. Caputo, A. kalmus and C. W. Roberts, *U. S. Govt. Res. Rep.,* 1958, **AD 209-669**,
49. R. Ratz, H. Schroeder, H. Ulrich, E. Kober and C. Grundmann, *J. Amer. Chem. Soc.,* 1962, **84**, 551.
50. H. R. Allcock and R. J. Best, *Can. J. Chem.,* 1964, **42**, 447.
51. J. O. Conecny and C. M. Douglas, *J. Polym. Sci.,* 1959, **36**, 195.
52. F. G. R. Gimblett, *J. Polym. Sci.,* 1962, **60**, 529.
53. A. V. Tobolsky and A. Eisemberg, *J. Amer. Chem. Soc.,* 1960, **82**, 289.
54. A. V. Tobolsky, *Properties and Structure of Polymers,* Wiley, New York, N. Y., 1960.
55. H. Lederle, E. Kober and G. Ottman, *J. Chem. Eng. Data,* 1966, **11**, 221.
56. G. Ottmann, H. Lederle and E. Kober, *Ind. eng. Chem., Prod. Res. Develop.,* 1966, **5**, 202.
57. E. Kober, H. Lederle and G. Ottmann, *Amer. Soc. Lubric. Eng. Trans.,* 1964, **7**, 389.

58. E. Kober, H. Lederle and G. Ottmann, *Inorg. Chem.*, 1966, **5**, 2239.
59. B. W. Fitzsimmons and R. A. Shaw, *Chem. Ind. (London)*, 1961, 109.
60. B. W. Fitzsimmons and R. A. Shaw, *J. Chem. Soc.*, 1964, 1735.
61. H. R. Allcock and R. L. Kugel, *Inorg. Chem.*, 1966, **5**, 1016.
62. B. W. Fitzsimmons and R. A. Shaw, *Inorg. Synt.*, 1966, **8**, 77.
63. H. R. Allcock, *J. Amer. Chem. Soc.*, 1963, **85**, 4050.
64. H. R. Allcock, *J. Amer. Chem. Soc.*, 1964, **86**, 2591.
65. J. Parrod and R. Pornin, *C. R. Acad. Sci.*, 1964, **258**, 3022.
66. M. S. Chang and A. J. Matuszko, *Chem. Ind. (London)*, 1962, 410.
67. B. Dishon, *J. Amer. Chem. Soc.*, 1949, **71**, 2251.
68. U. S. Pat. 2,876,247.
69. E. T. McBee, H. R. Allcock, R. Caputo, A. Kalmus and C. W. Roberts, *U. S. Govt. Astia Rep.*, 1959, **AD 209,669**,
70. H. R. Allcock and R. L. Kugel, *J. Amer. Chem. Soc.*, 1965, **87**, 4216.
71. H. R. Allcock, R. L. Kugel and K. J. Valan, *Inorg. Chem.*, 1966, **5**, 1709.
72. H. Lederle, E. Kober and G. Ottmann, *J. Chem. Eng. Data*, 1966, **11**, 221.
73. M. V. Lenton and B. Lewis, *J. Chem. Soc., A*, 1966, 665.
74. C. W. Allen and T. Moeller, *Inorg. Chem.*, 1968, **7**, 2178.
75. C. W. Allen and T. Moeller, *Inorg. Synth.*, 1970, **12**, 293.
76. G. Tesi and P. J. Slota, *Proc. Chem. Soc. (London)*, 1960, 404.
77. M. Biddlestone and R. A. Show, *J. Chem. Soc., Chem. Commun.*, 1968, 407.
78. M. Biddlestone and R. A. Shaw, *J. Chem. Soc.*, 1968, 178.
79. R. A. Shaw and M. Biddlestone, *J. Chem. Soc., Chem. Commun.*, 1965, 205.
80. U. S. Pat. 3,169,933.
81. F. Seel and J. Langer, *Angew. Chem.*, 1956, **68**, 461.
82. K. John and T. Moeller, *J. Am. Chem. Soc.*, 1960, **82**, 2647.
83. L. G. Lund, N. L. Paddock, J. E. Proctor and H. T. Searle, *J. Chem. Soc.*, 1960, 2542.
84. K. John and T. Moeller, *J. Inorg. Nucl. Chem.*, 1961, **22**, 199.
85. E. T. McBee, L. Brinkmann and H. P. Braendlin, *U. S. Govt. Res. Rep.*, 1960, **AD 254,982**,
86. M. Becke-Goehring, K. John and E. Fluck, *Z. Anorg. Chem.*, 1959, **302**, 103.
87. S. K. Ray and R. A. Show, *J. Chem. Soc.*, 1961, 872.
88. C. T. Ford, F. E. Dickson and I. I. Bezman, *Inorg. Chem.*, 1964, **3**, 177.
89. Y. Kobayashi, L. A. Chasin and L. B. Clapp, *Inorg.Chem.*, 1963, **3**, 177.
90. A. C. Chapman, D. H. Paine, H. T. Searle, E. R. Smith and R. F. M. White, *J. Chem. Soc.*, 1961, 1768.
91. A. P. Carroll and R. A. Shaw, *Chem. Ind.*, 1962, 1908.
92. J. L. Schmutz and H. R. Hallcock, *Inorg. Chem.*, 1975, **14**, 2433.
93. S. P. Kotun and D. D. DesMarteau, *Can. J. Chem.*, 1989, **67**, 1724.

94. D. P. Graham and V. Weinmayer, *J. Org. Chem.,* 1966, **31**, 957.
95. A. C. Knipe and W. E. Watts, *Organic Reaction Mechanism,* Wiley Interscience, 1978.
96. C. Walling, *Free-Radicals in Solution,* Wiley, New York, 1957.
97. W. A. Pryor, *Free-Radicals,* McGraw-Hill, New York, 1966.
98. J. M. Tedder, *Quart. Rev.,* 1960, **14**, 336.
99. G. Tesi and C. M. Douglas, *J. Am. Chem. Soc.,* 1962, **84**, 549.
100. T. Kitazume and N. Ishikawa, *Chem. Lett.,* 1981, 1679.
101. T. Kitazume and N. Ishikawa, *Chem. Lett.,* 1982, 137.
102. N. J. O'Reilly, M. Maruta and N.Ishikawa, *Chem. Lett.,* 1984, 517.
103. G. Santini, M. L. Blanc and J. G. Reiss, *J. Organom. Chem.,* 1977, **1**, 140.
104. G. Santini, M. L. Blanc and J. G. Reiss, *J. Chem. Soc., Chem. Commun.,* 1975, 678.
105. T. Kitazume and N. Ishikawa, *Nippon Kagau Kaishi,* 1984, 1725.
106. M. Stacey, J. C. Tatlow and A. B. Sharpe, *Adv. Fluorine Chem.,* 1963, **3**,
107. G. K. S. Prakash, R. Krishnamurti and G. Olah, *J. Am. Chem. Soc.,* 1989, **111**, 393.
108. I. Rupport, K. Schlich and W. Volbach, *Tetrahedron Lett.,* 1984, 2195.
109. G. Pawelke, *J. Fluorine Chem.,* 1989, **42**, 429.
110. W. Huang, C. Hu, Y. He and H. Zhou, *J. Fluorine Chem.,* 1990, **48**, 145.
111. W. T. Miller and A. L. Dittman, *J. Am. Chem. Soc.,* 1956, **78**, 2793.
112. W. T. Miller, S. D. Koch and F. W. McLafferty, *J. Am. Chem. Soc.,* 1956, **78**, 4992.
113. W. T. Miller and S. D. Kock, *J. Am. Chem. Soc.,* 1957, **79**, 3084.
114. U.S. Pat. 2,876,248.
115. C. E. Snyder and R. E. D. Jr., *ASLE Transactions,* 1976, **19**, 171.
116. U.S. 4,431,556.
117. U. S. 4,454,349.
118. U.S. 4,438,007.
119. M. H. Rock, Ph.D. Thesis, University of University of Durham, 1990.
119a. H. D. Jordan, J. W. Woods, *Proc. Int. Conf. Methods Prep. Stor. Label. Compounds,* J. Eur. At. Energy Community EURATOM, 1966
120. R. Fuss, Ph.D. Thesis, University of University of Durham, 1989.
120a. G. M. Burch, H. Goldwhite, and R. M. Haszeldine, *J. Chem Soc.,* 1963, 1083
121. R. Filler and Y. Kobayashi, *Biomedical Aspects of Fluorine Chemistry,* Elsevier, Amsterdam, 1982.
122. R. Filler, *Fluorine-The First Hundred Years,* Elsevier, Amsterdam, 1986.
123. G. T. Newbold, *Organofluorine Chemicals and Their Industiral Applications,* Ellis Horwood Ltd, Chirchester, 1979.
124. J. T. Welch, *Tet.,* 1987, **43**, 3123.

125. G. M. Trenholme, R. L. Williams, R. E. Desjardine, H. Frisher, P. E. Carson, K. H. Rieckmann and C. J. Canfield, *Science,* 1975, **190**, 792.
126. J. H. Brown, C. W. Suckling and W. B. Whally, *J. Chem. Soc.,* 1949, 95.
127. G. A. Boswell, W. C. Ripka, R. M. Scribner and C. W. Tullock, *Org. React.,* 1974, **21**, 1.
128. D. J. Burton and D. M. Wiemers, *J. Am. Chem. Soc.,* 1986, **108**, 832.
129. R. E. Banks, F. Cuthberton and W. K. R. Musgrave, *Anal. Chem. Acta,* 1955, **13**, 442.

INSTRUMENTATION AND REAGENTS

Gas Liquid Chromatographic Analysis

Analyses were carried out using a Hewlett Packard 5890A gas liquid chromatograph equipped with a 25 m cross-linked methyl silicone capillary column.

Preparative g.l.c. was performed on a Varian Aerograph Model 920 (catharometer detector) gas liquid chromatograph with packed columns, which was mainly a 3 m 10% SE 30.

Elemental Analysis

Carbon, hydrogen, and nitrogen elemental analyses were obtained using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Strumentazione 1106 Elemental Analyser. Analysis for halogens was performed as described in the literature[129]

NMR spectra

^{1}H, ^{19}F, ^{13}C n.m.r. spectra were recorded on a Bruker AC 250 (250 MHz), and a Varian VXR400S (400 MHz) n.m.r. spectrometer.

Infrared Spectra

Infrared spectra were recorded on a Perkin-Elmer 457 or 577 Grating spectrometer using KBr discs (for solid samples) or thin films between two KBr plates (for liquid samples). Gaseous samples were condensed into a cylindrical cell fitted with KBr plates.

Mass spectra

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

Ultraviolet spectra

Ultraviolet spectra were recorded on a Philips PU8720 UV/Vis scanning spectrometer.

Distillation

Fractional distillation of product mixtures was carried out using a Fischer Spahltroh MMS255 small concentric tube apparatus. Boiling points were recorded during the distillation.

Melting Points

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

Reagents and Solvent

Unless otherwise stated, reagents were used as supplied. Solvents were dried by standard methods and stored over a molecular sieve (type 4A).

CHAPTER 4
EXPERIMENTAL TO CHAPTER 1

4.A Preparation of remarkably stable fluorinated carbocations.

A series of observable carbocations were generated by mixing appropriate hydrofluorocarbon precursors with antimony pentafluoride. In a typical procedure hydrofluorocarbons listed in Table 14 were added slowly to antimony pentafluoride (~6 to 1 molar excess) under an inert atmosphere of nitrogen and stirred vigorously for 2 hours at room temperature. The mixture was then transferred into an n.m.r. tube and the correspondent ^{1}H, ^{19}F, ^{13}C n.m.r. spectra were acquired. In every case but for (20a) the observable carbocations were produced in almost quantitative yields. These carbocations showed no detectable signs of decomposition after storage at room temperature for several weeks.

Carbocation	Precursor g mmol	SbF_5 g mmol	n.m.r. spectrum
(9a)	(9) 0.48 g, 1.52 mmol	2.04 g, 2.1 mmol	1
(10a)	(10) 0.41 g, 1.07 mmol	1.4 g, 6.7 mmol	2
(11a)	(11) 0.52 g, 444 mmol	1.6 g, 7.4 mmol	3
(12a)	(12) 0.43 g, 0.8 mmol	1.17 g, 5.4 mmol	4
(10a)	(13) 0.47 g, 1.3 mmol	1.72 g, 7.9 mmol	2
(11a)	(14) 0.53 g, 1.3 mmol	1.7 g, 7.7 mmol	3
(12a)	(15) 0.6 g, 1.2 mmol	7.9 g, 1.7 mmol	4
(16a)	(16) 0.51 g, 1.4 mmol	8.7 g, 1.9 mmol	5
(17a)	(17) 0.49 g, 1.2 mmol	7.3 g, 1.6 mmol	6
(18a)	(18) 0.54 g, 1.1 mmol	1.5 g, 7.2 mmol	7
(19a)	(19) 0.4 g, 0.67 mmol	0.43 g, 0.95 mmol	8
(20a)	(20) 0.62 g, 0.85 mmol	5.3 g, 1.2 mmol	9

Table 14. Generation of carbocations.

4.B Preparation of Heptafluoro-2-iodopropane (25).

A mixture containing hexafluoropropene (275 g, 1.83 mol), iodine pentafluoride (83 g, 0.37 mol), and iodine (185 g, 0.73 mol) was sealed in a stainless steal autoclave (1175 ml capacity) degassed, and rocked under autogenous pressure for 28 hours at 150 °C. The autoclave was vented and HFP (1 g) was recovered. The liquid obtained was

washed with an aqueous solution of sodium metabisulphite and then distilled over anhydrous magnesium sulphate. The liquid was identified as heptafluoro-2-iodo propane (526 g, 97%) by comparison of its IR and n.m.r. spectra with that of an authentic sample.

4.C Telomerisation of vinylidene fluoride using perfluoroisopropyl iodide as initiator.

A mixture containing perfluoroisopropyl iodide (61 g, 0.206 mol) and vinylidene fluoride (VDF) (27 g, 0.432 mol) was condensed in a stainless steel autoclave (150 ml), degassed and rocked under autogenous pressure for 24 h at 180 °C. The autoclave was vented and no VDF was recovered. The liquid mixture obtained was separated by distillation (reduced pressure) and the components: $(CF_3)_2CFI$ (0.8 g) Bp 42 °C, $(CF_3)_2CF(CH_2CF_2)I$ (22.6 g, 30%) Bp 103-105°C, $(CF_3)_2CF(CH_2CF_2)_2I$ (38.4 g, 44%) Bp 92 °C/ 60 mmHg, $(CF_3)_2CF(CH_2CF_2)_3I$ (17 g, 17%) Bp 61-65 °C/ 1 mmHg, $(CF_3)_2CF(CH_2CF_2)_4I$ (4.5 g, 4%) Bp 92-96 °C/ 1 mmHg, $(CF_3)_2CF(CH_2CF_2)_5I$ (traces) were identified by comparison of their IR and n.m.r. spectra with those of authentic samples.

4.D Fluorodeiodination of telomer iodides.

4.D.1 Preparation of $(CF_3)_2CFCH_2CF_3$ (6).

A two necked round bottom flask was fitted with a dropping funnel, and a condenser. Antimony pentafluoride (4.3 g, 19 mmol.) in 1,1,2-trichloro-1,2,2-trifluoroethane (R-113) (10 ml) was added drop-wise to a stirred solution of $(CF_3)_2CF(CH_2CF_2)I$ (3.7 g, 10.4 mmol.) in R-113 (5 ml) over 20 minutes at -5° C. The mixture was stirred for a further hour . Water was added cautiously to the mixture which was allowed to warm up to room temperature and then thoroughly washed with a saturated sodium carbonate solution. The fluorinated layer was separated, dried over molecular sieves and distilled to give $(CF_3)_2CF(CH_2CF_2)F$ (1.7 g, 65 %) Bp 47-49 °C. The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N° 1, n.m.r. spectrum N°10, mass spectrum N°1.

4.D.2 Preparation of $(CF_3)_2CF(CH_2CF_2)_2F$ (9).

In a similar manner, using the apparatus described in 5.D.1, antimony pentafluoride (8.48 g, 39 mmol) in R-113 (10 ml) was added drop-wise to a solution of $(CF_3)_2CF(CH_2CF_2)_2I$ (8.3 g, 19 mmol) in R-113 (5 ml) at -5 °C to give $(CF_3)_2CF(CH_2CF_2)_2F$ (4.3 g, 70%).The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°2, n.m.r. spectrum N°11, mass spectrum.N°2.

4.D.3 Preparation of $(CF_3)_2CF(CH_2CF_2)_3F$ (10).

In a similar manner, using the apparatus described in 5.D.1, antimony pentafluoride (5.2 g, 24 mmol) in R-113 (10 ml) was added drop-wise to a solution of $(CF_3)_2CF(CH_2CF_2)_3I$ (6,2 g, 12 mmol) in R-113 (10 ml) at -5 °C to give $(CF_3)_2CF(CH_2CF_2)_3F$ (3.14 g, 68%).The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°3, n.m.r. spectrum N°12, mass spectrum N°3.

4.D.4 Preparation of $(CF_3)_2CF(CH_2CF_2)_4F$ (11).

In a similar manner, using the apparatus described in 5.D.1, antimony pentafluoride (5.6 g, 26 mmol) in R-113 (10 ml) was added drop-wise to a solution of $(CF_3)_2CF(CH_2CF_2)_4I$ (8.3 g, 15 mmol) in R-113 (10 ml) at -5 °C to give $(CF_3)_2CF(CH_2CF_2)_4F$ (4.06 g, 61%).The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°4, n.m.r. spectrum N°13, mass spectrum N°4.

4.D.5 Preparation of $(CF_3)_2CF(CH_2CF_2)_5F$ (12).

In a similar manner, using the apparatus described in 5.D.1, antimony pentafluoride (5.1 g, 23.6 mmol) in R-113 (10 ml) was added drop-wise to a solution of $(CF_3)_2CF(CH_2CF_2)_5I$ (6.2 g, 10.1 mmol) in R-113 (10 ml) at -5 °C to give $(CF_3)_2CF(CH_2CF_2)_5F$ (2.76 g, 54%).The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. N.m.r. spectrum N°14.

4.E Coupling reaction of telomer iodides using hν and mercury.

4.E.1 Preparation of $[(CF_3)_2CF(CH_2CF_2)]_2$ (21).

A mixture of $(CF_3)_2CF(CH_2CF_2)I$ (5 g, 9 mmol) and Hg (54 g) was sealed in a Carius tube and degassed. The Carius tube was then rolled whilst being irradiated for 2 days using a 1 Kw medium pressure Hanovia U.V. lamp. The Carius tube was cooled in liquid air, opened, and a mixture of gases (0.35 g) recovered. The mixture was analysed by GC/MS and the products identified as $(CF_3)_2CF(CH=CF_2)$ (5%), $(CF_3)_2CF(CH_2CF_2H)$ (5%), and $[(CF_3)_2CF(CH_2CF_2)]_2$ (85%) by comparison of their spectra with those of authentic samples. The remaining mixture containing mercury was extracted with dichloromethane and distilled under reduced pressure to give $[(CF_3)_2CF(CH_2CF_2)]_2$ (1.5 g, 82%).The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°14, n.m.r. spectrum N°27.

4.E.2 Preparation of $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (20).

A mixture of $(CF_3)_2CF(CH_2CF_2)_2I$ (5.3 g, 12.5 mmol) and Hg (90 g) was put into a Carius tube, degassed and sealed. The tube was then rolled whilst being irradiated for 2 days by a 1 Kw medium pressure Hanovia U.V. lamp. The tube was cooled in liquid air, then opened and a mixture of gases (0.3 g) recovered by distillation under reduced pressure. The mixture was analysed by GC/MS and the products identified as: $(CF_3)_2CF(CH_2CF_2)(CH=CF_2)$ (45%) and $(CF_3)_2CF(CH_2CF_2)(CH_2CF_2H)$ (55%). The involatiles were extracted with dichloromethane and the mixture obtained distilled under reduced pressure to give $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (1.55 g 42%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°15, n.m.r. spectrum N°28.

4.E.3 Preparation of $[(CF_3)_2CF(CH_2CF_2)_3]_2$ (19).

A mixture of $(CF_3)_2CF(CH_2CF_2)_3I$ (7 g, 14.3 mmol) and Hg (100 g) was degassed and sealed in a Carius tube. The tube was then rolled whilst being irradiated for 2 days by a 1 Kw medium pressure Hanovia U.V. lamp. The tube was cooled in liquid air, opened, and the contents extracted with dichloromethane. The mixture so obtained was purified by distillation (reduced pressure) to give $[(CF_3)_2CF(CH_2CF_2)_3]_2$ (2.3 g, 45%).Requires C, 29.9; H, 1.6; F, 68.3; found C, 30.1; H, 1.8; F, 68.7.
IR spectrum N°16, n.m.r. spectrum N°29, mass spectrum N°10.

4.F Coupling reaction of telomer iodides using zinc and acetic anhydride.

4.F.1 Preparation of $[(CF_3)_2CFCH_2CF_2\text{-}]_2$ (21).

A two necked round bottomed flask was fitted with a condenser topped by a drying tube and a super-seal. A mixture of zinc (0.19 g, 3 mmol) and acetic anhydride (5 ml) was stirred at temperature of reflux (external oil bath temperature 140 °C) for 2 hours to activate zinc and then allowed to cool down. A solution $(CF_3)_2CF(CH_2CF_2)I$ (1.08 g, 3 mmol) in dichloromethane (5 ml) was added drop-wise (by means of an hypodermic syringe) to the previously obtained mixture and stirred overnight. Following treatment with 10% sulphuric acid solution (20 ml), the resulting mixture separated into two layers. The organic layer was purified by distillation to give $[(CF_3)_2CF(CH_2CF_2)]_2$ (0.6 g, 85%) which was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample.

4.F.2 Preparation of $[(CF_3)_2CF(CH_2CF_2)_2]_2$ (20).

In a similar manner, using the apparatus described in 4.F.1, zinc (1.15 g, 22.9 mmol) was activated in acetic anhydride (10 ml). A solution of $(CF_2)_2CF(CH_2CF_2)_2I$ (7.5 g, 17,6 mmol) in acetic anhydride (5 ml) was added drop-wise to the zinc

suspension and stirred overnight. The reaction was worked up adding a 10% sulphuric acid solution (20 ml), and separating the fluorinated layer which was distilled to give $(CF_2)_2CF(CH_2CF_2)_2H$ (0.5 g, 10%), $[(CF_2)_2CF(CH_2CF_2)_2]_2$ (3.1 g, 58%), Bp 96-101 °C/ 1 mmHg, and $(CF_2)_2CF(CH_2CF_2)_2COCH_3$ (1.9 g, 32%), Bp 118-123 °C/ 1 mmHg. The products were identified by comparison of their IR and n.m.r. spectra with those of authentic samples.

4.G Dehydroiodination of telomers of vinylidene fluoride.

4.G.1 Synthesis of $(CF_3)_2CFCH=CF_2$ (8).

A three necked round bottomed flask was fitted with a condenser and a dropping funnel. Et_3N (6.5 g, 65 mmol) was added drop-wise to $(CF_3)_2CFCH_2CF_2I$ (21 g, 58.3 mmol) over 30 min. An exothermic reaction occurred with precipitation of the amine hydroiodide. The mixture was stirred for 2 hours, then the volatiles were pumped off under reduced pressure, washed with 5% hydrochloric acid solution (10 ml) (to remove the amine in excess) and distilled over anhydrous magnesium sulphate to give $(CF_3)_2CFCH=CF_2$ (9.7 g, 72%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°5, n.m.r. spectrum N°15.

4.G.2 Synthesis of $(CF_3)_2CFCH_2CF_2CH=CF_2$ (24).

In a similar manner, using the apparatus described in 4.G.1 Bu_3N (8.9 g, 48 mmol) was added drop-wise to $(CF_2)_2CF(CH_2CF_2)_2I$ (13.6 g, 32 mmol) over 30 min and stirred for 2 hours. The amine hydroiodide precipitated and the volatiles were distilled off under reduced pressure. The mixture was then washed with 5% hydrochloric acid solution (5 ml), the fluorinated layer was separated and distilled over magnesium sulphate to give $(CF_3)_2CFCH_2CF_2CH=CF_2$ (7.3 g, 78%) Bp 52 °C/ 200 mmHg. The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°6, n.m.r. spectrum N°16, mass spectrum N°5.

4.G.3 Synthesis of $(CF_3)_2CF(CH_2CF_2)_2CH=CF_2$ (13).

In a similar manner, using the apparatus described in 4.G.1 Bu_3N (2.9 g, 15.6 mmol) was added drop-wise to $(CF_2)_2CF(CH_2CF_2)_3I$ (5.88 g, 12.04 mmol) over 15 min and stirred for 30 minutes. The amine hydroiodide precipitated and the volatiles were distilled off under reduced pressure. The mixture was then washed with 5% hydrochloric acid solution (5 ml), the fluorinated layer was separated and distilled over magnesium sulphate to give $(CF_3)_2CF(CH_2CF_2)_2CH=CF_2$ (3.2 g, 74%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°7, n.m.r. spectrum N°17, mass spectrum N°6.

4.G.4 Synthesis of $(CF_3)_2CF(CH_2CF_2)_3CH=CF_2$ (14).

In a similar manner, using the apparatus described in 4.G.1 Bu_3N (3.51 g, 18.9 mmol) was added drop-wise to $(CF_2)_2CF(CH_2CF_2)_4I$ (8.05 g, 14.58 mmol) over 20 min and stirred for 30 min. The amine hydroiodide precipitated and the volatiles were distilled off under reduced pressure (heating with at 50°C). The mixture was then washed with 5% hydrochloric acid solution (5 ml), the fluorinated layer was separated and distilled over magnesium sulphate to give $(CF_3)_2CF(CH_2CF_2)_3CH=CF_2$ (4.2 g, 68%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N° 8, n.m.r. spectrum N°18.

4.G.5 Synthesis of $(CF_3)_2CF(CH_2CF_2)_4CH=CF_2$ (16).

In a similar manner, using the apparatus described in 4.G.1 Bu_3N (1.87 g, 10.1 mmol) was added drop-wise to $(CF_2)_2CF(CH_2CF_2)_5I$ (5.3 g, 8.6 mmol) over 20 min and stirred for 30 min. The amine hydroiodide precipitated and the volatiles were distilled off under reduced pressure (heating at 50°C). The mixture was then washed with 5% hydrochloric acid solution (5 ml), the fluorinated layer was separated and distilled over magnesium sulphate to give $(CF_3)_2CF(CH_2CF_2)_4CH=CF_2$ (2.56 g, 52%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. N.m.r. spectrum N°19.

4.G.6 Synthesis of $(CF_3)_2C=CHCF_3$ (7).

An 8 mm diameter silica Carius tube was charged with anhydrous caesium fluoride (0.7 g, 4.4 mmol), $(CF_3)_2CFCH=CF_2$ (0.7 g, 3 mmol) and anhydrous sulpholane (1.5 ml) under an inert atmosphere of nitrogen. The tube was degassed and sealed and heated at 90 °C in a rotating oil bath for 6 hours. The tube was cracked open and the volatiles were distilled off under reduced pressure to give $(CF_3)C=CHCF_3$ (0.5 g, 71%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°9, n.m.r. spectrum N°20, mass spectrum N°7.

4.G.7 Synthesis of $(CF_3)_2C=CHCF_2CH_2CF_3$ (24a).

In a similar manner an 8 mm diameter silica Carius tube was charged with anhydrous caesium fluoride (0.6 g, 3.7 mmol), $(CF_3)_2CFCH_2CF_2CH_2CF_3$ (1.8 g, 5.6 mmol) and sulpholane (1.5 ml), degassed sealed and heated to 120 °C in a rotating oil bath for 12 hours. The tube was cracked open and the volatiles pumped off under reduced pressure to give $(CF_3)_2C=CHCF_2CH_2CF_3$ (1.51 g, 85%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°10, n.m.r. spectrum N°21, mass spectrum N°8.

4.G.8 Synthesis of $(CF_3)_2C=CH(CF_2CH_2)_2CF_3$ (16).

In a similar manner an 8 mm diameter silica Carius tube was charged with anhydrous caesium fluoride (0.7 g, 4.4 mmol), $(CF_3)_2CFCH_2(CF_2CH_2)_2CF_3$ (0.98 g, 2.5 mmol) and sulpholane (1.5 ml), degassed sealed and heated to 120 °C in a rotating oil bath for 12 hours. The tube was cracked open and the volatiles distilled off (reduced pressure, 50 °C). The mixture was washed with water (2 ml) and the fluorinated layer was purified to give $(CF_3)_2C=CH(CF_2CH_2)_2CF_3$ (0.56 g, 63%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°11, n.m.r. spectrum N°22.

4.G.9 Synthesis of $(CF_3)_2C=CH(CF_2CH_2)_3CF_3$.(17).

In a similar manner an 8 mm diameter silica Carius tube was charged with anhydrous caesium fluoride (1.4 g, 3.1 mmol), $(CF_3)_2CFCH_2(CF_2CH_2)_3CF_3$ (0.98 g, 2.5 mmol) and sulpholane (1.5 ml), degassed sealed and heated to 120 °C in a Carius tube rotating oil bath for 12 hours. The tube was cracked open and the volatiles pumped off (reduced pressure, 70 °C). The mixture was washed with water (2 ml), to remove sulpholane, and the fluorinated layer was separated and purified to give $(CF_3)_2C=CH(CF_2CH_2)_3CF_3$ (0.68 g, 51%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°12, n.m.r. spectrum N°23.

4.G.10 (Z,Z) and (Z,E)-3,5-dihydro-2-trifluoromethylperfluorohex-2,4-ene (23a), (23b).

An 8 mm diameter quartz Carius tube was charged with anhydrous caesium fluoride (0.8 g, 5 mmol), $(CF_3)_2CFCH_2CF_2CH=CF_2$ (1.2 g, 4.3 mmol) in sulpholane (1.5 ml), degassed and sealed. The tube was heated in a rotating oil bath at 120 °C for 24 hours. The tube was cracked open and the volatiles pumped off under reduced pressure (0.8 g). Analysis by GLC showed two major components, in a 76/24 ratio (according to GLC peaks integration), which were separated by preparative GLC and identified as (23a) and (23b) (Z,Z) and (Z,E)-3,5-dihydro-2-trifluoromethylperfluorohex-2,4-ene. The product were identified by comparison of their IR and n.m.r. spectra with those of authentic samples. (23a) IR spectrum N°13, n.m.r. spectrum N°25, mass spectrum N°9; (23b) n.m.r. spectrum N°26.

4.G.11 Synthesis of $[(CF_3)_2C=CHCF_3]_2$ (22).

A three necked round bottomed flask (100 ml) was equipped with a dropping funnel a condenser and a vacuum tap connected to a vacuum pump through a trap (cooled down to liquid air temperature) containing sodium fluoride (5 g). $[(CF_3)_2CFCH_2CF_3]_2$ (5.4 g, 11.6 mmol) was added drop-wise to SbF_5 (7.9 g, 36.5 mmol) at room

temperature, the mixture was heated up to 120 °C and stirred for 2 h. The volatiles were then pumped off (reduced pressure) and collected into the sodium fluoride trap where they were allowed to rest for 1 h at room temperature. The volatiles were then transferred into another flask under reduced pressure, analysed and identified as $[(CF_3)_2C{=}CHCF_3]_2$ (4.5 g, 92%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°20, n.m.r. spectrum N°30, mass spectrum N°11.

4.H Preparation of 1,2-diiodotetrafluoroethane (37).

A mixture containing tetrafluoroethylene (TFE) (40 g, 0.4 mol) and iodine (104 g, 0.41 mol) was sealed in a stainless steal autoclave (1175 ml capacity) degassed, and rocked under autogenous pressure for 24 hours at 150 °C. The autoclave was vented and TFE (traces) was recovered. The liquid obtained was washed with an aqueous solution of sodium metabisulphite and distilled over anhydrous magnesium sulphate. The liquid was identified as 1,2-diiodotetrafluoroethane (138 g, 98%) Bp 110-111 °C. The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°17, n.m.r. spectrum N°31.

4.I Telomerisation of vinylidene fluoride using 1,2-diiodotetrafluoro-ethane as initiator.

A mixture containing 1,2-diiodotetrafluoroethane (60 g, 0.169 mol) and vinylidene fluoride (VDF) (27 g, 0.43 mol) was condensed in a stainless steel autoclave (150 ml), degassed and rocked under autogenous pressure for 24 h at 180 °C. The autoclave was vented and VDF (12.7 g) was recovered. The liquid mixture obtained was separated by distillation (reduced pressure) and the components: ICF_2CF_2I (8.4 g) Bp 110-111 °C, $ICF_2CF_2CH_2CF_2I$ (31.76 g, 45%) Bp 61-65 °C/ 1 mmHg, IR spectrum N°18, n.m.r. spectrum N°32, a ca.1:1 mixture of $ICF_2CH_2CF_2CF_2CH_2CF_2I$ and $ICF_2CF_2CH_2CF_2CH_2CF_2I$ (14.7 g, 18%) Bp 92-96 °C/ 1 mmHg, IR spectrum N°19, n.m.r. spectrum N°33 and higher molecular weight telomers (4.1 g) Bp 110- 114 °C / 1 mm Hg.

4.J Coupling reaction of telomer iodides using Zn and acetic anhydride.

4.J.1 Attempted preparation of 3,3,6,6-tetrahydroperfluoro-cyclohexane (35).

A three necked round bottomed flask (500 ml) was fitted with a condenser topped by a drying tube, a dropping funnel with a pressure equaliser and an inlet for nitrogen. A mixture of zinc (2.6 g, 40 mmol) and acetic anhydride (80 ml) was stirred at temperature of reflux (external oil bath temperature 140 °C) for 1 hour to activate zinc and then it was

allowed to cool down. A solution of $ICF_2CH_2CF_2CF_2CH_2CF_2I$ and $ICF_2CF_2CH_2CF_2CH_2CF_2I$ (1.08 g, 3 mmol) in acetic anhydride (10 ml) was added drop-wise to the previous mixture and stirred overnight. The reaction mixture was worked up by adding a 10% sulphuric acid solution (80 ml) in four portions (20 ml), the resulting mixture was extracted with dichloromethane. The organic layer was separated and purified by distillation to give a complex mixture of species of relatively high molecular weight which was difficult to separate. Attempts to isolate 3,3,5,5,tetrahydrooctafluorocyclohexane by means of vacuum sublimation did not prove to be successful.

4.K Fluorodeiodination of the telomer di-iodides. Preparation of $CF_3CF_2CH_2CF_3$ (38).

A two necked round bottom flask was fitted with a dropping funnel, and a condenser. Antimony pentafluoride (11.5 g, 53.2 mmol.) in 1,1,2-trichloro-1,2,2-trifluoroethane (R-113) (30 ml) was added drop-wise to a stirred solution of $(CF_3)_2CF(CH_2CF_2)I$ (7.4 g, 17.7 mmol.) in R-113 (10 ml) over 45 minutes at 0° C. The mixture was stirred for a further hour . Water was added cautiously to the mixture which was allowed to warm up to room temperature and then thoroughly washed with a saturated sodium carbonate solution till evolution of CO_2 ceased. The fluorinated layer was separated, dried on molecular sieves and distilled to give $CF_3CF_2CH_2CF_3$ (1.6 g, 55%). The product was identified by comparison of its n.m.r. spectra with those of an authentic sample. N.m.r. spectrum N°34.

CHAPTER 5
EXPERIMENTAL TO CHAPTER 2

5.A Reactions of halocyclotriphosphazenes with selected nucleophiles to investigate the reaction mechanism.

A two necked round bottom flask (100 ml) was equipped with a condenser a drying tube a super seal and a teflon coated magnetic stirring bar. Hexachlorocyclotriphosphazene (48) (5.56 g, 15.9 mmol) in anhydrous ether (20 ml) was reacted with sodium 2,2,2-trifluoroethoxide (20 ml of 4 x 10^{-1} M solution, 8 mmol). (The solution was prepared by reaction of 2,2,2-trifluoroethanol (2.5 g, 25 mmol) and sodium (0.57 g, 23 mmol) in anhydrous ether (62.5 ml)). The mixture was sampled every ten minutes for three times, then after 15' and 30', the reaction was quenched each time by immediate cooling of the sample. The degree of nucleophilic displacement was monitored by ^{31}P. Results are reported in Table 15.

In a similar manner sodium phenoxide, and sodium thiolate were reacted with hexachlorocyclotriphosphazene. The conditions and the results are reported in Table 15.

In a similar manner 2,2,2-trifluoroethanol, sodium phenoxide, and sodium thioethoxide were reacted with hexafluorocyclotriphosphazene (55), the conditions are reported in Table 15. No sign of reaction could be monitored at 0°C.

A 10 mm diameter n.m.r. tube was charged with hexachlorocyclotriphosphazene (0.56 g, 1.6 mmol) and an ethereal solution of sodium 2,2,2-trifluoroethanol (2 ml, 4 x 10^{-1} M, 0.8 mmol), under an inert atmosphere of nitrogen and at liquid air temperature. The mixture was allowed to warm up to room temperature and the kinetic of the reaction was followed by timed monitoring ^{31}P n.m.r. analysis. Results are reported in Table 15.

Reactants	$[NPX_2]_3$			Nu^-	AX_2		
		(g)	mmol	(mmol)	δ_1 (ppm)	δ_2 (ppm)	J_{1-2} (Hz)
$CF_3CH_2O^-Na^+$	(48)	5.6	16	8	23.2	16.8	~66
$C_6H_5O^-Na^+$	(48)	5.6	16	8	24.6	8.7	~60
$C_2H_5S^-Na^+$	(48)	5.6	16	8	19.2	39.7	~34
$CF_3CH_2O^-Na^+$	(48)	0.56	1.6	0.8	23.2	16.8	~66
$C_6H_5O^-Na^+$	(55)	3.98	16	8	no reaction		
$C_2H_5S^-Na^+$	(55)	3.98	16	8	no reaction		
$CF_3CH_2O^-Na^+$	(55)	3.98	16	9	no reaction		

Table 15. Reaction of halophosphazenes with selected nucleophiles

5.B Reactions of hexachlorocyclotriphosphazene (48) with nucleophiles.

5.B.1 Synthesis of hexafluorocyclotriphosphazene (55).

A three necked round bottom flask was equipped with a condenser, a drying tube, two stoppers and a teflon coated magnetic stirring bar. Hexachlorocyclotriphosphazene (48) (17 g, 0.04 mol) in anhydrous acetonitrile (200 ml) was mixed with anhydrous KF (18 g, 0.31 mol) and 18-crown-6 (0.5 g) under a stream of nitrogen. The mixture was stirred vigorously and heated up to reflux conditions for 4 hours. On cooling demineralised water (200 ml) was added to the mixture. The fluorinated layer was separated, further washed with water, and subsequently distilled over anhydrous sodium sulphate to give hexafluorocyclotriphosphazene (8.46 g, 85%). The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°21,.n.m.r. spectrum N°35, mass spectrum N°12.

5.B.2 formation of poly(fluoro)phosphazene (55b).

A 10 mm diameter quartz n.m.r.tube was filled with caesium fluoride (0.3 g, 2.1 mmol) and hexafluorocyclotriphosphazene (1.7 g, 0.7 mmol). The tube was degassed and sealed and heated up to 70°C. A very viscous liquid was obtained and identified as poly-hexafluorocyclotriphosphazene $[NPF_2]_n$ (found N, 15.73; P, 36.12; F, 44.1; requires N, 16.86; P, 37.34; F, 45.8%); IR spectrum N°29,.n.m.r. spectrum N°48.

5.B.3 Attempted synthesis of hexabromocyclotriphosphazene (54).

A one necked flask (25 ml) was fitted with a condenser and a teflon coated magnetic stirring bar. Sodium bromide (4.43 g, 43.05 mmol) was reacted with hexachlorocyclotriphosphazene (0.5 g, 1.4 mmol) in anhydrous acetone (8 ml) and in presence of a catalytic amount of 18-crown-6 (~5%). The mixture was stirred for four days. Celite (1 g) was added and the precipitate was filtered off. ^{31}P n.m.r. of the filtrate showed numerous doublet and triplets in the area between 0 - 20 ppm., but assignment could not be carried out.

5.B.4 Attempted synthesis of hexaiodocyclotriphosphazene (61).

A single necked flask (25 ml) was fitted with a condenser and a teflon coated magnetic stirring bar. Sodium iodide (6.4 g, 43.05 mmol) was reacted with hexachlorocyclotriphosphazene (0.5 g, 1.4 mmol) in anhydrous acetone (8 ml) and in presence of a catalytic amount of 18-crown-6 (~5%). The mixture was stirred for four days. Celite (1 g) was added and the precipitate was filtered off. ^{31}P n.m.r. of the filtrate showed that extensive decomposition had taken place.

5.B.5 Synthesis of hexakis(methoxy)cyclotriphosphazene (63).

A three necked round bottomed flask (250 ml) was fitted with a condenser, a dropping funnel with a pressure equaliser, a nitrogen inlet, and a teflon coated magnetic stirring bar. Sodium (3.3.g, 143 mmol) was added to a mixture of methanol (20 ml) and diethylether (20 ml). The mixture was then added drop-wise to a solution of hexachlorocyclotriphosphazene (6.25 g, 18 mmol) in diethylether (20 ml). The so obtained mixture was heated up to reflux temperature (oil bath temperature 70°C) for 3 hours. The reaction mixture was allowed to cool and celite (10 g) was added. The precipitate was then filtered off and the solvents removed under reduced pressure. The solid obtained was purified by vacuum sublimation (110°C, 4 x 10^{-2} bar) to give hexakis(methoxy)cyclotriphosphazene (4.25 g, 73%). The product was identified by comparison of the IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°22,.n.m.r. spectrum N°36, mass spectrum N°13.

5.B.6 Synthesis of hexakis(ethoxy)cyclotriphosphazene (64).

In a similar manner sodium hydride (3.42 g, 143 mmol) was added to a mixture of anhydrous ethanol (35 ml) and diethylether (10 ml). The mixture was then added drop-wise to a solution of hexachlorocyclotriphosphazene (6.25 g, 18 mmol) in diethylether (15 ml). The so obtained mixture was heated at temperature of reflux (oil bath temperature 70°C) for 3 hours. The reaction mixture was allowed to cool and celite (10 g) was added. The precipitate was then filtered off and the solvents removed under reduced pressure. The liquid obtained was purified by vacuum sublimation (90°C, 4 x 10^{-2} bar) to give hexakis(ethoxy)cyclotriphosphazene (4.25 g, 73%). The product was identified by comparison of the IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°23,.n.m.r. spectrum N°37, mass spectrum N°14.

5.B.7 Synthesis of hexakis(diethylamino)cyclotriphosphazene (66).

A stainless steel autoclave was charged with hexachlorocyclotriphosphazene and diethylamine in toluene, degassed and heated up to 150°C in a rocking furnace for 30 hours. The mixture was taken out of the autoclave, the solvent was removed under reduced pressure and the solid mixture recrystalised in toluene. The solid was identified as hexakis(diethylamino)cyclotriphosphazene by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°24,.n.m.r. spectrum N°38, mass spectrum N°15.

5.B.8 Synthesis of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50).

A three necked flask fitted with a condenser a dropping funnel and a teflon coated magnetic stirring bar. Sodium (1.6 g, 0.07 mol.) was added to a solution of 2,2,2-trifluoroethanol (16 g, 0.16 mol.) in anhydrous diethylether (30 ml) under a stream of nitrogen. A solution of hexachlorocyclotriphosphazene (3.4 g, 10 mmol) in anhydrous diethylether (20 ml) was added drop-wise to the previously obtained mixture and stirred for four hours at temperature of reflux. A precipitate of sodium chloride was filtered off and the filtrate was washed thoroughly with water to remove the excess of sodium 2,2,2-trifluoroethoxide. The organic layer was separated, and the solvent removed under reduced pressure to obtain a viscous oil which solidified on cooling to give hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (4.8 g, 65%) which was purified by vacuum sublimation at 70° C / 2 mmHg. The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°25,.n.m.r. spectrum N°39, mass spectrum N°16.

5.B.9 Synthesis of hexakis(2,2,3,3,3-pentafluoropropoxy)-cyclotriphosphazene (67).

A three necked flask (250 ml) was fitted with a condenser a dropping funnel and a teflon coated magnetic stirring bar. Sodium hydride (1.39 g, 58 mmol) was added to a solution of 2,2,3,3,3-pentafluoropropanol (9 g, 60 mmol) in anhydrous diethylether (30 ml) under a stream of nitrogen. A solution of hexachlorocyclotriphosphazene (2.78 g, 8 mmol) in anhydrous diethylether (20 ml) was added drop-wise to the previously obtained mixture and stirred for four hours at temperature of reflux. Sodium chloride was filtered off and the filtrate washed with water to quench the excess of sodium pentafluoropropoxide. The organic layer was separated, and the solvent removed under reduced pressure to obtain a viscous oil identified as hexakis(2,2,3,3,3-pentafluoropropoxy)cyclotriphosphazene (5.7 g, 69%) which was purified by vacuum sublimation at 70° C / 2 mmHg. The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°26,.n.m.r. spectrum N°40.

5.B.10 Synthesis of hexakis(2,2,3,3,4,4,4-heptafluorobutoxy)-cyclotriphosphazene (68).

In a similar manner sodium hydride (1.1 g, 46 mmol) was added to a solution of 2,2,3,3,4,4,4-heptafluorobutanol (10 g, 49 mmol) in anhydrous diethylether (30 ml) under a stream of nitrogen. A solution of hexachlorocyclotriphosphazene (2.34 g, 6.7 mmol) in anhydrous diethylether (20 ml) was added drop-wise to the previously obtained mixture and stirred for four hours at temperature of reflux. Sodium chloride was filtered

off and the filtrate washed with water to quench the heptafluoroalkoxide in excess. The organic layer was separated, and ether removed under reduced pressure to obtain a viscous oil identified as hexakis(2,2,3,3,4,4,4-heptafluoropropoxy)cyclotriphosphazene (5.7 g, 69%) which was purified by vacuum sublimation at 70° C / 2 mmHg. The product was identified by comparison of its IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°27,.n.m.r. spectrum N°41.

5.B.11 Synthesis of phosphazene (70a), fully substituted by Fomblin alcohol (69a).

In a similar manner sodium hydride (1.65 g, 42 mmol.) was added to a solution of perfluoropolyether alcohol (known as hydroxy-terminated Fomblin Y (fluid manufactured by Ausimont S.p.A.- Italy) of formula R_FCH_2OH (69), having an equivalent weight of 457 a.m.u. (69a), and a C_3/C_1 units ratio of 36.8.

$$T\text{-}O\text{-}\ (CF(CF_3)CF_2O)_m(CFXO)_n\text{-}CFZ\text{-}CH_2OH$$

(69)

where: T = $-CF_3$, $-C_2F_5$, $-C_3F_7$; X = -F, $-CF_3$; Z = -F, $-CF_3$; m and n are numbers so that the n/m ratio ranges from 0.01 to 0.5) (24 g, 50 mmol) in anhydrous tetrahydrofuran (30 ml) under a stream of nitrogen. A solution of hexachlorocyclotriphosphazene (2.34 g, 6.7 mmol) in anhydrous diethylether (20 ml) was added drop-wise to the previously obtained mixture and stirred for six hours at temperature of reflux. Sodium chloride was filtered off and the filtrate washed with water to quench the heptafluoroalkoxide in excess. The organic layer was separated, tetrahydrofuran was removed under reduced pressure and the perfluoropolyether-alcohol in excess was distilled off (90° C, 10^{-2} mbar) to obtain a viscous oil which was identified as hexakis(perfluoropolyether-alkoxy)-cyclotriphosphazene (16 g). Since the nature of the perfluoropolyether chains differ in structure the product was identified by the presence of a singlet in the ^{31}P n.m.r. spectrum at 17.2 ppm. IR spectrum N°28,.n.m.r. spectrum N°42.

5.B.12 Preparation of phosphazenes (70c)-(70g) partially substituted with Fomblin alcohol (69b).

In a similar manner a solution of Fomblin alcohol (equivalent weight 900 a.m.u.) (25.3 g, 28.1 mmol) in anhydrous diethylether (50 ml) was added drop-wise to a suspension of sodium hydride (0.61 g, 25.8 mmol) in anhydrous diethylether (100 ml). The resultant mixture was refluxed vigorously (oil bath temperature 65°C) for 1 hour and allowed to cool down. A solution of $[NPCl_2]_3$ (2.8 g, 8 mmol) in anhydrous diethylether (50 ml) was then added in a single portion. The resultant mixture was then refluxed for 1 hour, allowed to cool down. Demineralised water (200 ml) was then added, the ethereal layer was separated and ether removed under reduced pressure. Fomblin alcohol in excess was distilled off under reduced pressure (10^{-3} mbar) at 100°C. Further distillation

was carried out and two fractions were collected. The first fraction (6.2 g) Bp.100-150°C; 10^{-3} mbar, was analysed and identified as a mixture of mono-, di- and tri-substituted phosphazenes (70c)-(70e). The second fraction (9.58) Bp.150-180°C at 10^{-3} mbar was analysed and identified as a mixture of tri- and tetra- and penta-substitued phosphazenes (70e)-(70g). Identification was carried out by means of ^{31}P n.m.r. N.m.r. spectra N° 43-47.

5.C Thermal stability.

5.C.1 Thermal stability of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50).

A 4 mm diameter quartz tube was charged with a suitable amount of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (1.5 g, 1.8 mmol), degassed and sealed. The tube was put in a metal sleeve and heated up to 320°C for 3 hours. The colour of the material changed into light brown. The quartz tube was then put into an n.m.r. tube and analysed. The ^{31}P n.m.r. showed the presence of starting material (17.4 ppm, 84%) and of some degradation products (two singlets at -1.3 and -6 ppm, respectively 11 and 5%). The ^{19}F n.m.r. showed only the presence of a peak at -78 ppm attributed to the trifluoromethyl groups. No further analysis was carried out to determine the nature of the degradation products.

In a similar manner hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (1.5 g, 1.8 mmol) was pyrolysed at 420°C for 20 minutes. The ^{31}P n.m.r. showed the presence of starting material (17.4 ppm, 35%) and of some degradation products (a singlet at -1.3 ppm, 45% and two singlets at ~ -3 and ~ -6 ppm). The ^{19}F n.m.r. showed the presence of a peak at -78 ppm attributed to the trifluoromethyl groups and of some smaller peaks around -80 ppm. No further analysis was carried out to determine the nature of the degradation products.

5.C.3 Thermal stability of hexakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotriphosphazene (68).

A 4 mm diameter quartz tube was charged with hexakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotriphosphazene (1.8 g, 1.3 mmol), degassed and sealed. The tube was put in a metal sleeve and heated up to 320°C for 3 hours. The ^{31}P n.m.r. showed the presence of starting material (17.6 ppm, 90%) and the presence of a doublet and a triplet, respectively at 15 and 27 ppm in a 2 to 1 ratio J = 88.4 Hz. The ^{19}F n.m.r. showed only the presence of peaks at -84, -124 and -130 ppm attributed to heptafluoropropyl groups. No further analysis was carried out to determine the nature of the degradation products.

5.C.3 Thermal stability of hexakis(perfluoropolyether-alkoxy)cyclotriphosphazene (70a).

A 4 mm diameter quartz tube was charged with hexakis(perfluoropolyether-alkoxy)cyclotriphosphazene (1.5 g), degassed and sealed. The tube was put in a metal sleeve and heated up to 320°C for 3 hours. The quartz tube was analysed by ^{31}P n.m.r. which showed only the presence of the starting material (17.4 ppm, 100%), the ^{19}F and ^{1}H n.m.r. spectra were also unchanged, indicating that no degradation took place.

In a similar manner hexakis(perfluoropolyether-alkoxy)cyclotriphosphazene (1.5 g) was heated up to 420°C for 20 minutes. The ^{31}P n.m.r. showed the presence of starting material (17.4 ppm, 84%) and of degradation products (a triplet a ~10 ppm and some peaks between -2 and -15 ppm). The ^{19}F and ^{1}H n.m.r. did not show any relevant change. No further analysis was carried out to determine the nature of the degradation products.

5.D Hydrolytic stability.

Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50) (1.2 g), hexakis(heptafluoro-butoxy)cyclotriphosphazene (68) (1.4 g) and hexakis(perfluoropolyether-alkoxy)cyclo-triphosphazene (70a) were singularly reacted in a Carius tube with sodium hydroxide (2 x 10^{-2} M in a 25 vol % aqueous diglyme) and stirred at 70°C over 5 days. Analysis by ^{31}P n.m.r. did not show any sign of decomposition.

5.E Alcoholysis of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50).

A Rotaflo flask (100 ml) was equipped with a teflon coated magnetic stirring bar. Sodium (0.2 g, 8.6 mmol) and methanol (0.53 g, 16.8 mmol) were mixed in anhydrous tetrahydrofuran (1.5 ml), under a stream of nitrogen. When the evolution of hydrogen stopped, hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (0.5 g, 0.6 mmol) was added, the tube was closed and heated up to 75°C. The volatiles were removed under vacuum and analysed. Trifluoroethylmethylether $CF_3CH_2OCH_3$ was identified by GC/MS analysis by comparison of the mass spectrum (N°17) with that of an authentic sample prepared by another route. Analysis of the residue by ^{31}P n.m.r. showed the presence of numerous peaks which could not be assigned. Further investigation of the residue was not undertaken.

5.E.1 Preparation of 2,2,2-trifluoroethylmethylether ($CF_3CH_2OCH_3$) (71).

A two necked flask (100 ml) was fitted with a dropping funnel, a T joint , a Liebig condenser and a flask for collection. *N.B. special glass-wear is with smooth joint is needed to avoid explosions!!.* A solution of p-tolylsulphonylmethylnitrosamide (2.14 g, 10 mmol) in ether (30 ml) was added drop-wise to mixture potassium hydroxide (0.4 g, 7 mmol) was in ethanol (10 ml) and a few drops of demineralised water, heated at 60°C. A solution of 2,2,2-trifluoroethanol (1 g, 10 mmol) in ether was added to the previously obtained ethereal solution of diazomethane in presence of a catalytic amount of borotrifluoride etherate, at room temperature. The volatiles were removed under vacuum and $CF_3CH_2OCH_3$ (71) identified by GC/MS mass spectrum N°17.

5.F Interaction with Lewis acids.

A 5 mm diameter quartz n.m.r. tube was charged with hexakis(perfluoropolyether-alkoxy)cyclotriphosphazene (1.5 g) and aluminium trichloride (0.2 g, 1.4 mmol) degassed and sealed. The reaction was monitored by ^{31}P n.m.r. At room temperature no sign of reaction was detected. The mixture was then warmed up to 100°C, and ^{31}P n.m.r. showed a peak at 16.3 ppm 69%, a doublet at 7 ppm and a triplet at -4 ppm, J = 72 Hz.

5.G Attempted fluoride ion induced polymerisation.

Hexakis(2,2,2-2,2,3,3,4,4,4-hepatfluorobutoxy)cyclotriphosphazene (50) (1.4 g, 1.9 mmol) and hexakis(perfluoropolyether-alkoxy)cyclo-triphosphazene (70a) (1.5 g) were singularly mixed with an excess of caesium fluoride in acetonitrile in a sealed quartz tube and heated to 80°C to induce telomerisation. Monitoring by ^{31}P n.m.r. showed that no reaction took place.

5.H Synthesis of fluorinated tertiary alcohols.

5.H.1 $CF_3CF_2(CF_3)_2COH$ (72).

A three necked flask (2 l) was fitted with a Hanovia ultra-violet high pressure mercury lamp (1000 W), a pressure gauge and a vacuum tap connection. The flask was also equipped with two inlets at the side to allow top up of the gases when the reaction was taking place. A mixture of tetrafluoroethylene (300 mmHg) and hexafluoroacetone (490 mmHg) was irradiated overnight. The volatile were removed under reduced pressure and $C(CF_3)_2$-O- CF_2CF_2 (3 g, 11.2 mmol) separated by fractional distillation. The oxetane was then vacuum transferred into a stainless steel reactor (10 ml) containing

a SbF_5/HF (1/1.6 mixture, g 2.79). The tube was degassed and placed in a oil bath for 36 hours at 60° C. The mixture was vacuum transferred into a flask (125 ml) containing sodium fluoride (10 g, 0.5 mol). After two hours at room temperature with occasional shaking the volatiles were distilled off and fractionated through three cooled traps. The compound found in the trap at -80° C was identified as $CF_3CF_2C(CF_3)_2OH$ by comparison of its ^{19}F n.m.r. spectrum with that of an authentic sample. IR spectrum N°30, n.m.r. spectrum N°49.

5.H.2 $(CF_3)_2CF(CF_3)_2COH$ (73).

A two necked flask was fitted with a bladder and a vacuum tap connection. A mixture of anhydrous caesium fluoride (7.0 g, 46 mmol) in diglyme was put into the flask, degassed, and reacted with hexafluoroacetone (7.61 g 45.8 mmol) from a bladder. When the hexafluoroacetone-caesium fluoride complex was formed quantitatively, the mixture was frozen in liquid air, degassed and reacted with hexafluoropropene (7.9 g, 53 mmol) from a bladder. Solvent and the volatiles were removed under reduced pressure and gentle heating. The solid residue was treated with concentrated sulphuric acid and liquid was distilled off and identified as $(CF_3)_2CF(CF_3)_2COH$ (73) (11.9 g, 67%) by comparison of its ^{19}F n.m.r. spectrum with that of an authentic sample. IR spectrum N°31, n.m.r. spectrum N°50.

5.I Free radical additions to haxafluoropropene.

The free radical addition of hexafluoropropene to model compounds hexakis(methoxy)cyclotriphosphazene (63), hexakis(ethoxy)cyclotriphosphazene (64), hexakis(diethylamino)cyclotriphosphazene (66), hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50) and hexachlorocyclotriphosphazene (48) was carried out under the conditions reported in Table 16. A 8 millimetre diameter quartz tube was filled singularly with model compounds (63), (64), (66), (50), (48) in anhydrous acetone (1 ml) and hexafluoropropene (as indicated). The solution was degassed three times and the tube sealed. The mixtures were then irradiated for three weeks and the reactions were followed by ^{31}P n.m.r. monitoring. In all cases, complicated mixtures of products were obtained which could not be separated by column chromatography.

Model compounds (g, mmol)	HFP (g, mmol)	Solvent	Products
(63) 0.08, 0.23	6, 40	-	mixture
(63) 0.08, 0.23	1.3, 8.6	Acetone (1 ml)	mixture
(64) 0.22, 0.54	1.5, 10	Acetone (1 ml)	mixture
(66) 0.34, 0.59	1.7, 11.3	Acetone (1 ml)	mixture
(50) 0.11, 0.31	1.38, 9.2	Acetone (1 ml)	no reaction
(48) 0.15, 0.2	1.35, 9.04	Acetone (1 ml)	no reaction

Table 16. Free radical addition of hexafluoropropene to phosphazenes.

5.J Perfluoroalkylation of halophosphazenes.

5.J.1 Synthesis of trifluoromethyltrimethylsilane (78) by reaction of trifluoromethyl bromide and bis(diethylamino)phosphine.

A three necked flask (500 ml) was fitted with a pressure gauge, a vacuum tap, a stopper and a teflon coated magnetic stirring bar. Trimethylsilylchloride (7.2 g, 67 mmol) bis(diethylamino)phosphine (19.8 g, 80 mmol) were mixed in benzonitrile (60 ml). The mixture was cooled down in liquid air and trifluoromethyl bromide (10.5 g, 70.5 mmol) was condensed into the flask. The mixture was then allowed to warm up to -20°C while stirring for three hours. The mixture was then allowed to warm up to room temperature over-night, the volatiles were then removed under reduced pressure, and purified by distillation to give trifluoromethyltrimethylsilane (bp 44-46°C) (7.7 g, 81%). The product was identified by comparison of the IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°32, n.m.r. spectrum N°51, mass spectrum N°18.

5.J.2 Synthesis of trifluoromethyltrimethylsilane (78) by reaction of trifluoromethyliodide and tetrakis(dimethylamino)ethylene.

In a similar manner trimethylsilylchloride (4.3 g, 39 mmol) tetrakis(dimethylamino)ethylene (8.5 g, 42.5 mmol) were mixed in benzonitrile (60 ml). The mixture was cooled down in liquid air and trifluoromethyliodide (10.6 g, 36 mmol) was condensed into the flask. The mixture was then allowed to warm up to 0°C while stirring for three hours. The mixture was then allowed to warm up to room temperature over-night, the volatiles were then removed under reduced pressure, and purified by distillation to give trifluoromethyltrimethylsilane (4.3 g, 78%). The product was identified by comparison of the IR and n.m.r. spectra with those of an authentic sample.

5.J.3 Synthesis of pentafluoroethyltrimethylsilane (88).

In a similar manner trimethylsilylchloride (4.12 g, 38 mmol) bis(diethylamino)phosphine (9.9 g, 40 mmol) were mixed in benzonitrile (40 ml). The mixture was cooled down in liquid air and pentafluoroethyl iodide (7.8 g, 32 mmol) was condensed into the flask. The mixture was then allowed to warm up to -15°C while stirring for three hours, and then allowed to warm up to room temperature over-night. The volatiles were then removed under reduced pressure, and purified by distillation to give pentafluoroethyltrimethylsilane (88) (5.2 g, 72%) (requires C, 31.10; H, 4.70; F, 49.24%, found C, 31.32; H, 4.81; F, 49.8%). IR spectrum N°33, n.m.r. spectrum N°52, mass spectrum N°19.

5.J.4 Trifluoromethylation of halophosphazenes.

A two necked flask was equipped with a vacuum tap, a rubber septum and a teflon coated magnetic stirring bar. Hexafluorocyclotriphosphazene (0.6 g, 2.3 mmol), trifluoromethyltrimethylsilane (2.5 g, 17.6 mmol) and acetonitrile (3 ml) were condensed into the flask in presence of a catalytic amount of anhydrous potassium fluoride (0.1 g). The mixture was allowed to warm up to 0°C and stirred for three days in a cooling bath. Attempts to separate the mixture by fractional vacuum distillation proved not to be successful. However, the ^{31}P n.m.r. showed exclusively a septuplet at 3.9 ppm, J = 108 Hz the ^{19}F n.m.r. showed a doublet at -74.6 J = 108 Hz which are attributed to the presence of hexakis(trifluoromethyl)cyclotriphosphazene. The product, though, could not be isolated and fully characterised.

5.J.5 Attempted direct perfluoroalkylation of hexachlorocyclotriphosphazene.

A Carius tube containing a teflon coated magnetic stirring bar was charged with hexachlorocyclotriphosphazene (0.56 g, 1.6 mmol), tris(diethylamino)phosphine (4.1 g,

16.5 mmol), trifluoromethyl bromide (2.3 g, 15.4 mmol), and benzonitrile (10 ml). The Carius tube was then degassed sealed and the mixture was stirred over three days at 0°C, in a cooling bath. The Carius tube was then opened and the crude mixture (dark brown in colour) analysed. the ^{31}P n.m.r. showed as the main product a quartet at +73.8 ppm J = 91.05 and the ^{19}F n.m.r. showed the presence of a doublet at -61.5 ppm J = 92 Hz. This product was identified as tris(diethylamino)trifluoromethylphosphonium bromide (84).

5.J.6 Study of the trifluoromethylhalides-tris(diethylamino)phosphine interactions.

Trifluoromethyl bromide (81) and trifluoromethyliodide (85) were singularly reacted with tris(diethylamino)phosphine (82), in presence of different solvents. The mixtures were sealed in a 4 millimetre diameter n.m.r. tube and the reactions were followed by monitoring of ^{31}P, ^{19}F and ^{1}H n.m.r. spectra. Reaction conditions and results are reported in Table 17.

Reactant	g	mmol	Solvent (ml)	(82) (g) (mmol)	Products
(81)	0.29	2	-	(0.15) (0.6)	(84)
(81)	0.29	2	benzonitrile (0.2 ml)	(0.08 (0.32)	(84) 90% (83) 10%
(81)	0.31	2.1	diglyme (0.2 ml)	(0.09) (0.36)	(84) 90% (83) 10%
(81)	0.32	2.2	acetonitrile (0.2 ml)	(0.1) (0.4)	(83) ~100%
(85)	0.39	2	-	(0.09) (0.36)	complex mixture
(85)	0.39	2	benzonitrile (0.2 ml)	(0.12) (0.48)	complex mixture
(85)	0.37	1.9	diglyme (0.2 ml)	(0.09) (0.36)	complex mixture
(85)	0.39	2	acetonitrile (0.2 ml)	(0.09) (0.36)	complex mixture
(85)	0.39	2	CH_2Cl_2 (0.2 ml)	(0.1) (0.4)	complex mixture

Table 17. Interaction of trifluoromethyl halides and tris(diethylamino)phosphine.
(83) = trifluoromethane
(84) = trifluoromethyltris(diehtylamino)phosphonium bromide.

5.J.7 Perfluoroalkylation using heptafluoroisopropyl iodide and tris(diethylamino)phosphine

A Carius tube containing a teflon coated magnetic stirring bar was charged with hexachlorocyclotriphosphazene (0.56 g, 1.6 mmol), tris(diethylamino)phosphine (4.3 g, 17.3 mmol), heptafluoroisopropyl iodide (4.4 g, 14.8 mmol), and benzonitrile (10 ml). The tube was then degassed and sealed and the mixture was stirred over 3 days at 0°C. The mixture separated out into two layer and they both were analysed. Both ^{31}P and ^{19}F indicated the presence of a complex mixture whose separation was not attempted.

5.K Routes to per-haloalkoxy phosphazenes.

5.K.1 Reactions with hexafluoroacetone-cesium fluoride complexes.

A 8 millimetre diameter quartz tube was charged with hexafluorocyclotriphosphazene(0.71 g, 21 mmol), hexafluoroacetone (3.5 g, 21 mmol) in acetonitrile (1 ml) and in presence of a catalytic amount of caesium fluoride. The tube was degassed, sealed and heated up to 60°C for one day. The mixture was then worked up and analysed. Poly-fluorophosphazene was found to be the major product in the mixture, and was identified by comparison of the ^{31}P n.m.r. spectrum with that of an authentic sample.

5.K.2 Reactions with elemental fluorine.

A FEP (tetrafluoroethylene-propylene copolymer) tubing was fitted with a teflon capillary tube for fluorine inlet, and mounted into a teflon stopper, and an outlet with calcium oxide trap. The tube was charged with hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (0.34 g, 0.4 mmol) in acetonitrile (2 ml) and a 50% fluorine nitrogen mixture was bubbled through for one day. The 50% fluorine-nitrogen mixture was contained in a passivated stainless steel cylinder (1.5 l). The mixture was analysed and the major product of the reaction was identified as PF_6^- (ca. 60%) δ_P -144 , sept, J_{PF} = 705 Hz, δ_F -72.9, d, J_{FP} = 705 Hz together with a species of the type PF_5X^- where X is a substituent δ_P -144, sex, J_{PF} = 760 Hz, δ_F -58.63, d, J_{FP} = 760 Hz, and some other degradation products which gave resonance peaks between 1 and -29 ppm in the ^{31}P n.m.r spectrum. The nature of these degradation products was not investigated.

5.K.3 Reactions with elemental chlorine.

5.K.3.a Synthesis of hexakis(2,2-dichloro-1,1,1-trifluoroethoxy)-cyclotriphosphazene (93).

A quartz tube was fitted with a T joint, a chlorine inlet and a condenser connected to a trap containing a sodium hydroxide solution , and teflon coated magnetic stirring bar. Chlorine (40 g, 570 mmol) was bubbled through solution of hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (5.0 g, 6.8 mmol) in carbon tetrachloride (15 ml) over two days. The solvent was then removed under reduced pressure to give a white solid which was purified by vacuum sublimation and identified as hexakis(2,2-dichloro-1,1,1-trifluoroethoxy)-cyclotriphosphazene (6.9 g, 88%). The product was identified by comparison of the IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°34, n.m.r. spectrum N°54, mass spectrum N°20.

5.K.3.b Thermal stability of hexakis(2,2-dichloro-1,1,1-trifluoroethoxy)cyclotriphosphazene (93).

A 4 millimetre diameter quartz tube was charged with hexakis(2,2-dichloro-1,1,1-trifluoroethoxy)cyclotriphosphazene (0.7 g, 0.6 mmol) and oxygen was carefully removed. The tube was sealed, put into a metal sleeve and heated up to 200°C for two hours. The content of the tube was dissolved into deuterated chloroform and analysed. No sign of decomposition could be revealed by ^{31}P analysis.

5.K.3.c Synthesis of hexakis(dichloroperfluoroalkylpolyether-alkoxy)-cyclotriphosphazene (94).

A mixture of hexakis(dihydroperfluoroalkylpolyether-alkoxy)cyclotriphosphazene (1.38 g, 0.2 mmol) and chlorine (1.42 g, 20 mmol) in 1,1,2-trichloro-1,2,2-trifluoroethane (R-113, 5 ml) was put into a Pyrex Rotaflo tube, degassed and irradiated over 4 days by an Hanovia high pressure mercury lamp. Excess chlorine and solvent were removed under reduced pressure to give hexakis(dichloroperfluoroalkylpolyether-alkoxy)cyclotriphosphazene (8.3 g, 98% yield). IR spectrum N°35, n.m.r. spectrum N°55.

5.K.3.d Thermal stability of hexakis(dichloroperfluoroalkylpolyether-alkoxy)cyclotriphosphazene.

A 4 millimetre diameter quartz tube was charged with hexakis(dichloroperfluoroalkylpolyether-alkoxy)cyclotriphosphazene (0.8 g) and oxygen was carefully removed. The tube was sealed, put into a metal sleeve and heated up to 200°C for six hours. No sign of decomposition could be revealed by ^{31}P analysis.

5.L Fluorinated phosphazenes as potential additives for perfluoropolyether based fluids.

5.L.1 Preparation of phosphazene (97) fully substituted by perfluoroalkylpolyether-alcohol (69b) and cyclohexanol.

A three necked round bottom flask (500 ml) was equipped with a condenser topped by a nitrogen outlet, a dropping funnel with pressure equalizer topped by a nitrogen inlet, a stopper and a teflon coated magnetic stirring bar. All operations were carried out under an inert atmosphere of nitrogen.

A solution of cyclohexanol (2.81 g, 28.1 mmol) in anhydrous diethylether (25 ml) was added drop-wise to a suspension of sodium hydride (1.02 g, 25.8 mmol, 60% weight dispersion in wax) in anhydrous diethylether (50 ml). The sodium hydride had previously been washed with hexane (3 x 25 ml) to remove the wax. The resultant mixture was heated at reflux vigorously (oil bath temperature 65°C) for 1 hour and allowed to cool to room temperature. A solution of $[NPCl_2]_3$ (2.8 g, 8 mmol) in anhydrous diethylether (50 ml) was then added in a single portion. The resultant mixture was heated at reflux for 2 hours and analysed by means ^{31}P NMR spectrometry.

A three necked round bottom flask (1000 ml) was equipped with a condenser topped by a nitrogen outlet, a dropping funnel with pressure equalizer topped by a nitrogen inlet, a stopper and a teflon coated magnetic stirring bar.

A solution of Fomblin alcohol PE 900 (95) (25.3 g, 28.1 mmol) in anhydrous diethylether (25 ml) was added drop-wise to a suspension of sodium hydride (1.02 g, 25.8 mmol, 60% weight dispersion in wax) in anhydrous diethylether (50 ml). The sodium hydride had previously been washed with hexane (3 x 25 ml) to remove the wax. The resultant mixture was heated at reflux (oil bath temperature 65°C) for 1 hour and allowed to cool to room temperature, and the mixture obtained from the previous reaction was then added in a single portion, heated at reflux for 2 hours and stirred overnight. Demineralised water (200 ml) was added and after extraction with trichlorotrifluoroethane (R-113), solvents were removed under reduced pressure to give a viscous liquid which was purified by distilling off the Fomblin alcohol in excess at 120°C and 10^{-3} mbar and by flash-chromatography on a silica-gel column (R113 as eluent). The purified fluid was then extracted with dichloromethane (1 x 5 ml), analysed and identified as a mixture of phosphazenes (97) fully substituted by perfluoroalkylpolyether-alcohol (69b) and cyclohexanol in a ca. 3.4 to 2.6 ratio (18.3 g, 64% conversion). IR spectrum N°37, n.m.r. spectrum N°57.

5.L.2 Preparation of phosphazene (98) fully substituted by perfluoropolyether alcohol (69b) and 2,2,2-trifluoroethanol.

In a similar manner, a solution of 2,2,2-trifluoroethanol (2.8 g, 28 mmol) in ether (25 ml) was added to sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml), then $[NPCl_2]_3$ (2.8 g, 8 mmol) in ether (30 ml) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (26.3 g, 28.9 mmol) in ether (30 ml) was added to sodium hydride (0.6 g, 25.8 mmol) in ether (50 m), and then the mixture obtained from the reaction described above was added in a single portion and heated at reflux. The reaction was worked up and the products were purified as described previously. The mixture was then analysed and identified as a mixture of phosphazenes (98) fully substituted by perfluoropolyether alcohol (69b) and 2,2,2-trifluoroethanol in a ca. 2.8 to 3.2 ratio (21.8 g 75% conversion). IR spectrum N°38, n.m.r. spectrum N°58.

5.L.3 Preparation of phosphazene (96b)-(96d) fully substituted by perfluoropolyether alcohol (69b) and phenol.

In a similar manner, a solution of phenol (2.7 g, 28.7 mmol) in ether (25 ml) was added to sodium hydride (0.6 g, 25.8 mmol) in ether (50 m), then $[NPCl_2]_3$ (2.8 g, 8 mmol) in ether (30 ml) was then added in a single portion. A solution of Fomblin alcohol PE 900 (26.5 g, 29.4 mmol) in ether (30 ml) was added to sodium hydride (25.8 mmol) in ether (50 ml) when the mixture previously obtained was added in a single portion. The reaction was worked up and the products were purified as described previously. The purified liquid mixture was distilled under vacuum and two fractions were collected. The first fraction (6.4 g) Bp.170-180°C 10^{-3} mbar was analysed and identified as a mixture of phosphazenes (96b) fully substituted by Fomblin alcohol and phenol in a ca. 2.2 to 3.8 ratio. The second fraction (8.7 g) Bp.180-200°C at 10^{-3} mbar was analysed and identified as a mixture of phosphazenes (96c) fully substituted by Fomblin alcohol and phenol in a ca. 3.7 to 2.3 ratio. The non volatile material was further purified by flash-chromatography on a silica-gel column (R113 as eluent) and identified as a mixture of phosphazenes (96d) fully substituted by Fomblin alcohol and phenol in a ca. 5.4 to 0.6 ratio (7.2 g). IR spectrum N°39, n.m.r. spectrum N°56.

5.L.4 Preparation of phosphazene (100) fully substituted by perfluoropolyether alcohol (69b) and 4-methoxyphenol.

In a similar manner, a solution of 4-methoxyphenol.(3.48 g, 28 mmol) in ether (25 ml) was added to sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml), then $[NPCl_2]_3$ (3 g, 8.6 mmol) in ether (30 ml) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (27 g, 29.8 mmol) in ether (30 ml) was added to sodium hydride (0.6 g, 25.8 mmol) in ether (50 m), and then the mixture obtained from the reaction described above was added in a single portion and heated at reflux. The reaction was

worked up and the products were purified as described previously. The mixture was then analysed and identified as a mixture of phosphazenes (100) fully substituted by perfluoropolyether alcohol (69b) and 4-methoxyphenol in a ca. 3.6 to 2.4 ratio (22.1 g 76% conversion). IR spectrum N°40, n.m.r. spectrum N°59.

5.L.5 Preparation of phosphazene (101) fully substituted by perfluoropolyether alcohol (69b) and 3-nitrophenol.

In a similar manner, a solution of 3-nitrophenol (3.96 g, 28.5 mmol) in ether (25 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml). The resultant mixture was refluxed for 1 hour when a solution of $[NPCl_2]$ (2.8 g, 8 mmol) in ether (30 ml) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (26.3 g, 28.9 mmol) in ether (30 ml) was added drop-wise to a suspension of sodium hydride (25.8 mmol) in ether (50 ml). The resultant mixture was heated at reflux for 1 hour when the mixture obtained from the previously described reaction was added in a single portion. The reaction was worked up and purified as described previously and the products analysed and identified as a mixture of phosphazenes (101) fully substituted by perfluoropolyether alcohol (69b) and 3-nitrophenol (15 g, 52 % conversion) in a ca. 3.9 to 2.1 ratio. IR spectrum N°41, n.m.r. spectrum N°60.

5.L.6 Preparation of phosphazene (102) fully substituted by perfluoropolyether alcohol (69b) and 2-methoxy-5-nitrophenol.

In a similar manner, a solution of 2-methoxy -5-nitrophenol (3.96 g, 28.5 mmol) in ether (25 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml) and then a solution of $[NPCl_2]_3$ (2.8 g, 8 mmol) in ether (30 m) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (26.3 g, 28.9 mmol) in ether (30 ml) was added drop-wise to a suspension of sodium hydride (25.8 mmol) in ether (50 ml). The resultant mixture was heated at reflux for 1 hour when the mixture obtained from the previously described reaction was added in a single portion. The reaction was worked up and purified as described previously and the products analysed and identified as a mixture of phosphazenes (102) fully substituted by perfluoropolyether alcohol (69b) and 2-methoxy-5-nitrophenol (16.4 g, 56 % conversion) in a ca. 3.5 to 2.5 ratio. IR spectrum N°42, n.m.r. spectrum N°61.

5.L.7 Preparation of phosphazene (103) fully substituted by perfluoropolyether alcohol (69b) 3-N,N-dimethylaminophenol.

In a similar manner, a solution of 3-N,N-dimethylaminophenol (3.9 g, 28.5 mmol) in ether (25 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml). The resultant mixture was heated at reflux for 1 hour when a solution of $[NPCl_2]$ (2.8 g, 8 mmol) in ether (30 ml) was added in a single portion. A

solution of Fomblin alcohol PE 900 (95) (26.3 g, 29.2 mmol) in ether (30 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml). The resultant mixture was refluxed for 1 hour when the mixture obtained from the previously described reaction was added in a single portion. The reaction was worked up and purified as described previously and the products analysed and identified as a mixture of phosphazenes (103) fully substituted by perfluoropolyether alcohol (69b) and 3-N,N-dimethylaminophenol in a ca. 3.3 to 2.7 ratio. IR spectrum N°43, n.m.r. spectrum N°62.

5.L.8 Preparation of phosphazene (104) fully substituted by perfluoropolyether alcohol (69b) and α-naphthol.

In a similar manner, a solution of α-naphthol (4.1 g, 28.5 mmol) in ether (25 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml). The resultant mixture was heated up to reflux for 1 hour when a solution of $[NPCl_2]_3$ (2.8 g, 8 mmol) in ether (30 ml) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (26.3 g, 29.2 mmol) in ether (30 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml). The resultant mixture was heated at reflux for 1 hour when the mixture obtained from the previously described reaction was added in a single portion. The reaction was worked up and purified as described previously and the products analysed and identified as a mixture of phosphazenes (104) fully substituted by perfluoropolyether alcohol (69b) and and α-naphthol in a ca. 5.4 to 0.6 ratio. IR spectrum N°44, n.m.r. spectrum N°63.

5.L.9 Preparation of phosphazene (105) fully substituted by perfluoropolyether alcohol (69b) and catechol.

In a similar manner, a solution of catechol (2.07 g, 18.8 mmol) in ether (25 ml) was added drop-wise to a suspension of sodium hydride (1.44 g, 36 mmol) in ether (50 ml). The resultant mixture was heated at reflux for 1 hour when a solution of $[NPCl_2]_3$ (2.8 g, 8 mmol) in ether (30 ml) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (16.9 g, 18.8 mmol) in ether (30 ml) was added drop-wise to a suspension of sodium hydride (0.43 g, 18 mmol) in ether (50 ml). The resultant mixture was refluxed for 1 hour when the mixture obtained from the previously described reaction was added in a single portion. The reaction was worked up and purified as described previously and the products analysed and identified as a mixture of phosphazenes (105) fully substituted by perfluoropolyether alcohol (69b) and catechol in a ca. 5.8 to 0.2 ratio. IR spectrum N°45, n.m.r. spectrum N°64.

5.L.10 Preparation of phosphazene (106) fully substituted by perfluoropolyether alcohol (69b) and aniline.

In a similar manner, a solution of aniline (2.6 g, 28.3 mmol) in ether (25 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml). The resultant mixture was heated at reflux for 1 hour when a solution of $[NPCl_2]_3$ (2.8 g, 8 mmol) in ether (30 ml) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (26.0 g, 28.8 mmol) in ether (30 ml) was added drop-wise to a suspension of sodium hydride (25.8 mmol) in ether (50 ml). The resultant mixture was refluxed for 1 hour when the mixture obtained from the previously described reaction was added in a single portion. The reaction was worked up and purified as described previously and the products analysed and identified as a mixture of phosphazenes (106) fully substituted by perfluoropolyether alcohol (69b) and aniline in a ca. 5.3 to 0.7 ratio. IR spectrum N°46, n.m.r. spectrum N°65.

5.L.11 Preparation of phosphazene (107) fully substituted by perfluoropolyether alcohol (69b) and α-naphthylamine.

In a similar manner, a solution of α-naphtyylamine (4.1 g, 28.5 mmol) in ether (25 ml) was added drop-wise to a suspension of sodium hydride (0.6 g, 25.8 mmol) in ether (50 ml). The resultant mixture was heated up to reflux for 1 hour when a solution of $[NPCl_2]_3$ (2.8 g, 8 mmol) in ether (30 ml) was added in a single portion. A solution of Fomblin alcohol PE 900 (95) (26.3 g, 29.2 mmol) in ether (30 ml) was added drop-wise to a suspension of sodium hydride (25.8 mmol) in ether (50 ml). The resultant mixture was heated at reflux for 1 hour when the mixture obtained from the previously described reaction was added in a single portion. The reaction was worked up and purified as described previously and the products analysed and identified as a mixture of phosphazenes (107) fully substituted by perfluoropolyether alcohol (69b) and α-naphthylamine in a ca. 5.2 to 0.8 ratio. IR spectrum N°47, n.m.r. spectrum N°66.

CHAPTER 6
EXPERIMENTAL TO CHAPTER 3

6.A Pericyclic reactions of fluorinated olefins.

6.A.1 Synthesis of heptafluorobut-2-ene.

A three necked round bottomed flask (3 l) was fitted with a dropping funnel topped with a nitrogen inlet, a mechanical stirrer, a double layer condenser, and a trap cooled in liquid air was used to collect the volatiles. Hexachloro-1,3-butadiene (334 g, 1.29 mmol) was added drop-wise over a period of 3 hours to a suspension of potassium fluoride (600 g , 59.1 mmol) in anhydrous sulpholane (2 l) at 180-200°C. After completing the addition the mixture was stirred for 3 further hours at the same temperature. Fractional distillation of the collected volatiles at room temperature and atmospheric pressure gave (Z)-heptafluorobut-2-ene (115 g, 49% yield). The product was identified by comparison of the IR and n.m.r. spectra with those of an authentic sample. IR spectrum N°48, n.m.r. spectrum N°67, mass spectrum N°21. Fractional distillation of the residue of the former distillation gave a mixture of isomers of 5-hydroperfluoro-3,4-bis(trifluoromethyl)hexa-2,4-diene (6.2 g) Bp.78°- 81°C IR spectrum N°50, n.m.r. spectrum N°69, mass spectrum N°23, and a mixture of isomers of the trimer of 2-hydroheptafluorobut-2-ene (1.5 g), Bp 119°- 121°C (full characterisation has not been attempted).

6.A.2 Synthesis of 2,3-dihydrohexafluorobut-2-ene.

A mixture of tributyltin hydride (9.6 g, 33 mmol) and 1,1,1,2,4,4,4-2-Hydroheptafluorobut-2-ene (5.72 g, 31 mmol) were put into a Carius tube, degassed, sealed and rotated for 2 days under exposition of a U.V. lamp. The volatile materials were pumped out and distilled at low temperatures (from -30°C to 10°C) to give identified as 2,3-dihydrohexafluorobut-2-ene (4.6 g, 90% yield), Bp ~4°C. IR spectrum N°49, n.m.r. spectrum N°68.

6.B Pericyclic reactions.

6.B.1 Reaction of 2-hydroheptafluorobut-2-ene with furan.

A mixture of furan (5.47 g, 80.3 mmol), (E)-2-hydroheptafluorobut-2-ene was (13.66 g, 75.3 mmol) and tetrahydrofuran (12 g) was put in an autoclave (150 ml) and heated under autogenous pressure at 120°C in a rocking furnace for 15 hours. Excess alkene, and solvent were removed by distillation under reduced pressure to give a mixture of the two pair of enantiomers of 5-fluoro-5,6,-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (9 g, 48% yield), IR spectrum N°51. The set of isomers were characterised in detail:

a) endo-5-fluoro-5,6,-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (121a), n.m.r. spectrum N° 70.

b) exo-5-fluoro-5,6,-bis(trifluoromethyl)-7-oxabicyclo[2.2.1]hept-2-ene (121b), n.m.r. spectrum N°71.

6.B.2 Reaction of 2-hydroheptafluorobut-2-ene with cyclopentadiene.

An 8 mm diameter quartz tube was charged with 2-hydroheptafluorobut-2-ene (1.27 g, 6.9 mmol), cyclopentadiene (0.34 g, 5.2 mmol)and anhydrous tetrahydrofuran (1 ml), degassed and sealed. The reaction proceeded rapidly at room temperature, the mixture was distilled under reduced pressure through three traps cooled at 0°, -40° and -190°C. The mixture of products collected in the trap at -40°C was analysed by ^{19}F and ^{1}H n.m.r. which showed the presence of exo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (121c) n.m.r. spectrum N°72, endo-5-fluoro-5,6-bis(trifluoromethyl)-bicyclo[2.2.1]hept-2-ene (121d), n.m.r. spectrum N°73, and 5,6-bis(trifluoromethyl)-bicylo-[2.2.1]heptadi-2,5-ene, in a 4.2 / 3.2 / 2.6 ratio. The products were identified by comparison of the n.m.r. spectra with those of an authentic sample, but were not isolated.

6.B.3 Reaction of 2,3-dihydrohexafluorobut-2-ene with cyclopentadiene.

An 8 mm diameter quartz tube was charged with 2,3-dihydrohexafluorobut-2-ene (0.52 g, 3.2 mmol), cyclopentadiene (0.2 g, 3 mmol) and anhydrous tetrahydrofuran (1 ml), degassed and sealed. The tube was heated at 80°C for 12 hours, and the so obtained mixture was distilled under reduced pressure through three traps cooled at 0°, -40° and -190°C. The mixture of products collected in the trap at -40°C was analysed by ^{19}F and ^{1}H n.m.r. which showed the presence of 5,6-bis(trifluoromethyl)bicyclo-[2.2.1]-hept-2-ene (126), n.m.r. spectrum N°74. The product was identified by comparison of the n.m.r. spectra with those of an authentic sample, was not isolated.

6.B.4 Reaction of 2,3-dihydrohexafluorobut-2-ene with furan.

An 8 mm diameter quartz tube was charged with 2,3-dihydrohexafluorobut-2-ene (1.7 g, 10 mmol), furan (0.61 g, 9 mmol) and anhydrous tetrahydrofuran (1 ml), degassed and sealed. The tube was heated at 130°C for 12 hours, and the so obtained mixture was distilled under reduced pressure through three traps cooled at 0°, -40° and -190°C. The mixture of products collected in the trap at -40°C was analysed by ^{19}F and ^{1}H n.m.r. which showed the presence of 5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene (131) n.m.r. spectrum N°75. The product was identified only by means of n.m.r. spectrometry and so far, it has not been isolated. In addition, 5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene was heated at 130°C in presence of

a catalytic amount of p-toluensulphonic acid in a seal quartz tube for 12 hours, but no rearrangement took place.

6.B.5 Reaction of 2,3-dihydrohexafluorobut-2-ene with 2,3,5-trimethyloxazole.

An 8 mm diameter quartz tube was charged with 2,3-dihydrohexafluorobut-2-ene (0.94 g, 5.85 mmol), 2,3,5-trimethyloxazole (0.65 g, 5.85 mmol) and anhydrous tetrahydrofuran (1 ml), degassed and sealed. The tube was heated at 130°C for 12 hours, and the so obtained mixture was distilled under reduced pressure through three traps cooled at 0°, -40° and -190°C. The mixture of products collected in the trap at -40°C was analysed by ^{19}F and ^{1}H n.m.r. which showed the presence of the two stereoisomers 5,6-bis(trifluoromethyl)-1,3,4-trimethyl-2-aza-7-oxabicyclo-[2.2.1]-hept-2-ene (132a), and (132b). n.m.r. spectrum N°76. The products were identified only by means of n.m.r. spectrometry and so far, they have not been isolated. In addition, 5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene was heated at 130°C in presence of a catalytic amount of p-toluensulphonic acid in a seal quartz tube for 12 hours, but no rearrangement took place.

APPENDIX 1
N.M.R. SPECTRA

N° 1 3,5-dihydro-2-trifluoromethylperfluorohexyl cation (9a)

N°2 3,3,5,7,7-pentahydro-2-trifluoromethylperfluorooctyl cation (10a)

N°3 3,3,5,7,9,9-hexahydro-2-trifluoromethylperfluorodecyl cation (11a)

N°4 3,3,5,7,9,11,11-heptahydro-2-trifluoromethylperfluorododecyl cation (12a).

N°5 3,5,7,7-tetrahydro-2-trifluoromethylperfluorooctyl cation (16a).

N°6 3,5,7,9,9-pentahydro-2-trifluoromethylperfluorodecyl cation (17a).

N°7 3,5,7,9,11,11-hexahydro-2-trifluoromethylperfluorododecyl cation (18a).

N°8 3,3,5,7,7,10,10,12,14,14-decahydro-2,15-bis(trifluoromethyl)-perfluoro-hexadecyl di-cation (19a).

N°9 3,3,5,8,10,10-hexahydro-2,11-bis(trifluoromethyl)perfluoro-dodecyl di-cation (20a).

N°10 3,3-dihydro-2-trifluoromethylperfluorobutane (6).

N°11 3,3,5,5-tetrahydro-2-trifluoromethylperfluorohexane (9).

N°12 3,3,5,5,7,7-hexahydro-2-trifluoromethylperfluorooctane (10).

N°13 3,3,5,5,7,7,9,9-octahydro-2-trifluoromethylperfluorodecane (11).

N°14 3,3,5,5,7,7,9,9,11,11-decahydro-2-trifluoromethylperfluoro-dodecane (12).

N°15 2-hydro-3-trifluoromethylperfluorobut-1-ene (8).

N°16 2,4,4-trihydro-5-trifluoromethylperfluorohex-1-ene (24).

N°17 2,4,4,6,6-pentahydro-7-trifluoromethylperfluorooct-1-ene (13).

N°18 2,4,4,6,6,8,8-heptahydro-9-trifluoromethylperfluorodec-1ene (14).

N°19 2,4,4,6,6,8,8,10,10-nonahydro-11-trifluoromethylperfluorododec-1-ene (15).

N°20 3-hydro-2-trifluoromethylperfluorobut-2-ene (7).

N°21 3,5,5-trihydro-2-trifluoromethylperfluorohex-2-ene (24a).

N°22 3,5,5,7,7-pentahydro-2-trifluoromethylperfluorooct-2-ene (16).

N°23 3,5,5,7,7,9,9-heptahydro-2-trifluoromethylperfluorodec-2-ene (17).

N°24 3,5,5,7,7,9,9,11,11-nonahydro-2-trifluoromethylperfluorododec-2-ene (18).

N°25 (Z,Z) 3,5-dihydro-2-trifluoromethylperfluorohexa-2,4-di-ene (23a).

N°26 (Z,E) 3,5-dihydro-2-trifluoromethylperfluorohexa-2,4-di-ene (23b).

N°27 3,3,6,6-tetrahydro-2,7-bis(trifluoromethyl)perfluorooctane (21).

N°28 3,3,5,5,8,8,10,10-octahydro-2,11-bis(trifluoromethyl)perfluoro-dodecane (20).

N°29 3,3,5,5,7,7,10,10,12,12,14,14-dodecahydro-2,15-bis(trifluoromethyl)perfluoro-hexadecane (19).

N°30 3,6-dihydro-2,7-bis(trifluoromethyl)perfluorooctadi-2,6-ene (22).

N°31 1,2-diiodotetrafluoroethane (37)

N°32 2,2-dihydro-1,4-diiodoperfluorobutane (36a)

N°33 isomer mixture: 2,2,5,5-tetrahydro-1,6-diiodoperfluorohexan (36) and 2,2,4,4-tetrahydro-1,6-diiodoperfluorohexan (36b)

N°34 2,2,-dihydroperfluorobutane (38).

N°35 Hexafluorophosphazene (55).

N°36 Hexakis(methoxy)cyclotriphosphazene (63).

N°37 Hexakis(ethoxy)cyclotriphosphazene (64).

N°38 Hexakis(diethylamino)cyclotriphosphazene (66).

N°39 Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50).

N°40 Hexakis(2,2,3,3,3-pentafluoropropoxy)cyclotriphosphazene (67).

N°41 Hexakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotriphosphazene (68).

N°42 Hexakis(perfluoropolyether-alkoxy)cyclotriphosphazenes.

N°43 Pentachloro-mono(perfluoropolyether-alkoxy)cyclotriphosphazene (70c).

N°44 Tetrachloro-bis(perfluoropolyether-alkoxy)cyclotriphosphazene (70d).

N°45 Trichloro-tris(perfluoropolyether-alkoxy)cyclotriphosphazene (70e).

N°46 Dichloro-tetrakis(perfluoropolyether-alkoxy)cyclotriphosphazene (70f).

N°47 Chloro-pentakis(perfluoropolyether-alkoxy)cyclotriphosphazene (70g).

N°48 Poly(fluoro)phosphazene (55b).

N°49 1,1-bis(trifluoromethyl)perfluoropropanol (72).

N°50 1,1,3-tris(trifluoromethyl)perfluoropropanol (73).

N°51 Trifluoromethyltrimethylsilane (78).

N°52 Pentafluoroethyltrimethylsilane (88).

N°53 Hexakis(trifluoromethyl)cyclotriphosphazene (89).

N°54 Hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)cyclotriphosphazene (93).

N°55 Hexakis(1,1-dichloro-perfluoropolyether-alkoxy)cyclotriphosphazene (94).

N°56 Cyclotriphosphazenes (96a)-(96d).

N°57 Cyclotriphosphazene (97).

N°58 Cyclotriphosphazene (98).

N°59 Cyclotriphosphazene (100).

N°60 Cyclotriphosphazene (101).

N°61 Cyclotriphosphazene (102).

N°62 Cyclotriphosphazene (103).

N°63 Cyclotriphosphazene (104).

N°64 Cyclotriphosphazene (105).

N°65 Cyclotriphosphazene (106).

N°66 Cyclotriphosphazene (107).

N°67 2-hydroperfluorobut-2-ene (109).

N°68 2,3-dihydroperfluorobut-2-ene (112).

N°69 5-hydroperfluoro-3,4-bis(trifluoromethyl)hexadi-2,4-ene (110a).

N°70 endo-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene (121a).

N°71 exo-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene (121b).

N°72 exo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo-[2.2.1]-hept-2-ene (121c).

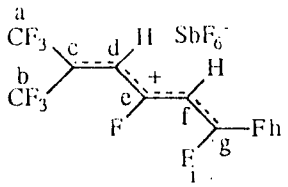
N°73 endo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo-[2.2.1]-hept-2-ene (121d).

N°74 5,6-bis(trifluoromethyl)bicyclo-[2.2.1]-hept-2-ene (126).

N°75 5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene (131).

N°76 5,6-bis(trifluoromethyl)-1,3,4-trimethyl-2-aza-7-oxabicyclo-[2.2.1]-hept-2-ene (132a) (132b).

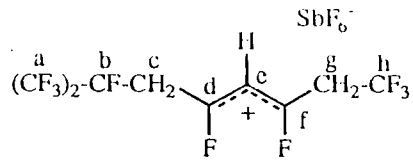
N° 1 3,5-dihydro-2-trifluoromethylperfluorohexyl cation (9a)



(400MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	6.8	m	2	d,f
^{19}F	+ 35.4	AB system J_{Fh-Fi} = 274Hz J_{Fh-Fe} = 142Hz, J_{Fh-Hf} = 17.6Hz	1	h
	+ 34.2	AB system J_{Fh-Fi} = 274Hz J_{Fi-Fe} = 63Hz,	1	i
	+ 16.7	m	1	e
	- 61.9	d of q, J_{F-F} = 32Hz, J_{F-F} = 8Hz	3	a
	- 68.7	q, J_{F-F} = 8Hz	3	b
^{13}C	96.1	d, J_{C-F} = 23Hz		d
	116.9	q, J_{C-F} = 277Hz		a or b
	117.7	q, J_{C-F} = 277Hz		b or a
	125.6	s		f
	146.5	sept, J_{C-F} = 36Hz		c
	177.9	t, J_{C-F} = 365Hz		g
	199.8	d, J_{C-F} = 354Hz		e

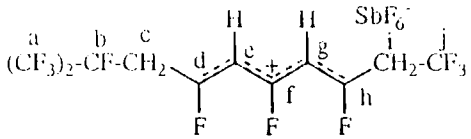
N°2 3,3,5,7,7-pentahydro-2-trifluoromethylperfluorooctyl cation (10a)



(400MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.2	m	4	c,g
	6.7	m	1	e
^{19}F	+ 58.5	m	2	d,f
	- 63.2	s	3	h
	- 79.7	s	6	a
	- 181.9	s	1	b
^{13}C	35.9	m		c or g
	40.1	m		g or c
	91.3	d of sept, J_{C-Fb} 217Hz, J_{C-Fa} 35Hz		b
	111.9	s		e
	117.6	q of d, J_{C-Fa} 288Hz, J_{C-Fb} 27Hz		a
	118.8	q, J_{C-Fh} 279Hz		h
	209.4	d, J_{C-F} 371Hz		d or f
	210.6	d, J_{C-F} 379Hz		f or d

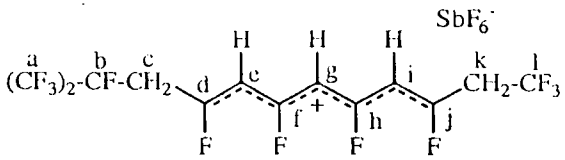
N°3 3,3,5,7,9,9-hexahydro-2-trifluoromethylperfluorodecyl cation (11a)



(400MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.2	m	4	c,i
	6.5	m	2	e,g
^{19}F	+ 1 - -8	small peaks	3	d,f,h
	- 64.1	s	3	j
	- 79.4	s	6	a
	- 183.2	s	1	b
^{13}C	35.7	m		c or i
	40.9	m		i or c
	91.7	d of sept, J_{C-Fb} 223Hz, J_{C-Fa} 35Hz		b
	108.2	s		e or g
	109.4	s		g or e
	118.2	q of d, J_{C-Fa} 288Hz, J_{C-Fb} 26Hz		a
	121.3	q, J_{C-F} 279Hz		j
	190.5 - 195.4	m		d,f,h

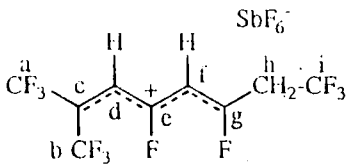
N°4 3,3,5,7,9,11,11-heptahydro-2-trifluoromethylperfluorododecyl cation (12a).



(400MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.1	m broad	4	c,k
	6.2 - 6.7	m broad	3	e,g,i
^{19}F	-13 - -26	small peaks	4	d,f,h,j
	- 64.4	s	3	l
	- 79.7	s	6	a
	- 183.5	s	1	b
^{13}C	35.3	m		c or k
	40.7	m		k or c
	91.6	d of sept, J_{C-Fb} 219Hz, J_{C-Fa} 34Hz		b
	106.6	s		e or g or i
	107.2	s		e or g or i
	107.9	s		e or g or i
	118.1	q of d, J_{C-Fa} 287Hz, J_{C-Fb} 27Hz		a
	120.7	q, J_{C-F} 278Hz		l
	177.3	m		d or f or h or j
	182.8	m		d or f or h or j
	184.7	m		d or f or h or j
	190.1	m		d or f or h or j

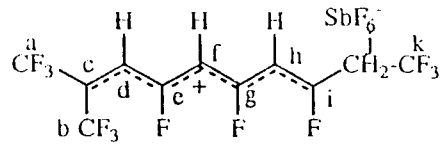
N°5 3,5,7,7-tetrahydro-2-trifluoromethylperfluorooctyl cation (16a).



(400MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.2	m broad	2	h
	6.4	m	1	d or f
	6.6	m	1	f or d
^{19}F	+ 57.6	m	1	f or g
	+ 24.7	m	1	f or g
	- 62.5	m	3	a or b
	- 62.8	m	3	a or b
	- 68.9	s	3	i
^{13}C	42.8	m		h
	116.9	s		f
	117.8	q, J_{C-F} = 277Hz		a or b
	118.3	q, J_{C-F} = 278Hz		b or a
	120.7	q, J_{C-F} = 278Hz		i
	127.1	s		d
	149.4	sept, J_{C-F} = 36Hz		c
	195.1	d, J_{C-F} = 368Hz		e or g
	211.6	d, J_{C-F} = 371Hz		e or g

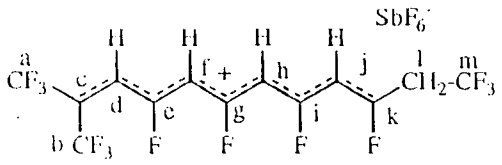
N°6 3,5,7,9,9-pentahydro-2-trifluoromethylperfluorodecyl cation (17a).



(400MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.2	m broad	2	j
	6.3 - 6.8	m	3	d,f,h
^{19}F	+2 - -10	small peaks	3	e,g,i
	- 62.4	m	3	a or b
	- 62.8	m	3	a or b
	- 69.1	s	3	k
^{13}C	42.7	m		j
	107.5	s		f or h
	107.9	s		f or h
	118.2	q, J_{C-F} = 277Hz		a or b
	118.6	q, J_{C-F} = 278Hz		b or a
	120.8	q, J_{C-F} = 278Hz		k
	123.3	s		d
	143.3	sept, J_{C-F} = 36Hz		c
	190.3	m		e or g or i
	193.6	m		e or g or i
	195.4	m		e or g or i

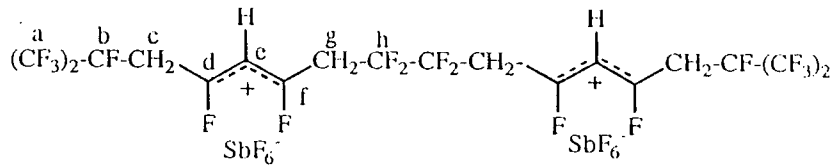
N°7 3,5,7,9,11,11-hexahydro-2-trifluoromethylperfluorododecyl cation (18a).



(400MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.1	m broad	2	l
	6.4 - 6.9	m	4	d,f,h,j
^{19}F	-12 - -28	small peaks	4	e,g,i,k
	- 62.1	m	3	a or b
	- 62.6	m	3	a or b
	- 68.8	s	3	m
^{13}C	42.3	m		l
	106.3	s		f or h or j
	106.9	s		f or h or j
	107.4	s		f or h or j
	117.8	q, J_{C-F} = 277Hz		a or b
	118.1	q, J_{C-F} = 278Hz		b or a
	119.3	q, J_{C-F} = 279Hz		m
	120.1	s		d
	135.2	sept, J_{C-F} = 36Hz		c
	177.9	m		e or g or i or k
	183.1	m		e or g or i or k
	184.9	m		e or g or i or k
	190.8	m		e or g or i or k

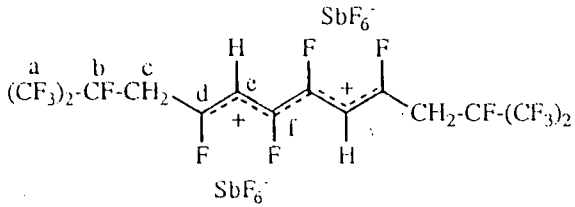
N°8 3,3,5,7,7,10,10,12,14,14-decahydro-2,15-bis(trifluoromethyl)-perfluorohexadecyl di-cation (19a).



(250MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.0	m	4	c,g
	6.7	m	1	e
^{19}F	+ 60.5	s	2	d,f
	- 78.7	s	6	a
	- 107.1	s	2	h
	- 181.9	s	1	b
^{13}C	37.5	m		c or g
	39.3	m		g or c
	90.7	d of sept, J_{C-Fb} 218Hz, J_{C-Fa} 34Hz		b
	114.1	s		e
	115.0	t, J_{C-Fh} 300Hz		h
	118.8	q of d, J_{C-Fa} 299Hz, J_{C-Fb} 27Hz		a
	210.2	d, J_{C-F} 372Hz		d or f
	212.5	d, J_{C-F} 379Hz		f or d

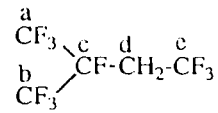
N°9 3,3,5,8,10,10-hexahydro-2,11-bis(trifluoromethyl)perfluoro-dodecyl di-cation (20a).



(250MHz, neat)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.5	m	4	c,g
	6.9	m	1	e
^{19}F	+ 42	m	1	d or f
	+ 40	m	1	d or f
	- 79.0	m	6	a
	- 182.1	s	1	b
^{13}C	41.4	m		c
	94.5	d of sept, J_{C-Fb} 232Hz, J_{C-Fa} 36Hz		b
	122.1	s		e
	123.1	q of d, J_{C-Fa} 287Hz, J_{C-Fb} 26Hz		a
	210.4	d, J_{C-F} 372Hz		d
	224.8	d of d, J_{C-F} 371Hz, J_{C-F} 41Hz		f

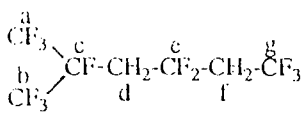
N° 10 3,3-dihydro-2-trifluoromethylperfluorobutane (6).



(400MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	2.9	quin J_{H-F} 9.2Hz	2	d
^{19}F	- 60.2	s	3	e
	- 76.7	s	6	a,b
	- 185.3	s	1	c
^{13}C	33.7	q of d, J_{C-Fe} 34Hz, J_{C-Fc} 20Hz		d
	88.7	d of sept, J_{C-Fc} 209Hz, $J_{C-Fa,b}$ 36Hz		c
	120.1	q of d, J_{C-Fa} 282Hz, J_{C-Fc} 43Hz		a,b
	122.8	q, J_{C-F} 272Hz		e

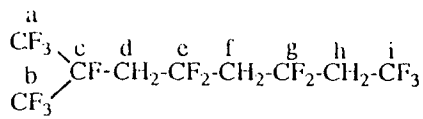
N° 11 3,3,5,5-tetrahydro-2-trifluoromethylperfluorohexane (9),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.84	t of q, $J_{f-e} = J_{f-g}$ 14 Hz	2	f
	2.87	t of d J_{d-e} 14Hz, J_{d-e} 9.59	2	d
^{19}F	- 61.5	s	3	g
	- 76.3	s	6	a,b
	- 90.0	s	2	e
	-185.6	s	1	c
^{13}C	36.4	t of d, J_{C-Fe} 29Hz, J_{C-Fe} 19Hz		d
	41.2	t of q, $J_{C-Fe} = J_{C-Fg}$ 27Hz		f
	89.7	d of sept, J_{C-Fe} 209Hz, J_{C-Fa} 33Hz		c
	116.9	t of q, J_{C-Fe} 248Hz, J_{C-Fg} 3.2Hz		e
	120.1	q of d, J_{C-Fa} 288Hz, J_{C-Fe} 27Hz		a,b
	122.8	q of t, J_{C-Fg} 276Hz, J_{C-Fe} 6Hz		g

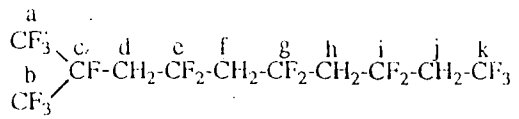
N°12 3,3,5,5,7,7-hexahydro-2-trifluoromethylperfluorooctane (10),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.12	t of t, $J_{f-g} = J_{f-e}$ 32Hz	2	f
	3.22	t of q, $J_{h-g} = J_{h-i}$ 15.9Hz	2	h
	3.23	d of t, J_{d-e} 17.5Hz, J_{d-e} 15.5Hz	2	d
^{19}F	- 62.5	s	3	i
	- 77.8	s	6	a,b
	- 94.53	s	2	e or g
	- 95.05	s	2	g or e
	-185.9	s	1	c
^{13}C	36.4	t of d, J_{C-Fe} 26Hz, J_{C-Fe} 19Hz		d
	41.3	t of q, $J_{C-Fg} = J_{C-Fi}$ 29Hz		h
	44.2	t of t, $J_{C-Fe} = J_{C-Fg}$ 25Hz		f
	91.3	d of sept, J_{C-Fe} 209Hz, J_{C-Fa} 34Hz		c
	119.5	t of q, J_{C-Fg} 245Hz, J_{C-Fi} 2.6Hz		g
	120.1	t, J_{C-Fe} 239Hz		e
	120.1	q of d, J_{C-Fa} 287Hz, J_{C-Fe} 27Hz		a,b
	122.8	q of t, J_{C-Fi} 276Hz, J_{C-Fg} 4Hz		i

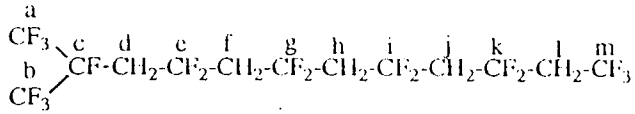
N°13 3,3,5,5,7,7,9,9-octahydro-2-trifluoromethylperfluorodecane (12).



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.01 - 3.19	m	8	d, f, h, j
^{19}F	- 62.1	s	3	k
	- 77.2	s	6	a,b
	- 94.3	s	2	e or g or i
	- 94.5	s	2	e or g or i
	- 94.9	s	2	e or g or i
	-183.8	s	1	c
^{13}C	35.4	t of d, J_{C-Fe} 26Hz, J_{C-Fc} 19Hz		d
	40.3	t of q, $J_{C-Fg} = J_{C-Fi}$ 29Hz		j
	42.9	t of t, $J_{C-Fg} = J_{C-Fi}$ 25Hz		h
	43.2	t of t, $J_{C-Fe} = J_{C-Fg}$ 25Hz		f
	90.3	d of sept, J_{C-Fc} 209Hz, J_{C-Fa} 34Hz		c
	118.7	t of q, J_{C-Fi} 245Hz, J_{C-Fk} 2.6Hz		i
	119.1	t, J_{C-Fe} 239Hz		e
	119.1	q of d, J_{C-Fa} 287Hz, J_{C-Fc} 27Hz		a,b
	119.4	t , J_{C-Fg} 241Hz		g
	122.8	q of t, J_{C-Fk} 276Hz, J_{C-Fi} 4Hz		k

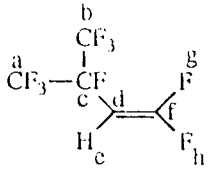
N°14 3,3,5,5,7,7,9,9,11,11-decahydro-2-trifluoromethylperfluoro-dodecane (12).



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.9 - 3.3	m	10	d, f, h, j, l
^{19}F	- 63.1	s	3	m
	- 78.1	s	6	a,b
	- 93.5		2	e or g or i or k
	- 94.7	s	2	e or g or i or k
	- 95.2	s	2	e or g or i or k
	- 95.6	s	2	e or g or i or k
	-183.8	s	1	c
^{13}C	36.2	m		d
	41.1	m		f or h or j or l
	42.8	m		f or h or j or l
	43.8	m		f or h or j or l
	44.3	m		f or h or j or l
	91.5	d of sept, J_{C-Fc} 211Hz, J_{C-Fa} 35Hz		c
	119.3	t, J_{C-F} 245Hz		i or g or e or k
	120.5	t , J_{C-F} 241Hz		i or g or e or k
	120.7	t, J_{C-F} 240Hz		i or g or e or k
	120.8	t,J_{C-F} 243Hz		i or g or e or k
	120.8	q of d, J_{C-Fa} 287Hz, J_{C-Fc} 27Hz		a,b
	122.8	q, J_{C-Fm} 276Hz		m

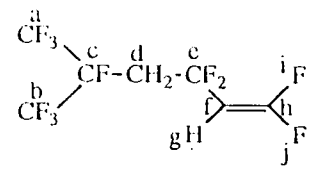
N°15 2-hydro-3-trifluoromethylperfluorobut-1-ene (8).



(400MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.57	d of d, $J_{e\text{-}g}$ = $J_{e\text{-}c}$ 21Hz	1	e
^{19}F	- 70.34	d, $J_{h\text{-}g}$ 9Hz	1	h
	-70.8	m	1	g
	-78..35	m	6	a,b
	-185.2	m	1	c
^{13}C	69.6	d of d of d, $J_{d\text{-}Fe}$ 30Hz ,$J_{d\text{-}g}$=$J_{d\text{-}h}$ 15Hz		d
	88.3	d of sept, $J_{C\text{-}Fe}$ 208Hz, $J_{C\text{-}Fa}$ 38Hz		c
	120.1	q of d, $J_{C\text{-}Fa}$ 286Hz, $J_{C\text{-}Fe}$ 28Hz		a,b
	159.1	d of d, $J_{C\text{-}F}$ 304Hz, $J_{C\text{-}F}$ 293Hz		f

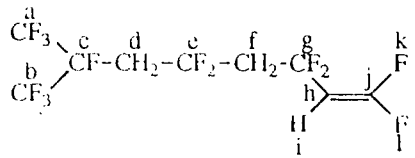
N°16 2,4,4-trihydro-5-trifluoromethylperfluorohex-1-ene (24).



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.26	t of d, $J_{d\text{-}e}$ 18Hz, $J_{d\text{-}c}$ 15Hz	2	d
	5.26	d of t of d, $J_{g\text{-}i}$ 24Hz, $J_{g\text{-}e}$ 12Hz, $J_{g\text{-}j}$ 3Hz	1	g
^{19}F	- 80.4	d of d of t,$J_{i\text{-}g}$ 24Hz, $J_{i\text{-}j}$ 22Hz, $J_{i\text{-}e}$ 21Hz	1	i
	- 81.7	q, $J_{a\text{-}b}$ 6Hz	6	a,b
	- 84.5	d of t of d, $J_{j\text{-}i}$ 22Hz, $J_{j\text{-}e}$ 8Hz, $J_{j\text{-}g}$ 3Hz	1	j
	- 92.5	m	2	e
	- 190.0	m	1	c
^{13}C	36.7	t of d, $J_{C\text{-}Fe}$ 29Hz, $J_{C\text{-}Fe}$ 19Hz		d
	80.3	d of t of d, $J_{C\text{-}Fi}$ 31Hz, $J_{C\text{-}Fe}$ 28Hz, $J_{C\text{-}Fj}$ 12Hz		f
	90.9	d of sept, $J_{C\text{-}Fe}$ 208Hz, $J_{C\text{-}Fa}$ 34Hz		c
	117.7	t of d, $J_{C\text{-}Fe}$ 243Hz, $J_{C\text{-}F}$ 14Hz		e
	121.5	q of d, $J_{C\text{-}Fa}$ 288Hz, $J_{C\text{-}Fe}$ 27Hz		a,b
	158.4	d of d of t, $J_{C\text{-}F}$ 300Hz, $J_{C\text{-}F}$ 290Hz, $J_{C\text{-}Fe}$ 8Hz		h

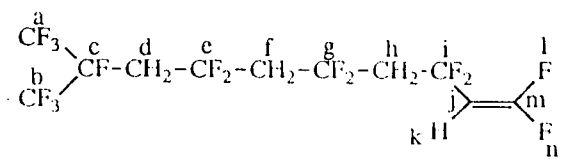
N°17 2,4,4,6,6-pentahydro-7-trifluoromethylperfluorooct-1-ene (13).



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.10	t of t, $J_{f-e} = J_{f-g}$ 15Hz	2	f
	3.22	d of t, J_{d-e} 19Hz, J_{d-e} 17Hz	2	d
	5.20	d of t of d, J_{i-k} 23.5Hz, J_{i-g} 11.7Hz, J_{i-l} 2.8Hz	1	i
^{19}F	- 81.4	d of d of t, J_{k-i} 23.5Hz, J_{k-l} 22Hz, J_{k-g} 21Hz,	1	k
	- 81.7	q, J_{a-b} 6.3Hz	6	a,b
	- 85.5	d of t of d, J_{l-k} 22Hz, J_{l-g} 8Hz, J_{l-i} 3Hz	1	l
	- 91.7	m	2	g
	- 99.2	m	2	e
	- 189.9	m	1	c
^{13}C	36.7	t of d, J_{C-Fe} 28Hz, J_{C-Fe} 19.5Hz		d
	45.3	t of t, $J_{C-Fe} = J_{C-Fg}$ 25Hz		f
	80.3	d of t of d, J_{C-Fk} 31Hz, J_{C-Fg} 28Hz, J_{C-Fl} 12Hz		h
	91.2	d of sept, J_{C-Fe} 208Hz, J_{C-Fa} 37Hz		c
	118.3	t of d, J_{C-Fg} 243z, J_{C-F} 13Hz		g
	120.0	t J_{C-Fe} 239Hz		e
	121.5	q of d, J_{C-Fa} 286Hz, J_{C-Fe} 26Hz		a,b
	158.4	d of d of t, J_{C-F} 299Hz, J_{C-F} 290Hz, J_{C-Fg} 8Hz		j

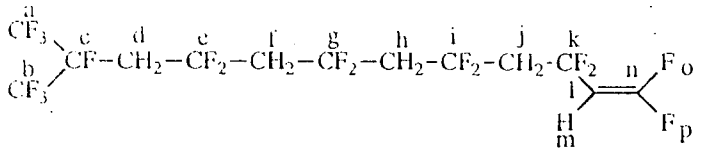
N°18 2,4,4,6,6,8,8-heptahydro-9-trifluoromethylperfluorodec-1ene (14).



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.10 - 3.4	m	6	d, f, h
	5.20	m	1	k
^{19}F	- 80.7	m	1	l
	- 81.2	m	6	a,b
	- 84.8	m	1	n
	- 90.8	s	2	i
	- 98.2	s	2	g or e
	-98.9	s	2	e or g
	- 189.1	s	1	c

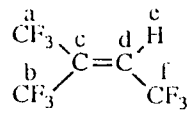
N°19 2,4,4,6,6,8,8,10,10-nonahydro-9-trifluoromethylperfluorododec-1-ene (15).



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.8 - 3.4	m	8	d, f, h, j
	5.2	m	1	m
^{19}F	- 80.9	m	1	o
	- 81.3	m	6	a,b
	- 84.8	m	1	p
	- 91.7	m	2	k
	- 97.8	s	2	e or g or i
	- 98.2	s	2	e or g or i
	- 99.3	s	2	e or g or i
	- 183.5	s	1	c

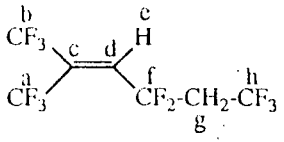
N° 20 3-hydro-2-trifluoromethylperfluorobut-2-ene (7).



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	7.57	q, $J_{e\text{-}f}$ 8Hz	1	e
^{19}F	- 64.4	q of q, $J_{b\text{-}f}$ 17.6Hz, $J_{b\text{-}a}$ 8.6Hz	3	b
	- 64.9	q of d, $J_{f\text{-}b}$ 17.6Hz, $J_{f\text{-}e}$ 8Hz	3	f
	- 70.2	q of d of q, $J_{a\text{-}b}$ 8.6Hz, $J_{a\text{-}e}$ 1.5Hz, $J_{a\text{-}f}$ 1.5Hz	3	a
^{13}C	119.9	q, J 274Hz		a
	121.0	q, J 273Hz		b,f
	129.7	sept, J 38Hz		c
	134.6	q, J 41Hz		d

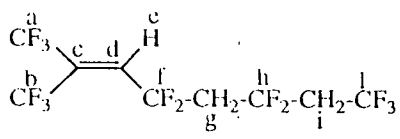
N°21 3,5,5-trihydro-2-trifluoromethylperfluorohex-2-ene (24a),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.15	t of q, $J_{g-f} = J_{g-h}$ 16 Hz	2	g
	7.27	t J_{c-f} 14Hz	1	c
^{19}F	- 64.6	t of q, J_{b-f} 16Hz J_{b-a} 8Hz	3	b
	- 67.2	m	3	h
	- 70 5	q, J_{a-b} 8Hz	3	a
	- 101.2	m	2	f
^{13}C	45.6	t of t, $J_{C-Ff} = J_{C-Fh}$ 24Hz		g
	118.2	t, J_{C-F} 244Hz		f
	120.9	q, J_{C-F} 274Hz		a or b
	122.1	q, J_{C-F} 275Hz		b or a
	125.3	q of t J_{C-Fl} 276, J_{C-Fh} 4Hz		h
	126.7	sept, $J_{C-Fa,b}$ 24Hz		c
	139.4	t $_{C-Ff}$ 31Hz		d

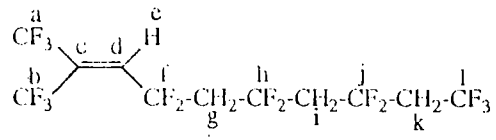
N° 22 3,5,5,7,7-pentahydro-2-trifluoromethylperfluorooct-2-ene (16),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{1}H	3.26	t of q, $J_{i-h} = J_{i-l}$ 16 Hz	2	i
	3.30	m	2	g
	7.32	t J_{c-f} 14Hz	1	c
^{19}F	- 63.3	t of q, J_{b-f} 16Hz J_{b-a} 8Hz	3	b
	- 66.4	m	3	l
	- 70 0	q, J_{a-b} 8Hz	3	a
	- 96.4	m	2	f
	- 99.3	m	2	h
^{13}C	41.2	t of q, J_{C-Fh} 26 Hz, J_{C-Fl} 29Hz		i
	44.2	t of t, $J_{C-Ff} = J_{C-Fh}$ 24Hz		g
	117.7	t, J_{C-F} 244Hz		f
	119.3	t of q, J_{C-Fh} 242Hz, J_{C-Fl} 3Hz		h
	120.6	q, J_{C-F} 274Hz		a or b
	121.6	q, J_{C-F} 275Hz		b or a
	124.9	q of t J_{C-Fl} 276, J_{C-Fh} 4Hz		l
	126.38	sept, $J_{C-Fa,b}$ 24Hz		c
	140.5	t $_{C-Ff}$ 31Hz		d

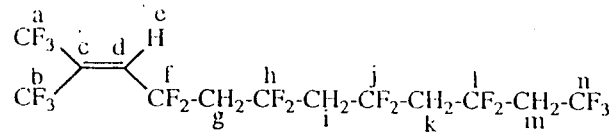
N°23 3,5,5,7,7,9,9-heptahydro-2-trifluoromethylperfluorodec-2-ene (17),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.2- 3.3	m	6	g, i, k
	7.35	t J_{e-f} 14Hz	1	e
^{19}F	- 63.3	m	3	b
	- 67.8	m	3	l
	- 72.6	m	3	a
	- 97.4	s	2	f
	- 99.3	s	2	j or h
	- 100.1	s	2	h or j
^{13}C	40.7	t of q, J_{C-Fh} 26 Hz, J_{C-Fl} 29Hz		k
	42.4	t of t, $J_{C-Ff} = J_{C-Fh}$ 25Hz		i or g
	44.9	t of t, $J_{C-Ff} = J_{C-Fh}$ 24Hz		g or i
	118.3	t, J_{C-F} 244Hz		j
	118.6	t, J_{C-F} 245Hz		f
	119.9	t, J_{C-Fh} 242Hz,		h
	120.4	q, J_{C-F} 274Hz		a or b
	121.8	q, J_{C-F} 275Hz		b or a
	124.9	q of t J_{C-Fl} 276, J_{C-Fh} 4Hz		l
	127.2	sept, $J_{C-Fa,b}$ 24Hz		c
	141,5	t J_{C-Ff} 30Hz		d

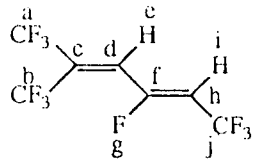
N°24 3,5,5,7,7,9,9,11,11-nonahydro-2-trifluoromethylperfluorododec-2-ene (18),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.2- 3.3	m	8	g, i, k,m
	7.35	t J_{e-f} 13Hz	1	e
^{19}F	- 63.3	m	3	b
	- 66.4	s	3	n
	- 70 0	m	3	a
	- 93.7	m	2	f
	- 97.7	s	2	j or h or l
	- 98.5	s	2	j or h or l
	- 99.3	s	2	j or h or l

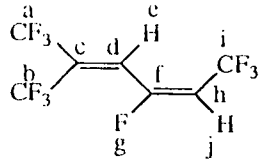
N°25 (Z,Z) 3,5-dihydro-2-trifluoromethylperfluorohexa-2,4-di-ene (23a),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	6.56	d of q, $J_{i\text{-}Fg}$ 30Hz, $J_{i\text{-}Fj}$ 8Hz	1	i
	7.58	d, $J_{e\text{-}Fg}$ 27Hz	1	e
^{19}F	- 62.9	d of q, $J_{b\text{-}g}$ 32Hz, $J_{b\text{-}a}$ 8Hz	3	b
	- 64.2	d of d $J_{j\text{-}g}$ 17Hz, $J_{j\text{-}i}$ 8Hz	3	j
	- 69.4	q, $J_{a\text{-}b}$ 8Hz	3	a
	- 106.7	m	1	g
^{13}C	109.5	sept $J_{C\text{-}Fa,b}$ 35Hz		c
	112.1	q of d, $J_{C\text{-}Fj}$ 37Hz, $J_{C\text{-}Fg}$ 8Hz		h
	120.8	q $J_{C\text{-}F}$ 274Hz		a or b
	121.8	q $J_{C\text{-}F}$ 273Hz		j
	122.1	q $J_{C\text{-}F}$ 269Hz		b or a
	133.8	d of spet, $J_{C\text{-}Fg}$ 25Hz, $J_{C\text{-}Fa,b}$ 3Hz		e
	157.4	d of q, $J_{C\text{-}Fg}$ 276Hz, $J_{C\text{-}Fj}$ 6Hz		f

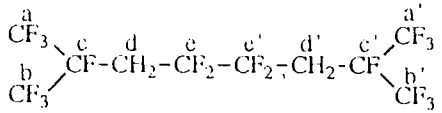
N°26 (Z,E) 3,5-dihydro-2-trifluoromethylperfluorohexa-2,4-di-ene (23b),



(400MHz, d-Acetone, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	6.63	d of q, $J_{j\text{-}Fg}$ 18Hz, $J_{j\text{-}Fi}$ 7Hz		j
	7.68	d, $J_{e\text{-}Fg}$ 19Hz	1	e
^{19}F	- 64.7	d of q, $J_{b\text{-}g}$ 24Hz, $J_{b\text{-}a}$ 8Hz	3	b
	- 66.1	d of d, $J_{i\text{-}g}$ 14Hz, $J_{i\text{-}j}$ 7Hz	3	i
	- 69.7	q, $J_{a\text{-}b}$ 8Hz	3	a
	- 99.6	m	1	g

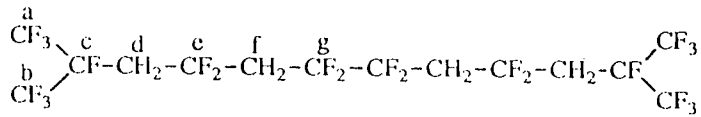
N°27 3,3,6,6-tetrahydro-2,7-bis(trifluoromethyl)perfluorooctane (21).



(400MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.86	d of t $J_{d\text{-}e(e')} = J_{d\text{-}e(e')}$ 18Hz	4	d, d'
^{19}F	- 76.7	s	12	a, b, a', b'
	- 112.4	s	4	e, e'
	- 184.9	s	2	c, c'
^{13}C	28.3	d of t $J_{C\text{-}Fe(e')} = J_{C\text{-}Fe(e')}$ 19Hz		d, d'
	89.8	d of sept, $J_{C\text{-}Fe(e')}$ 212Hz $J_{C\text{-}Fa(a',b,b')}$ 33.9Hz		c, c'
	115.7	t of t, $J_{C\text{-}Fe(e')}$ 260Hz, $J_{C\text{-}Fe'(e)}$ 37.5Hz		e, e'
	120.4	q of d, $J_{C\text{-}Fa(a',b,b')}$ 287Hz, $J_{C\text{-}Fe(e')}$ 27.5Hz		a, a', b, b'

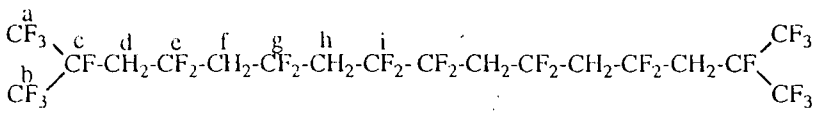
N°28 3,3,5,5,8,8,10,10-octahydro-2,11-bis(trifluoromethyl)perfluoro-dodecane (20).



(400MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.77	m	2	d or f
	2.84	m	2	f or d
^{19}F	- 77.4	s	12	a, b
	- 88.4	s	4	e
	- 113.8	s	4	g
	-185.6	s	2	c
^{13}C	36.4	t of d, $J_{C\text{-}Fe}$ 28Hz, $J_{C\text{-}Fe}$ 19Hz		d
	37.0	m		f
	90.6	d of sept, $J_{C\text{-}Fe}$ 209Hz, $J_{C\text{-}Fa}$ 33Hz		c
	116.7	t of t, $J_{C\text{-}Fg}$ 256Hz, $J_{C\text{-}Fg'}$ 38Hz		g
	118.8	t, $J_{C\text{-}Fe}$ 247Hz		e
	121.1	q of d, $J_{C\text{-}Fa}$ 287Hz, $J_{C\text{-}Fe}$ 27Hz		a,b

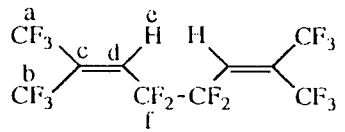
N°29 3,3,5,5,7,7,10,10,12,12,14,14-dodecahydro-2,15-bis(trifluoromethyl)-perfluorohexadecane (19),



(400MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.7 - 2.8	m	12	d or f or h
^{19}F	- 76.9	s	12	a, b
	- 88.7	s	4	e or g
	- 89.6	s	4	g or e
	- 113.6	s	4	i
	-185.6	s	2	c
^{13}C	35.9	m		d,f
	43.6	m		h
	89.7	d of sept, J_{C-Fc} = 209Hz, J_{C-Fa} = 33Hz		c
	115.8	t of t, J_{C-F} = 247Hz, J_{C-F} 29Hz		i
	118.1	t, J_{C-F} = 246Hz,		g or e
	118.6	t, J_{C-F} 249Hz		e or g
	120.2	q of d, J_{C-Fa} 289Hz, J_{C-Fc} 27Hz		a,b

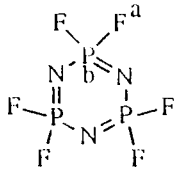
N°30 3,6-dihydro-2,7-bis(trifluoromethyl)perfluorooctadi-2,6-ene (22),



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	7.54	t J_{e-f} 15Hz	2	e
^{19}F	- 59.6	s	3	a or b
	- 66.2	s	3	b or a
	- 110.6	s	2	f

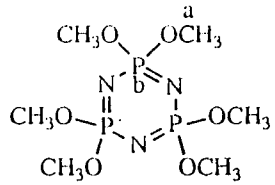
N°35 Hexafluorophosphazene (55).



(250MHz, $CDCl_3$, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	- 70.55	d, J_{P-F} = 957Hz	6	a
^{31}P	10.1	t of m, J_{P-F} = 957Hz	3	b

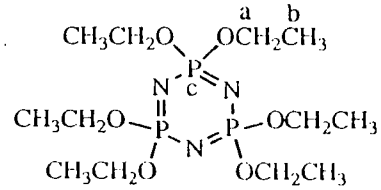
N°36 Hexakis(methoxy)cyclotriphosphazene (63).



(250MHz, $CDCl_3$, TMS)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.67	broad	18	a
^{31}P	20.9	s	3	b

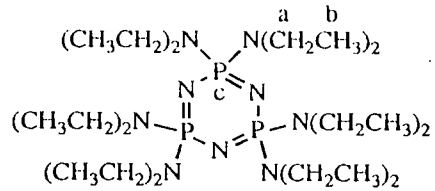
N°37 Hexakis(ethoxy)cyclotriphosphazene (64).



(250MHz, $CDCl_3$, TMS)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	1.9	broad	3	b
	4.6	broad	2	a
^{31}P	17.5	s	3	c

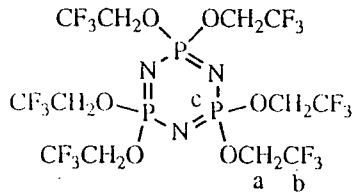
N°38 Hexakis(diethylamino)cyclotriphosphazene (66).



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	1.03	broad	3	b
	3.04	broad	2	a
^{31}P	22.3	s	3	c

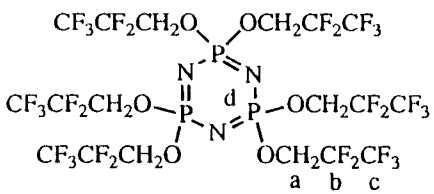
N°39 **Hexakis(trifluoroethoxy)cyclotriphosphazene (50).**



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	- 75.7	s	3	b
^{31}P	17.2	s	3	c

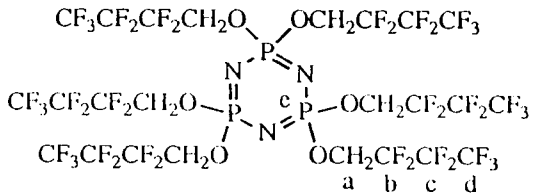
N°40 **Hexakis(pentafluoropropoxy)cyclotriphosphazene (67).**



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	- 83.9	s	3	c
	- 124.6	s	2	b
^{31}P	17.2	s	3	d

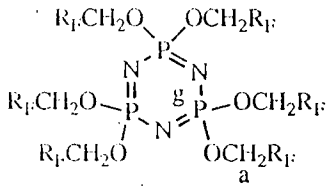
N°41 **Hexakis(heptafluorobutoxy)cyclotriphosphazene (68).**



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	- 83.7	s	3	d
	- 123.8	s	2	b
	- 129.9	s	2	c
^{31}P	17.2	s	3	c

N°42 Hexakis(perfluoropolyether-alkoxy)cyclotriphosphazenes.
(70a) R_F = PFPE (69a) equivalent weight 457 a.m.u.
(70b) R_F = PFPE (69b) equivalent weight 900 a.m.u.



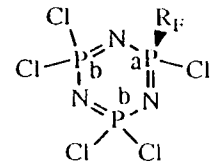
R_F= T-O-($CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-
c b d e f

where: T = $-CF_3$, $-C_2F_5$, $-C_3F_7$; X = -F, $-CF_3$; Z = -F, $-CF_3$; m and n are numbers so that the n/m ratio ranges from 0.01 to 0.5 and the molecular weight is in the above mentioned range.

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	- 55.2	s	-	-
	- 56.4	s	-	-
	- 57.1	s	3	b
	- 58.2	s	-	-
	- 77.4	s	-	-
	- 77.8	s	-	-
	- 81.4	s	2	d
	- 85.7	s	-	-
	- 86.4	s	2	e
	- 87.7	s	-	-
	- 146.3	s	1	c
	- 146.4	s	-	-
	-146.5	s	-	-
^{31}P	17.2	s	3	g

N°43 Pentachloro-mono(perfluoropolyether-alkoxy)cyclotriphosphazene (70c).

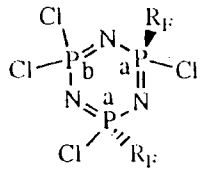


R_F= T-O-($CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-
c

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	as in (70a)			
^{31}P	16.2	t, J_{P-P} = 67Hz	1	a
	22.4	d, J_{P-P} = 67Hz	2	b

N°44 Tetrachloro-bis(perfluoropolyether-alkoxy)cyclotriphosphazene (70d).

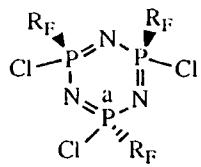


R_F= T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-
c

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	as in (70a)			
^{31}P	19.2	d, J_{P-P} = 69Hz	2	a
	25.1	t, J_{P-P} = 67Hz	1	b

N°45 Trichloro-tris(perfluoropolyether-alkoxy)cyclotriphosphazene (70e).

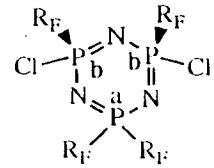


R_F= T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	as in (70a)			
^{31}P	16.2	d, J_{P-P} = 7Hz	3	a

N°46 Dichloro-tetrakis(perfluoropolyether-alkoxy)cyclotriphosphazene (70f).

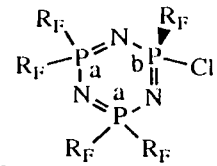


R_F= T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	as in (70a)			
^{31}P	11.5	t, J_{P-P} = 85Hz	1	a
	24.7	d, J_{P-P} = 85Hz	2	b

N°47 Chloro-pentakis(perfluoropolyether-alkoxy)cyclotriphosphazene (70g).

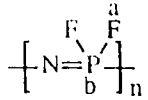


R_F= T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	2	a
^{19}F	as in (70a)			
^{31}P	9.8	d, J_{P-P} = 67Hz	2	a
	18.5	t, J_{P-P} = 67Hz	1	b

N°48 Poly(fluoro)phosphazene (55b).



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	- 71.7	d, J_{P-F} = 200Hz	2	a
^{31}P	-4.5	t, J_{P-F} = 200Hz	1	b

N°49 1,1-bis(trifluoromethyl)perfluoropropanol (72).

CF_3-CF_2-$C(CF_3)_2$-OH
a b c

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	- 73.2	s	6	c
	-80.4	s	3	a
	-119.5	s	2	b

N°50 1,1,3-tris(trifluoromethyl)perfluoropropanol (73).

$(CF_3)_2$CF-$C(CF_3)_2$-OH
a b c

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	- 70.9	s	6	a or c
	- 71,8	s	6	c or a
	-180.2	s	1	b

N°51 Trifluoromethyltrimethylsilane (78).

b
CF_3SiMe_3
a

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	0.26	s	9	b
^{19}F	- 67.5	s	3	a

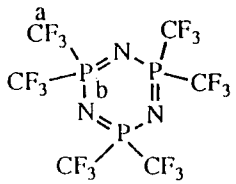
N°52 Pentafluoroethyltrimethylsilane (88).

CF_3-CF_2SiMe_3
a b c

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	0.22	s	9	c
^{19}F	- 82.5	s	3	a
	- 132.13	s	2	b

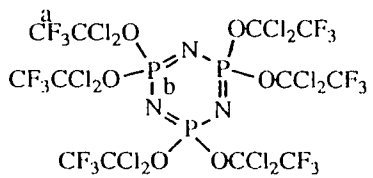
N°53 Hexakis(trifluoromethyl)cyclotriphosphazene (89).



(250MHz, $CDCl_3$, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	- 74.7	d, J_{P-F} = 109Hz	3	a
^{31}P	3.9	sept, J_{F-P} = 109Hz	1	b

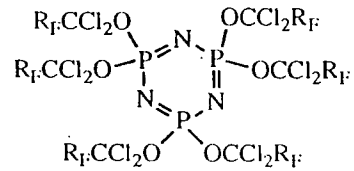
N°54 Hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)cyclotriphosphazene (93).



(250MHz, $CDCl_3$, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	- 84.9	s	3	a
^{31}P	- 0.23	s	1	b

N°55 Hexakis(1,1-dichloro-perfluoropolyether-alkoxy)cyclotriphosphazene (94).

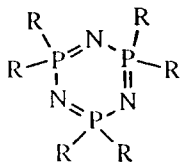


R_F= T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-

(250MHz, $CDCl_3$, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	as in (70a)			
^{31}P	- 0.28	s	1	b

N°56 Cyclotriphosphazenes (96a)-(96d).



$R = R_F = T\text{-}O\text{-}(CF(CF_3)CF_2O)_m(CFX)_n\text{-}CFZ\text{-}CH_2\text{-}O\text{-}$ (a)

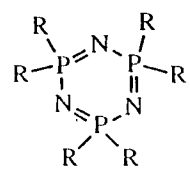
R = O– (b, c, d)

(69a) R = R_F and phenol in a ca. 3.2 / 2.8 ratio
(69b) R = R_F and phenol in a ca. 2.2 / 3.8 ratio
(69c) R = R_F and phenol in a ca. 3.7 / 2.3 ratio
(69d) R = R_F and phenol in a ca. 5.4 / 0.6 ratio

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	-	a
	6.9	m	1	b
	7.1	m	2	c or d
	7.2	m	2	d or c
^{19}F	as in (70a)			
^{31}P	8.2	s	-	-
	11.6	s	-	-
	14.1	s	-	-
	16.9	s	-	-
	24.4	s	-	-
	26.5	s	-	-
	26.8	s	-	-

N°57 Cyclotriphosphazene (97).



$R = R_F = T\text{-}O\text{-}(CF(CF_3)CF_2O)_m(CFX)_n\text{-}CFZ\text{-}CH_2\text{-}O\text{-}$ (a)

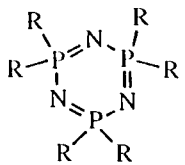
R = O– (b, c, d)

(97) R = R_F and cyclohexanol in a ca.3.4 / 2.6 ratio

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	broad	1.3	a
	5.8	m	1	b
	6.0	m	2	c or d
	6.2	m	2	d or c
^{19}F	as in (70a)			
^{31}P	9.4	s	-	-
	11.7	s	-	-
	12.4	s	-	-
	14.7	s	-	-

N°58 Cyclotriphosphazene (98).



R = R_F = T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-
a

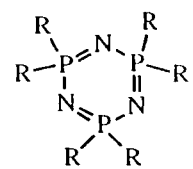
R = OCH_2CF_3
b

(98) R = R_F and trifluoroethanol in a ca.2.8 / 3.2 ratio

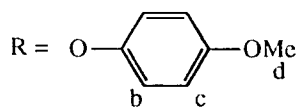
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.9	broad	1.1	b
	4.2	broad	1	a
^{19}F	as in (70a)			
^{31}P	17.4	s broad	-	-

N°59 Cyclotriphosphazene (100).



R = R_F = T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-
a

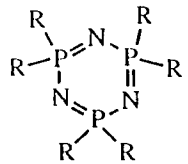
R = 

(100) R = R_F and 4-methoxyphenol in a ca.3.6 / 2.4 ratio

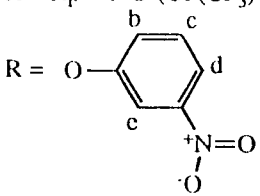
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.5	s	3	d
	4.2	broad	3	a
	6.7	m	2	b or c
	6.9	m	2	c or b
^{19}F	as in (70a)			
^{31}P	9.4	s	-	-
	11.7	s	-	-
	12.4	s	-	-
	14.7	s	-	-

N°60 Cyclotriphosphazene (101).



R = R_F = T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-
a

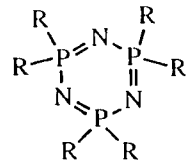


(101) R = R_F and 3-nitrophenol in a ca.3.9 / 2.1 ratio

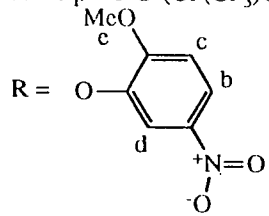
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	s broad	1.85	a
	7.1	m	1	
	7.3	m	1	b,c,d,e
	7.6	m	1	
	7.9	m	1	
^{19}F	as in (70a)			
^{31}P	12.6	s	-	-
	12.9	s	-	-
	16.1	s	-	-

N°61 Cyclotriphosphazene (102).



R = R_F = T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-
a

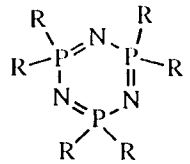


(102) R = R_F and 2-methoxy-5-nitrophenol in a ca.3.5 / 2.5 ratio

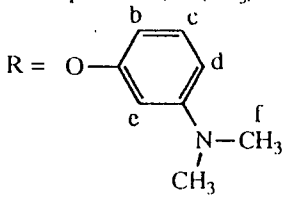
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.4	s	3	e
	4.2	s broad	1.4	a
	7.3	m	1	
	7.6	m	1	b,c,d
	7.9	m	1	
^{19}F	as in (70a)			
^{31}P	11.3 - 21.4	numerous peaks	-	-

N°62 Cyclotriphosphazene (103).



R = R_F = T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-

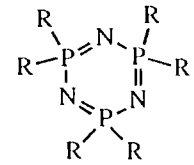


(103) R = R_F and 3-dimethylaminophenol in a ca.3.3 / 2.7 ratio

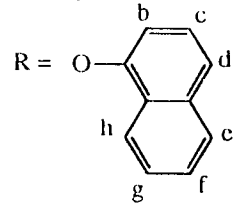
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.2	s	6	f
	4.2	s broad	2.45	a
	7.2	m	2	
	7.5	m	2	b,c,d,e
^{19}F	as in (70a)			
^{31}P	12.5	s	-	-
	13.85	s	-	-
	15.95	s	-	-
	16.7	s	-	-

N°63 Cyclotriphosphazene (104).



R = R_F = T-O-$(CF(CF_3)CF_2O)_m(CFX)_n$-CFZ-CH_2-O-

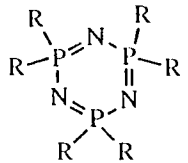


(104) R = R_F and α-napthol in a ca.5.4 / 0.6 ratio

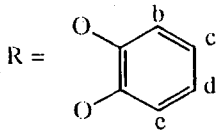
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	s broad	9	a
	6.6 - 8.0	m	1	b,c,d,e,f,g,h
^{19}F	as in (70a)			
^{31}P	13 - 17	numerous peaks	-	-
	21 - 26	numerous peaks	-	-

N°64 Cyclotriphosphazene (105).



$R = R_F = T\text{-}O\text{-}(CF(CF_3)CF_2O)_m(CFX)_n\text{-}CFZ\text{-}CH_2\text{-}O\text{-}$ (a)

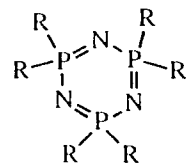
R = 

(105) R = R_F and catechol in a ca.5.8 / 0.2 ratio

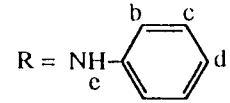
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	4.2	s broad	9	a
	6.9 - 7.5	m	1	b,c,d,e
^{19}F	as in (70a)			
^{31}P	11 - 27	numeorus peaks	-	-

N°65 Cyclotriphosphazene (106).



$R = R_F = T\text{-}O\text{-}(CF(CF_3)CF_2O)_m(CFX)_n\text{-}CFZ\text{-}CH_2\text{-}O\text{-}$ (a)

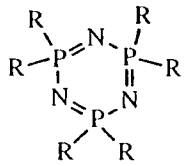
R = 

(106) R = R_F and anylin in a ca.5.3 / 0.7 ratio

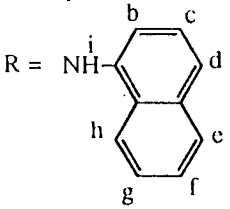
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.2	very broad	-	e
	4.2	s broad	7.6	a
	6.9 - 7.5	m	1	b,c,d
^{19}F	as in (70a)			
^{31}P	12.5 - 24	numerous peaks	-	-

N°66 Cyclotriphosphazene (107).



$R = R_F = T\text{-}O\text{-}(CF(CF_3)CF_2O)_m(CFX)_n\text{-}CFZ\text{-}CH_2\text{-}O\text{-}$ (a)

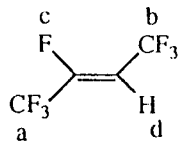
R = 

(107) R = R_F and α-napthylamine in a ca.5.2 / 0.8 ratio

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts (ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.2	very broad	-	i
	4.2	s broad	6.5	a
	6.9 - 7.5	m	1	b,c,d,e,f,g,h
^{19}F	as in (70a)			
^{31}P	15.6 - 23.8	numerous peaks	-	-

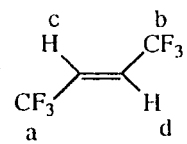
N° 67 2-hydroperfluorobut-2-ene (109).



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	6.55	d of q, J_{Fc-H} = 30.0Hz, J_{Fb-H} = 6.9Hz	1	d
^{19}F	- 61.5	d, J_{Fc-F} = 17.4Hz	3	a
	- 75.8	d, J_{H-F} = 6.9Hz	3	b
	- 120.8	m	1	c

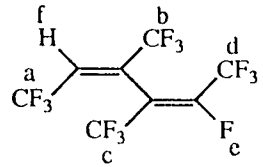
N° 68 2,3-dihydroperfluorobut-2-ene (109).



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	6.8	s	2	c,d
^{19}F	- 66.5	s	6	a,b

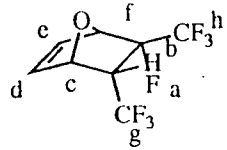
N° 69 5-hydroperfluoro-3,4-bis(trifluoromethyl)hexadi-2,4-ene (110a).



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	7.59	broad	1	f
^{19}F	- 60.78	d, J_{Fa-F} = 15.7Hz	3	d
	- 62.12	d, J_{H-F} = 6.9Hz	3	a
	- 67.90	s	3	b
	- 70.09	s	3	c
	- 104.98	m	1	e

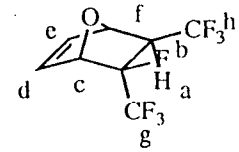
N° 70 endo-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo-[2,2,1]-hept-2-ene (121a),



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.62	d of q of d, J_{H-F} = 12.6Hz, J_{CF3-H} = 8.9Hz, J_{H-H} = 4.3Hz	1	b
	5.4	broad	2	c,f
	6.68	m	1	e
	6.91	m	1	d
^{19}F	- 61.81	s	3	g
	- 79.23	s	3	h
	- 183.75	s	1	a

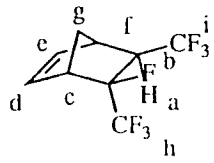
N° 71 exo-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo-[2,2,1]-hept-2-ene (121b),



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	3.17	d of q of d, J_{H-F} = 12.2Hz, J_{CF3-H} = 9.0Hz,	1	a
	5.4	broad	2	c,f
	6.42	m	1	e
	6.74	m	1	d
^{19}F	- 64.96	s	3	g
	- 75.99	s	3	h
	- 182.91	s	1	b

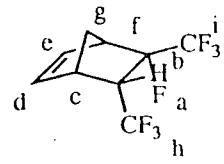
N° 72 exo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo-[2,2,1]-hept-2-ene (121c).



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.54	m	1	b
	3.23	broad	2	c,f
	va 1.30, vb 1.48	AB system J= 7.85Hz	2	g
	5.95	m	1	e
	6.15	m	1	d
^{19}F	- 65.18	s	3	h
	- 78.59	s	3	i
	- 177.44	s	1	a

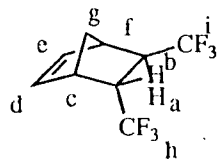
N° 73 endo-5-fluoro-5,6-bis(trifluoromethyl)bicyclo-[2,2,1]-hept-2-ene (121d).



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.75	m	1	a
	3.39	broad	2	c,f
	va 1.84, vb 2.17	AB system J= 8.6Hz	2	g
	6.23	m	1	e
	6.43	m	1	d
^{19}F	- 63.8	s	3	h
	- 78.6	s	3	i
	- 180.8	s	1	a

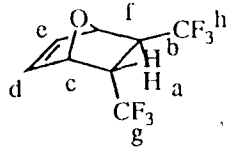
N° 74 **5,6-bis(trifluoromethyl)bicyclo-[2,2,1]-hept-2-ene (126).**



(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.15	m	1	a
	2.83	m	1	b
	va 1.53, vb 1.68	AB system J= 8.6Hz	2	g
	3.18	broad	1	c or f
	3.19	broad	1	f or c
	6.19	m	1	e or d
	6.32	m	1	d or e
^{19}F	- 66.8	s	3	h
	- 68.3	s	3	i

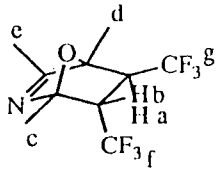
N° 75 **5,6-bis(trifluoromethyl)-7-oxabicyclo-[2,2,1]-hept-2-ene (131).**



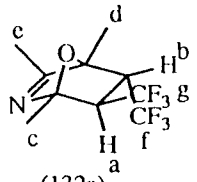
(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^1H	2.34	m	1	a
	2.83	m	1	b
	5.17	broad	2	c, f
	6.45	m	1	e
	6.57	m	1	d
^{19}F	- 65.89	s	3	g
	- 68.92	s	3	h

N° 76 5,6-bis(trifluoromethyl)-1,3,4-trimethyl-2-aza-7-oxabicyclo-[2,2,1]-hept-2-ene (132a) (132b),



(132b)



(132a)

(250MHz, $CDCl_3$, TMS, $CFCl_3$)

	Chemical Shifts(ppm)	Multiplicity Coupling Costants (Hz)	Relative Intensity	Assignment
^{19}F	- 65.7	s	3	f (132a)
	- 65.9	s	3	g (132a)
^{19}F	- 65.4	s	3	f (132b)
	- 66.8	s	3	g (132b)

APPENDIX 2
INFRARED SPECTRA

N°1 3,3-dihydro-2-trifluoromethylperfluorobutane (6).

N°2 3,3,5,5-tetrahydro-2-trifluoromethylperfluorohexane (9).

N°3 3,3,5,5,7,7-hexahydro-2-trifluoromethylperfluorooctane (10).

N°4 3,3,5,5,7,7,9,9-octahydro-2-trifluoromethylperfluorodecane (11).

N°5 2-hydro-3-trifluoromethylperfluorobut-1-ene (8).

N°6 2,4,4-trihydro-5-trifluoromethylperfluorohex-1-ene (24).

N°7 2,4,4,6,6-pentahydro-7-trifluoromethylperfluorooct-1-ene (13).

N°8 2,4,4,6,6,8,8-heptahydro-9-trifluoromethylperfluorodec-1ene (14).

N°9 3-hydro-2-trifluoromethylperfluorobut-2-ene (7).

N°10 3,5,5-trihydro-2-trifluoromethylperfluorohex-2-ene (24a).

N°11 3,5,5,7,7-pentahydro-2-trifluoromethylperfluorooct-2-ene (16).

N°12 3,5,5,7,7,9,9-heptahydro-2-trifluoromethylperfluorodec-2-ene (17).

N°13 (Z,Z) 3,5-dihydro-2-trifluoromethylperfluorohexa-2,4-di-ene (23a).

N°14 3,3,6,6-tetrahydro-2,7-bis(trifluoromethyl)perfluorooctane (21).

N°15 3,3,5,5,8,8,10,10-octahydro-2,11-bis(trifluoromethyl)perfluoro-dodecane (20).

N°16 3,3,5,5,7,7,10,10,12,12,14,14-dodecahydro-2,15-bis(trifluoromethyl)perfluoro-hexadecane (19).

N°17 1,2-diiodotetrafluoroethane (37)

N°18 2,2-dihydro-1,4-diiodoperfluorobutane (36a)

N°19 isomer mixture: 2,2,5,5-tetrahydro-1,6-diiodoperfluorohexan (36) and 2,2,4,4-tetrahydro-1,6-diiodoperfluorohexan (36b)

N°20 3,6-dihydro-2,7-bis(trifluoromethyl)perfluorooctadi-2,6-ene (22).

N°21 Hexafluorophosphazene (55).

N°22 Hexakis(methoxy)cyclotriphosphazene (63).

N°23 Hexakis(ethoxy)cyclotriphosphazene (64).

N°24 Hexakis(diethylamino)cyclotriphosphazene (66).

N°25 Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50).

N°26 Hexakis(2,2,3,3,3-pentafluoropropoxy)cyclotriphosphazene (67).

N°27 Hexakis(2,2,3,3,4,4,4-heptafluorobutoxy)cyclotriphosphazene (68).

N°28 Hexakis(perfluoropolyether-alkoxy)cyclotriphosphazenes.

N°29 Poly(fluoro)phosphazene (55b).

N°30 1,1-bis(trifluoromethyl)perfluoropropanol (72).

N°31 1,1,3-tris(trifluoromethyl)perfluoropropanol (73).

N°32 Trifluoromethyltrimethylsilane (78).

N°33 Pentafluoroethyltrimethylsilane (88).

N°34 Hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)cyclotriphosphazene (93).

N°35 Hexakis(1,1-dichloro-perfluoropolyether-alkoxy)cyclotriphosphazene (94).

N°36 Chloro-perfluoropolyether-alkoxycyclotriphosphazene (70c)-(70g).

N°37 Cyclotriphosphazene (97).

N°38 Cyclotriphosphazene (98).

N°39 Cyclotriphosphazenes (96a)-(96d).

N°40 Cyclotriphosphazene (100).

N°41 Cyclotriphosphazene (101).

N°42 Cyclotriphosphazene (102).

N°43 Cyclotriphosphazene (103).

N°44 Cyclotriphosphazene (104).

N°45 Cyclotriphosphazene (105).

N°46 Cyclotriphosphazene (106).

N°47 Cyclotriphosphazene (107).

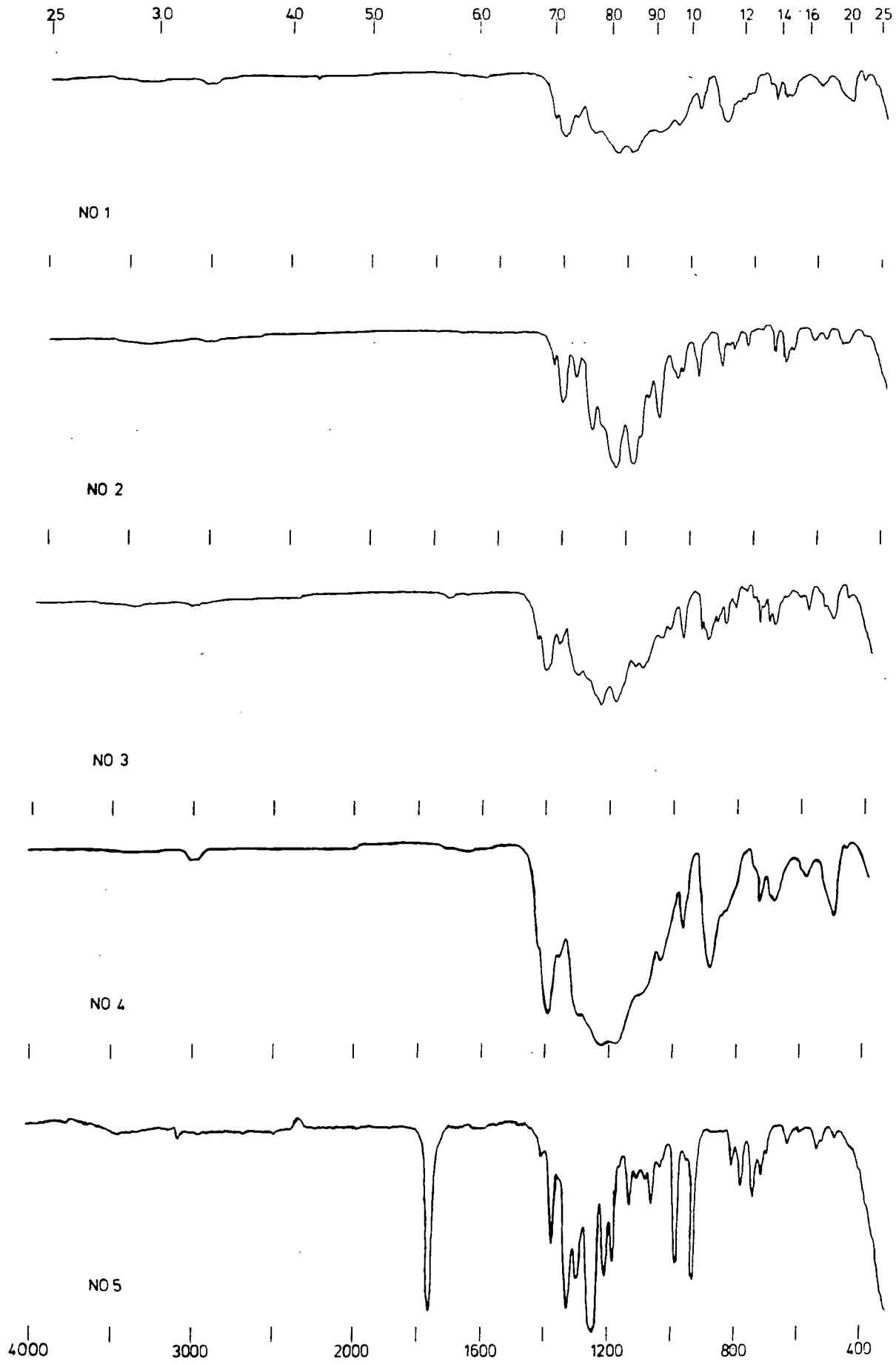
N°48 2-hydroperfluorobut-2-ene (109).

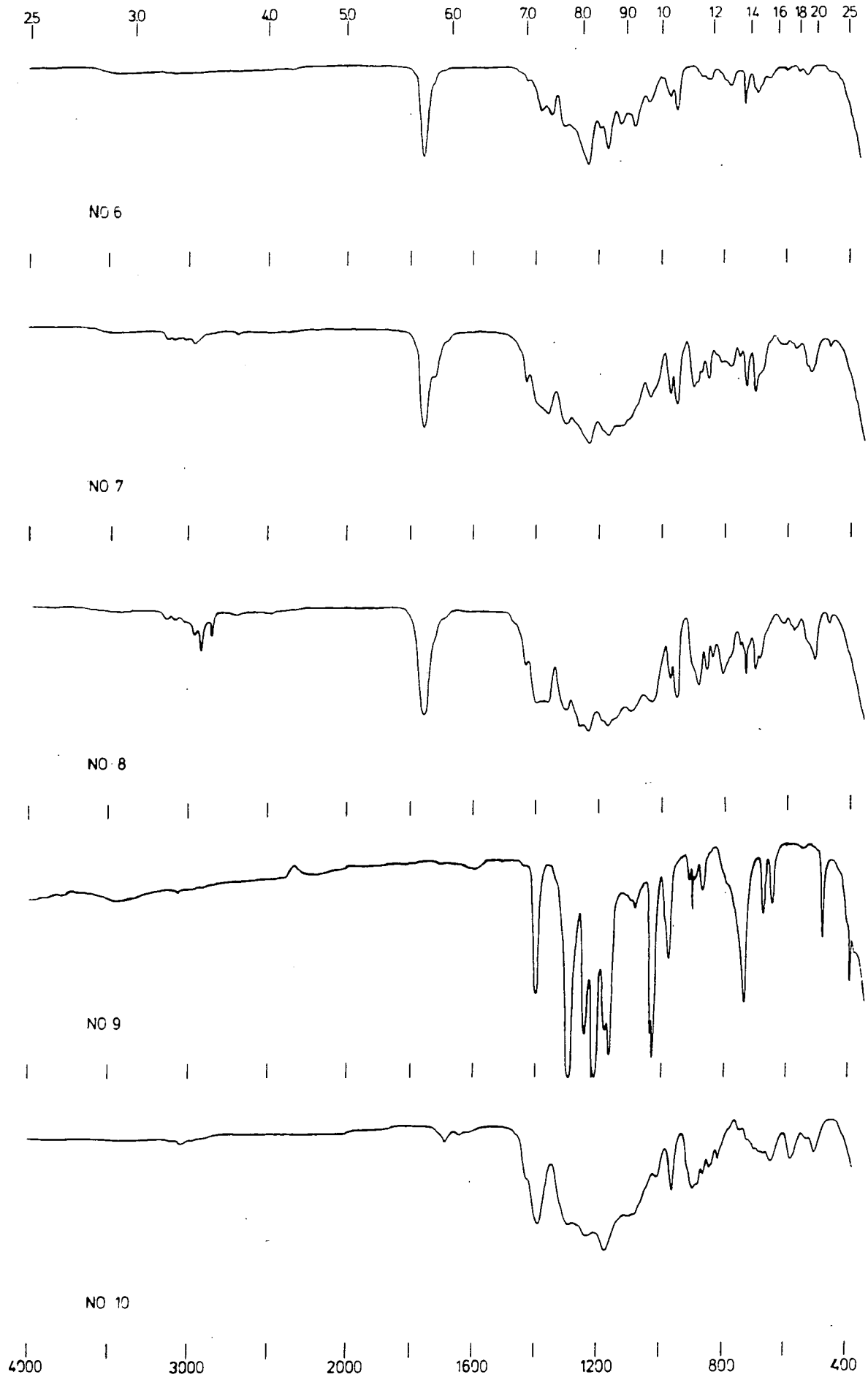
N°49 2,3-dihydroperfluorobut-2-ene (112).

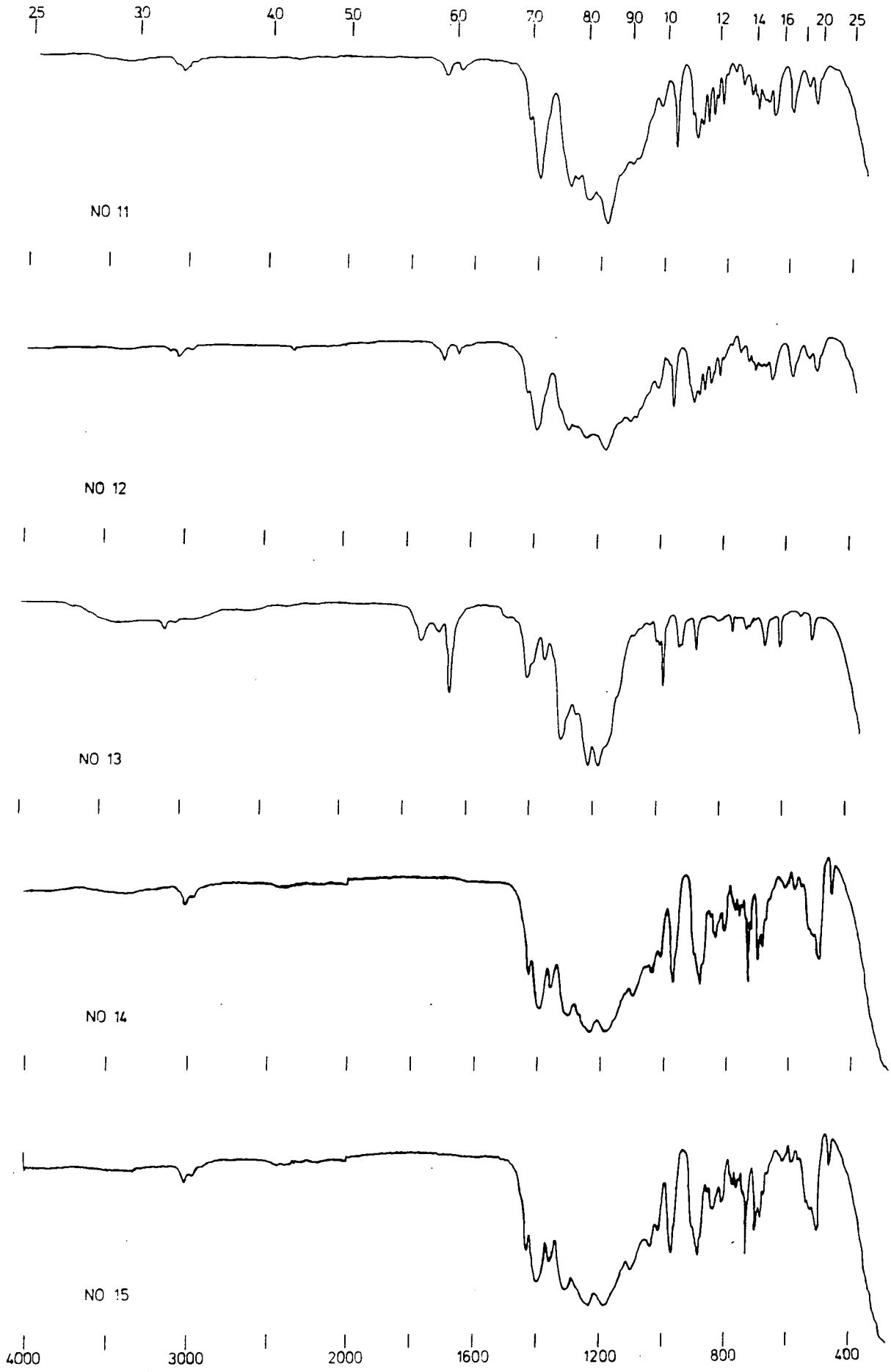
N°50 5-hydroperfluoro-3,4-bis(trifluoromethyl)hexadi-2,4-ene (110a).

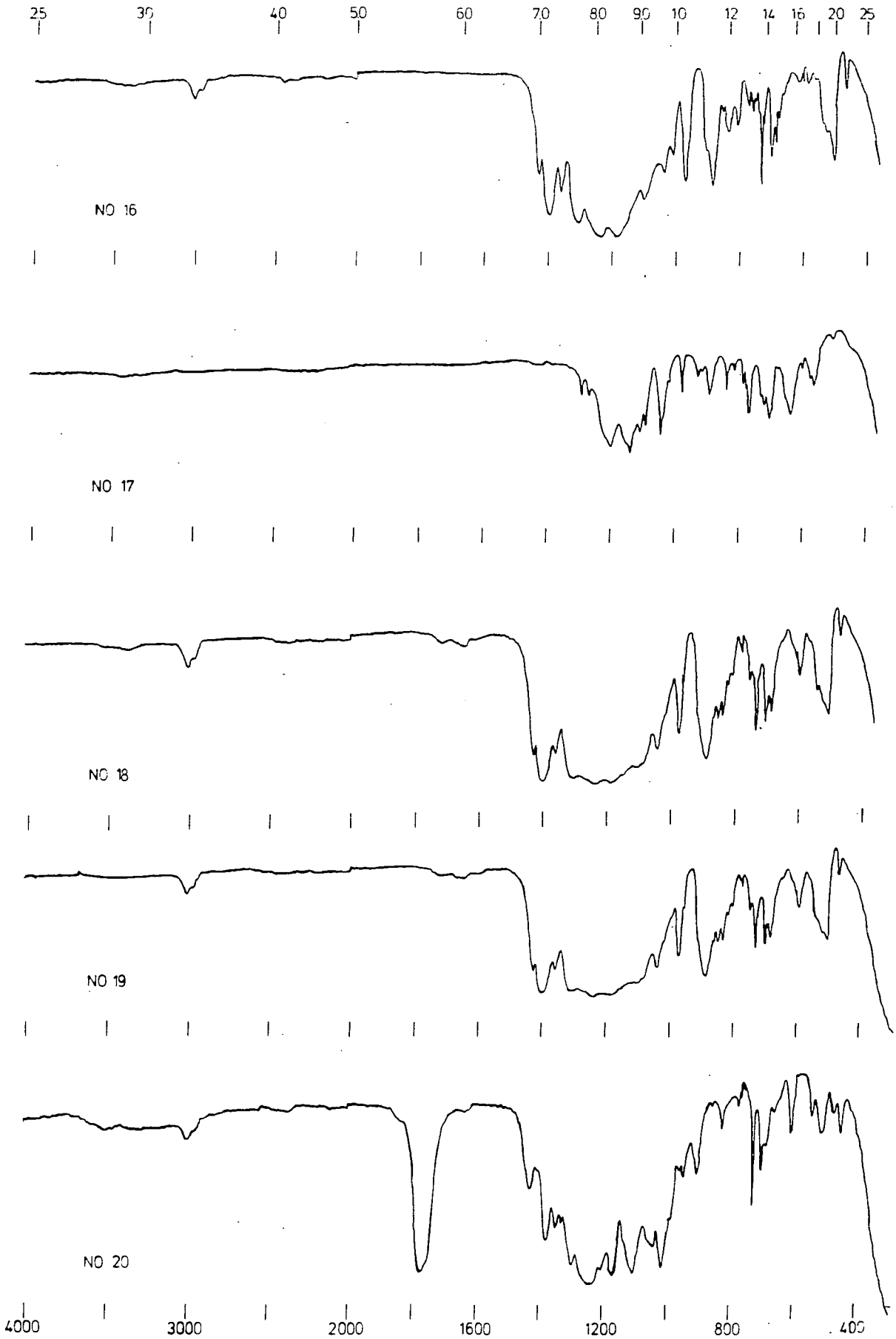
N°51 endo-5-fluoro-5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene (121a).

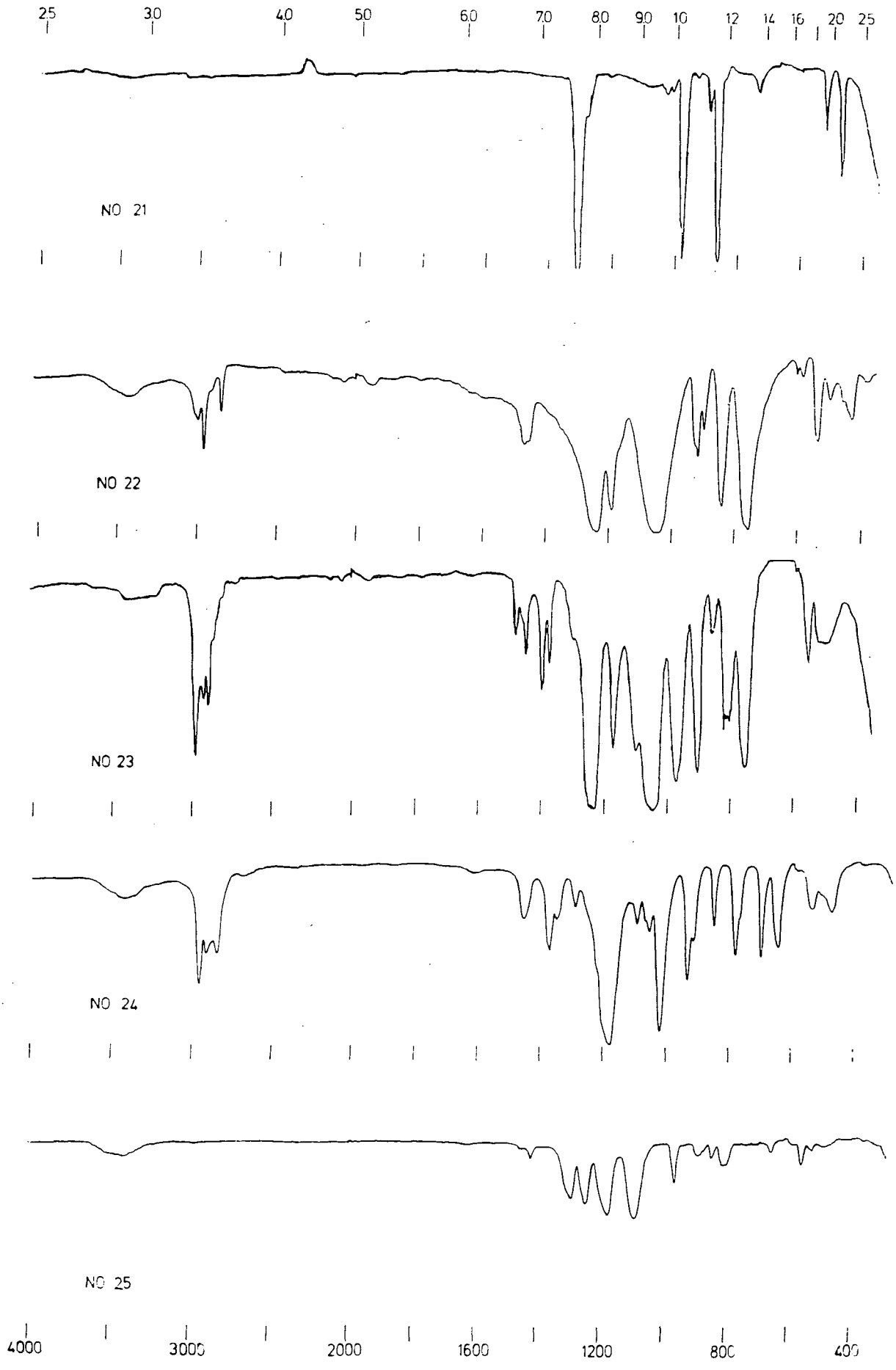
N°52 5,6-bis(trifluoromethyl)-7-oxabicyclo-[2.2.1]-hept-2-ene (131).

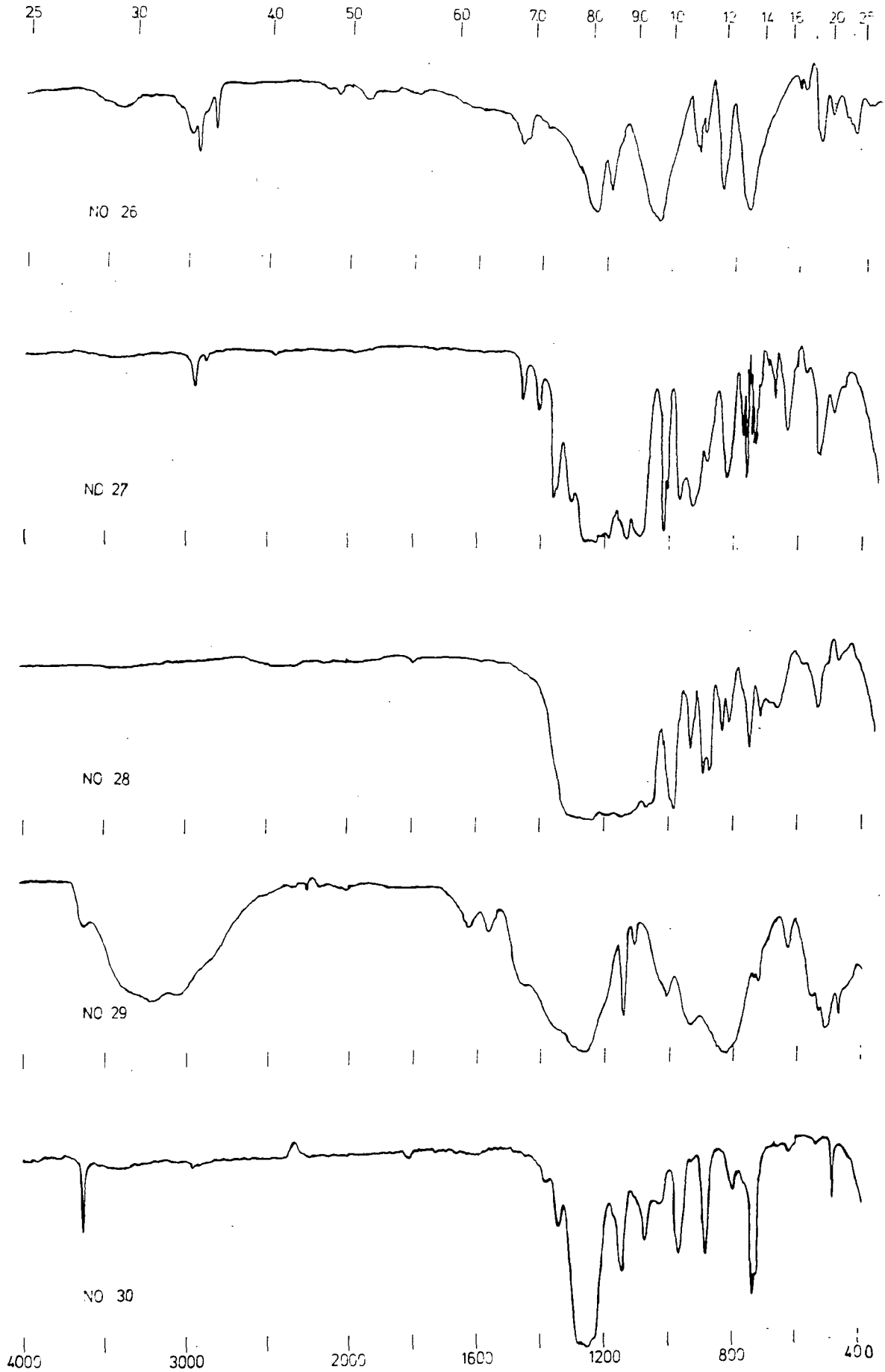

25
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
NO 1
NO 2
NO 3
NO 4
NO 5
4000
3000
2000
1600
1200
800
400

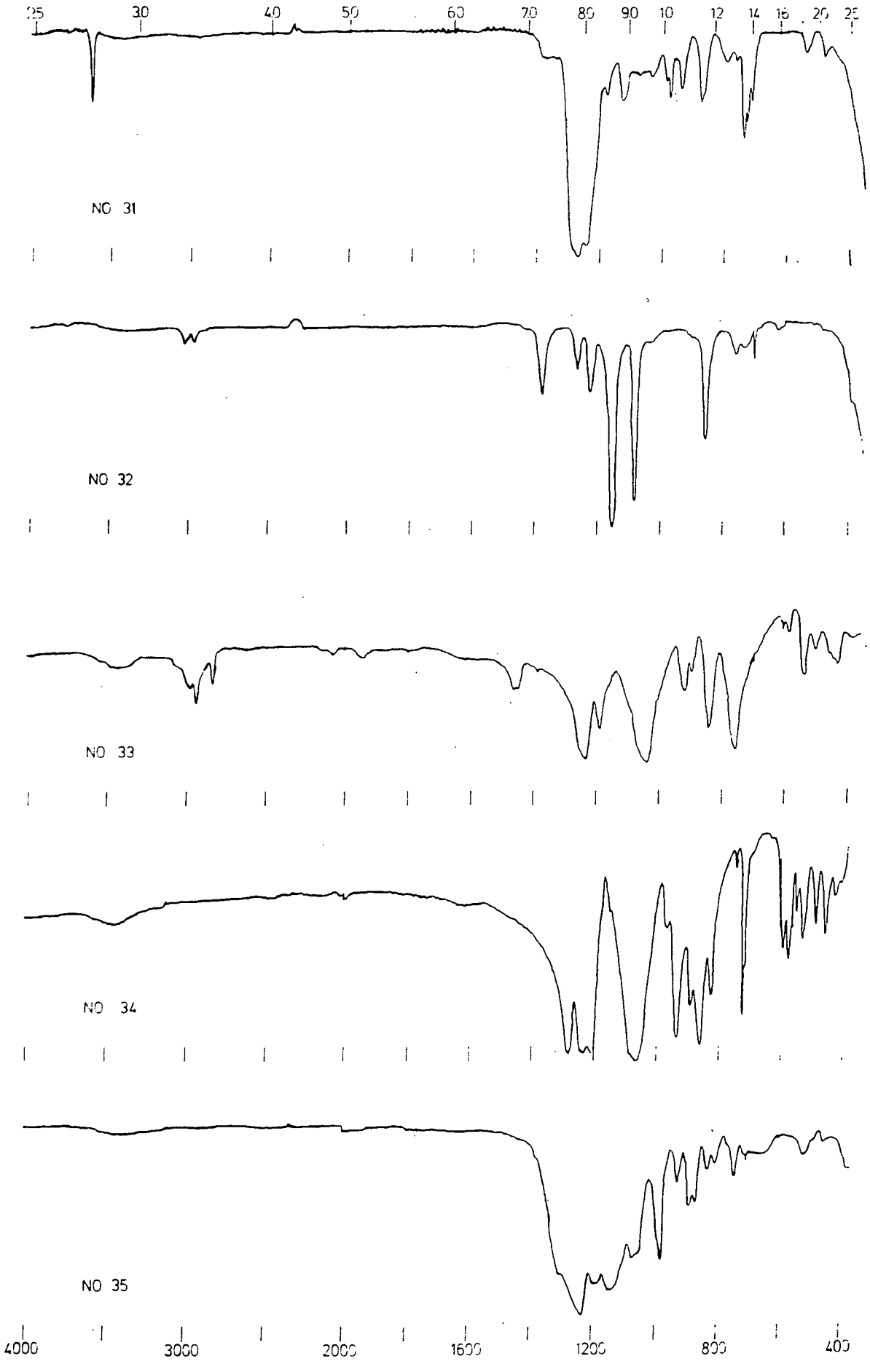

25
30
40
50
60
70
80
90
10
12
14
16
18
20
25
NO 6
NO 7
NO 8
NO 9
NO 10
4000
3000
2000
1600
1200
800
400

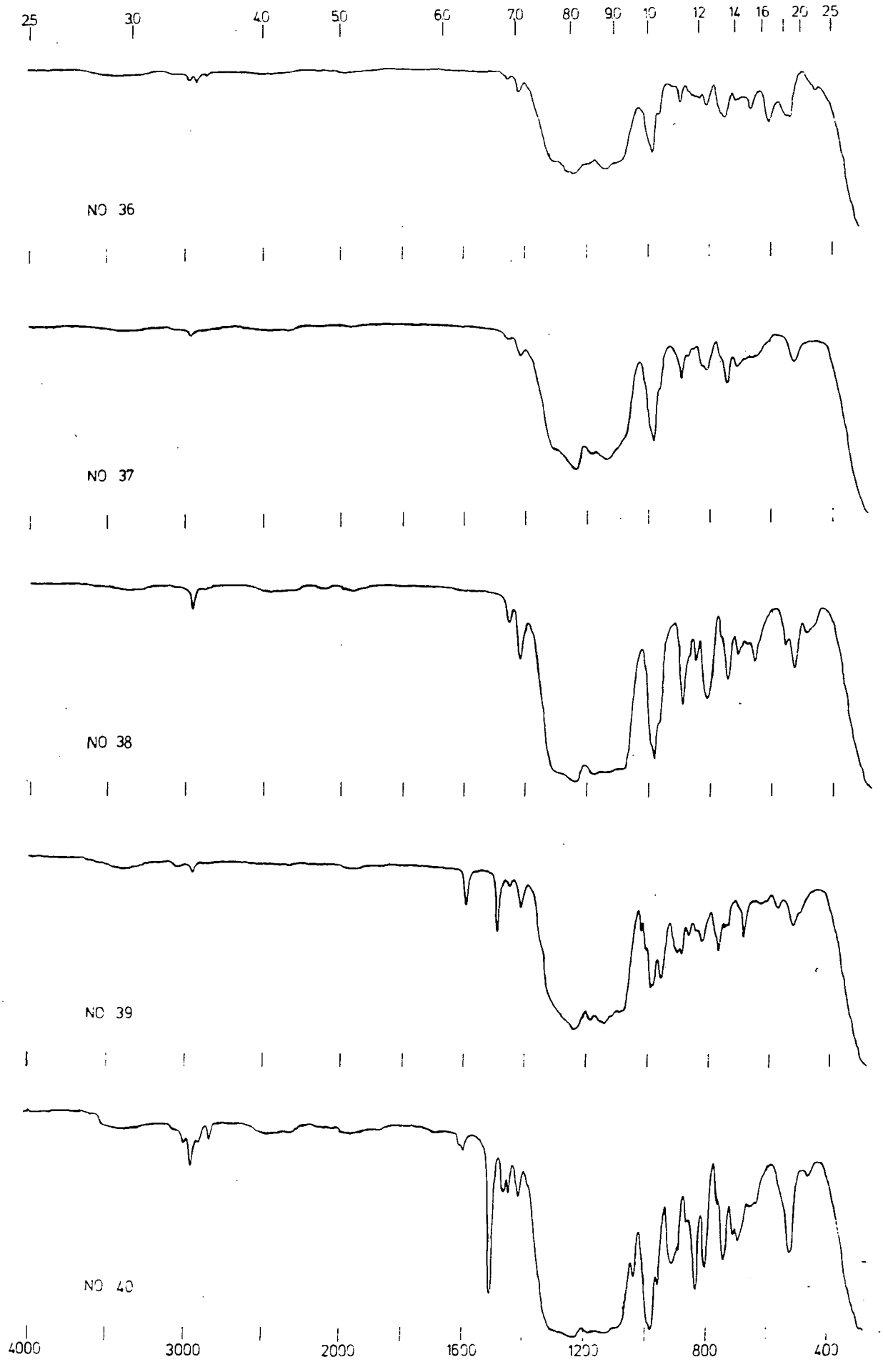

25
30
40
50
60
70
80
90
10
12
14
16
20
25
NO 11
NO 12
NO 13
NO 14
NO 15
4000
3000
2000
1600
1200
800
400

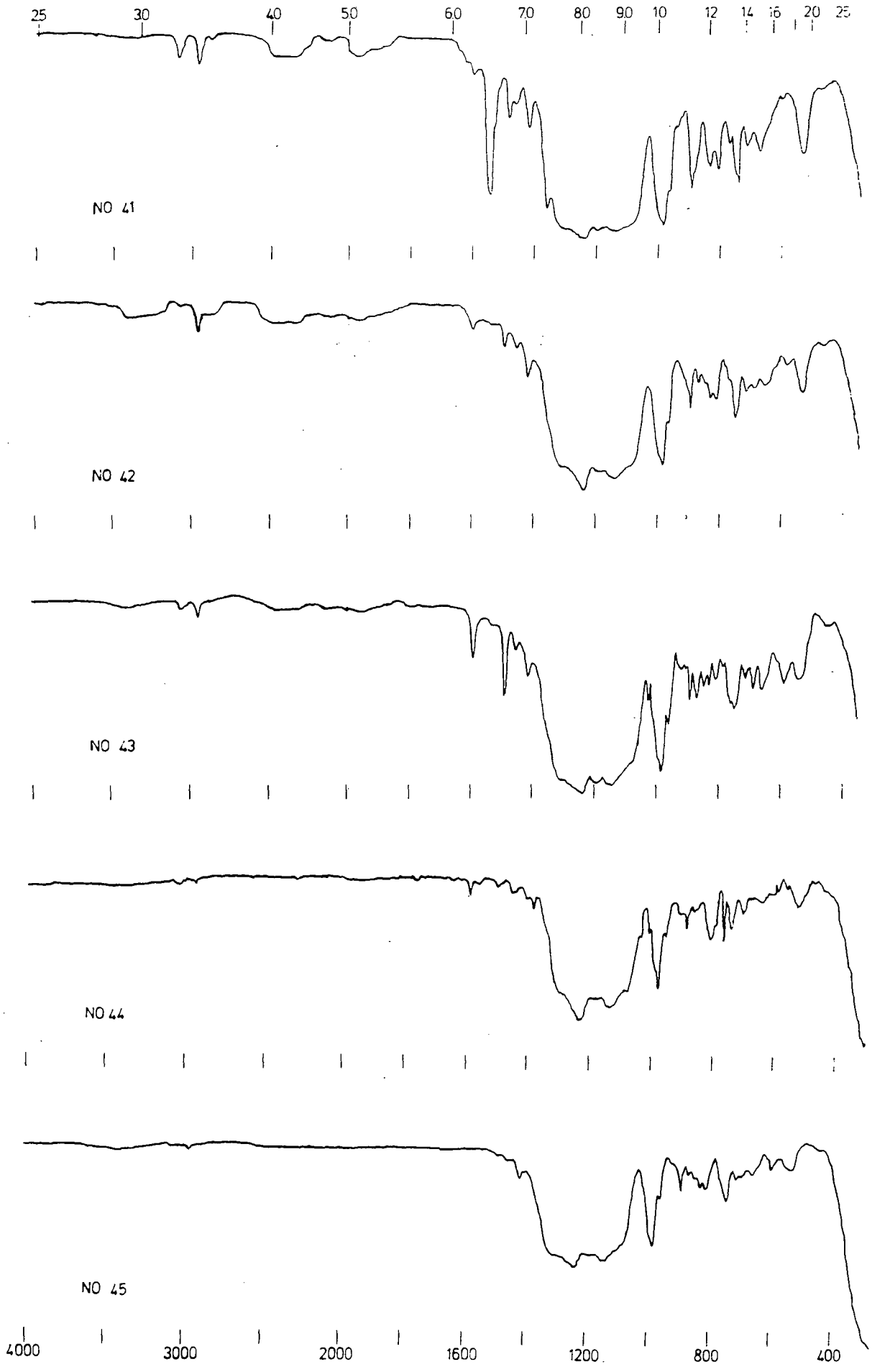

25
30
40
50
60
70
80
90
10
12
14
16
20
25
NO 16
NO 17
NO 18
NO 19
NO 20
4000
3000
2000
1600
1200
800
400

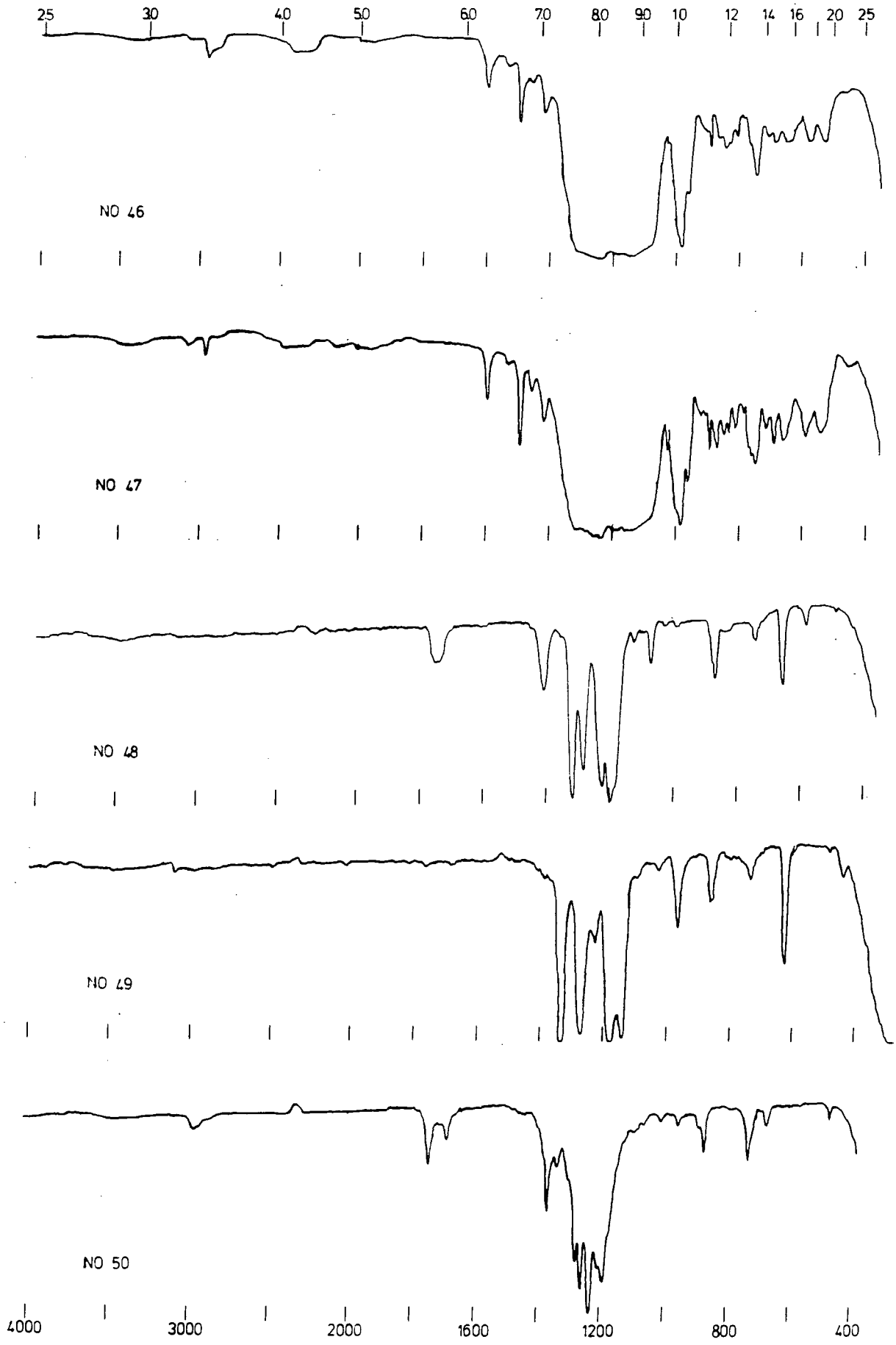

2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
NO 21
NO 22
NO 23
NO 24
NO 25
4000
3000
2000
1600
1200
800
400

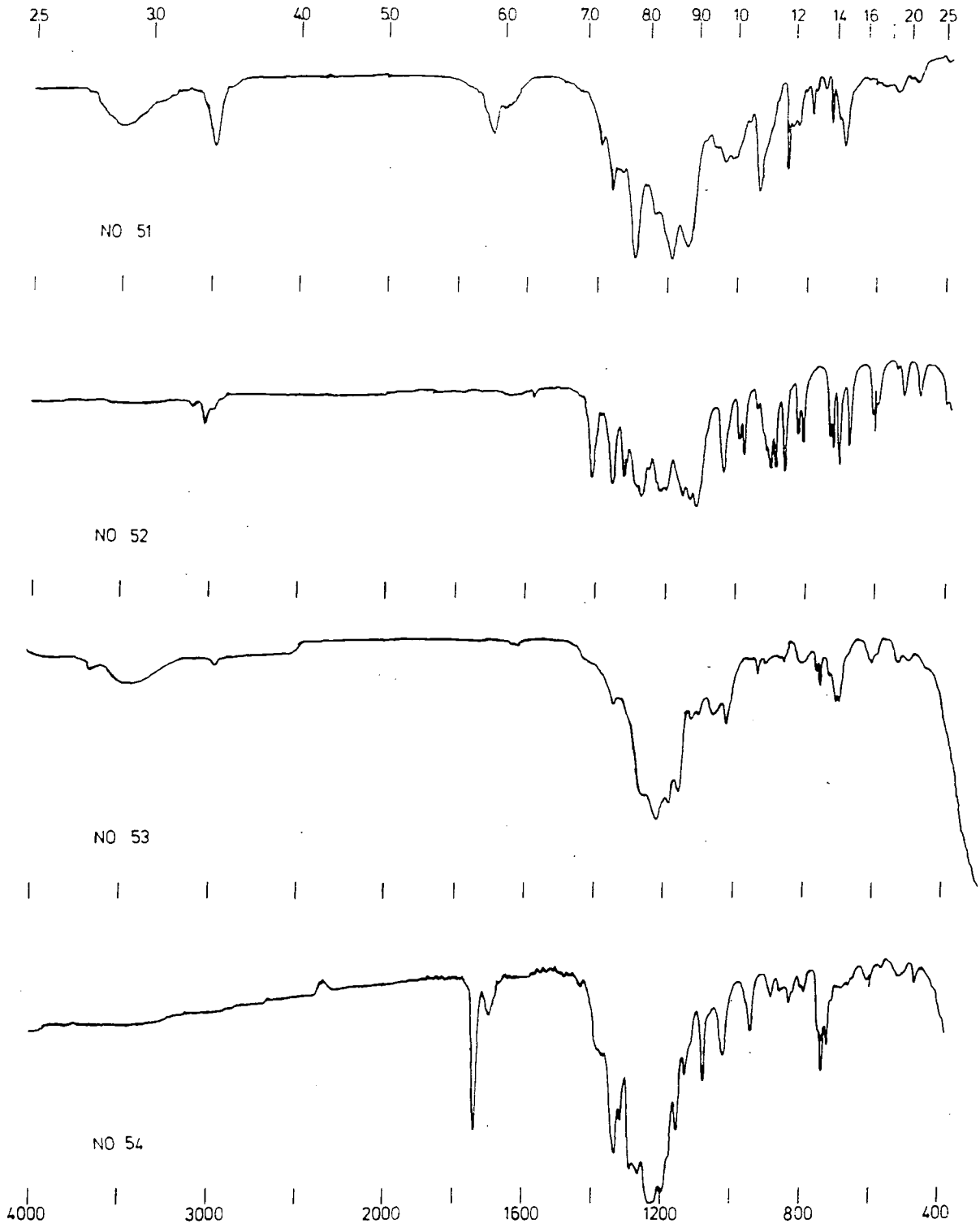

25
30
40
50
60
70
80
90
NO 26
NO 27
NO 28
NO 29
NO 30
4000
3000
2000
1600
1200
800
400


25
30
40
50
60
70
80
90
10
12
14
16
20
25
NO 31
NO 32
NO 33
NO 34
NO 35
4000
3000
2000
1600
1200
800
400


25
30
40
50
60
70
80
90
10
12
14
16
20
25
NO 36
NO 37
NO 38
NO 39
NO 40
4000
3000
2000
1600
1200
800
400


25
30
40
50
60
70
80
90
10
12
14
16
20
25
NO 41
NO 42
NO 43
NO 44
NO 45
4000
3000
2000
1600
1200
800
400


25
30
40
50
60
70
80
90
10
12
14
16
20
25
NO 46
NO 47
NO 48
NO 49
NO 50
4000
3000
2000
1600
1200
800
400


2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
20
25
NO 51
NO 52
NO 53
NO 54
4000
3000
2000
1600
1200
800
400

APPENDIX 3
MASS SPECTRA

N°1 3,3-dihydro-2-trifluoromethylperfluorobutane (6).

N°2 3,3,5,5-tetrahydro-2-trifluoromethylperfluorohexane (9).

N°3 3,3,5,5,7,7-hexahydro-2-trifluoromethylperfluorooctane (10).

N°4 3,3,5,5,7,7,9,9-octahydro-2-trifluoromethylperfluorodecane (11).

N°5 2,4,4-trihydro-5-trifluoromethylperfluorohex-1-ene (24).

N°6 2,4,4,6,6-pentahydro-7-trifluoromethylperfluorooct-1-ene (13).

N°7 3-hydro-2-trifluoromethylperfluorobut-2-ene (7).

N°8 3,5,5-trihydro-2-trifluoromethylperfluorohex-2-ene (24a).

N°9 (Z,Z) 3,5-dihydro-2-trifluoromethylperfluorohexa-2,4-di-ene (23a).

N°10 3,3,5,5,7,7,10,10,12,12,14,14-dodecahydro-2,15-bis(trifluoromethyl)perfluoro-hexadecane (19).

N°11 3,6-dihydro-2,7-bis(trifluoromethyl)perfluorooctadi-2,6-ene (22).

N°12 Hexafluorophosphazene (55).

N°13 Hexakis(methoxy)cyclotriphosphazene (63).

N°14 Hexakis(ethoxy)cyclotriphosphazene (64).

N°15 Hexakis(diethylamino)cyclotriphosphazene (66).

N°16 Hexakis(2,2,2-trifluoroethoxy)cyclotriphosphazene (50).

N°17 2,2,2-trifluoroethylmethylether (71)

N°18 Trifluoromethyltrimethylsilane (78).

N°19 Pentafluoroethyltrimethylsilane (88).

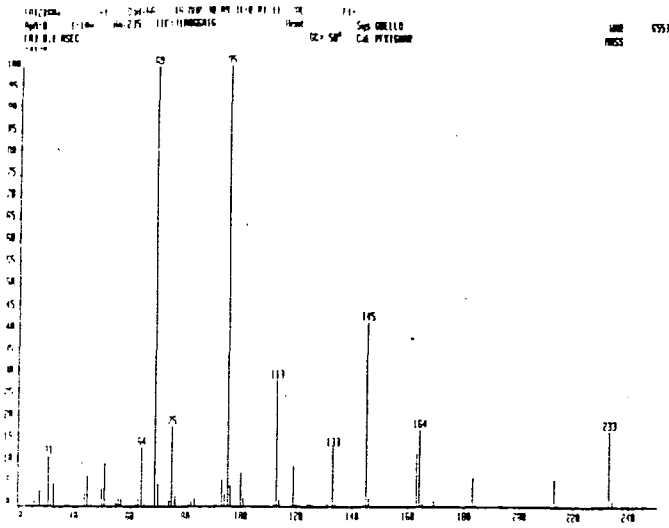
N°20 Hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)cyclotriphosphazene (93).

N°21 2-hydroperfluorobut-2-ene (109).

N°22 2,3-dihydroperfluorobut-2-ene (112).

N°23 5-hydroperfluoro-3,4-bis(trifluoromethyl)hexadi-2,4-ene (110a).

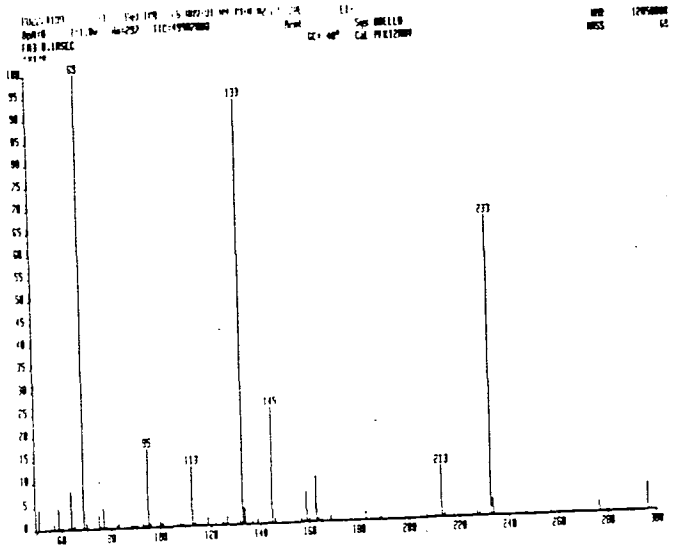
N°1 3,3-dihydro-2-trifluoromethylperfluorobutane (6).



?012#68# A1 Bgd=66 16-MAR-90 09:31+0:01:11 70E EI+
BpM=0 I=10v HM=235 TIC=318066000 Acnt: Sys:00EL..
FA3 0.1 MSEC GC= 50 Cal:PFK16H+

Mass	% Base		Mass	% Base
24.77	0.21		169.01	1.26
25.78	1.07		180.99	0.16
27.78	3.43		182.99	6.59
30.79	11.25		184.00	0.26
31.79	1.09		213.01	6.22
32.82	5.13		214.01	0.28
36.83	0.37		230.99	0.10
37.84	0.18		233.01	17.34
42.86	0.16		234.02	1.10
43.87	2.71			
44.88	6.76			
45.89	0.14			
49.89	3.96			
50.91	9.65			
54.92	0.72			
55.05	0.12			
55.93	1.60			
56.94	1.52			
61.94	0.27			
62.96	1.70			
63.97	13.48			
64.98	0.33			
69.00	100.00	0		
69.98	5.08			
71.98	0.11			
73.99	1.27			
75.00	18.26			
76.01	2.31			
81.00	0.50			
82.01	1.04			
83.02	1.74			
90.17	0.10			
90.47	0.13			
90.68	0.10			
93.00	5.99			
94.00	2.85	F		
95.02	100.00	F0		
[illegible]	[illegible]			
100.00	7.25			
101.01	1.33			
106.01	0.22			
112.00	2.30			
113.00	28.69			
114.01	1.33			
118.97	9.13			
119.99	0.23			
123.97	0.65			
124.98	0.43			
126.01	0.10			
130.98	0.78			
131.97	0.21			
132.99	13.26			
134.00	0.32			
143.02	0.36			
144.02	0.85			
145.02	42.17			
146.03	1.76			
163.01	12.15			
164.02	17.73			
165.03	0.68			

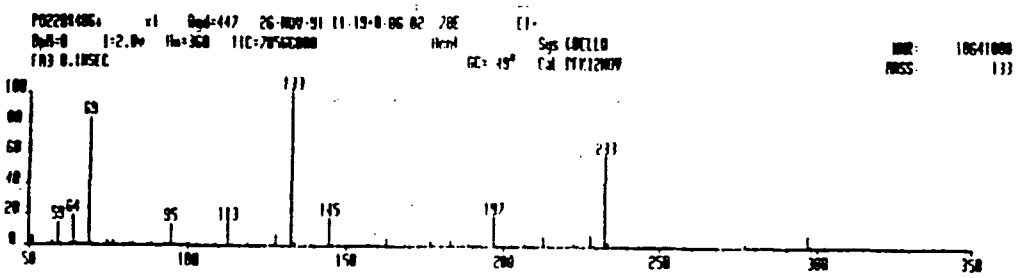
N°2 3,3,5,5-tetrahydro-2-trifluoromethylperfluorohexane (9).



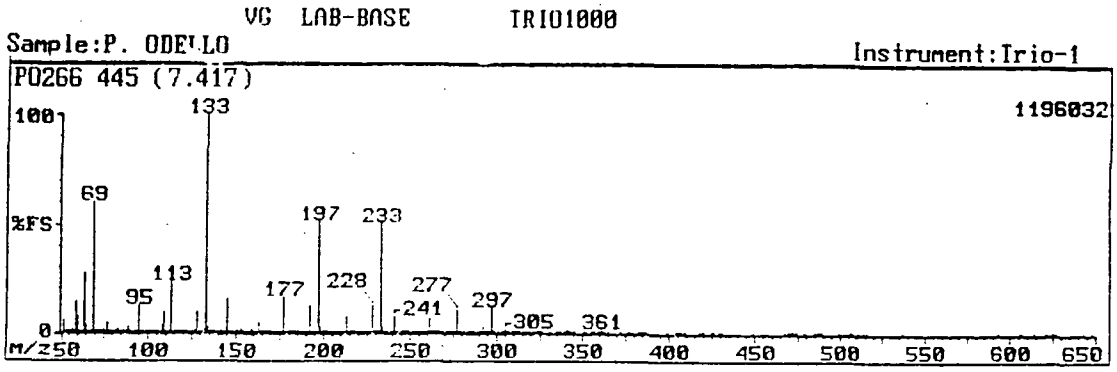
20227#198★ Bgd=180 26-NOV-91 09:39+0:02.27
BpM=0 I=1.8v mm=297 TIC=49902000
FA3 0.1MSEC

Mass	% Base
49.98	0.50
50.98	4.25
56.99	1.07
59.01	4.41
62.98	0.41
63.99	8.00
64.99	0.52
68.96	100.00
69.97	1.11
74.97	2.78
75.98	0.49
76.98	4.25
81.96	0.58
82.97	1.05
87.97	0.48
88.97	0.46
92.95	1.15
93.95	0.57
94.96	16.98
95.97	0.83
99.94	1.06
100.96	0.73
107.96	0.66
112.95	12.84
113.95	0.56
118.93	1.63
124.95	0.43
126.95	1.79
131.93	0.87
132.93	93.39
133.94	3.62
138.94	0.84
143.89	0.42
144.92	25.21
145.92	0.96
156.92	0.89
158.93	6.37
159.94	0.46
162.90	9.72
163.90	0.66
168.89	1.04
182.89	1.69
188.91	0.41
206.89	0.58
212.87	11.01
213.87	0.57
226.88	0.85
227.88	0.55
232.86	65.82
233.86	3.45
256.85	0.78
276.84	2.18
296.83	5.77
297.85	0.32

N°3 3,3,5,5,7,7-hexahydro-2-trifluoromethylperfluorooctane (10).

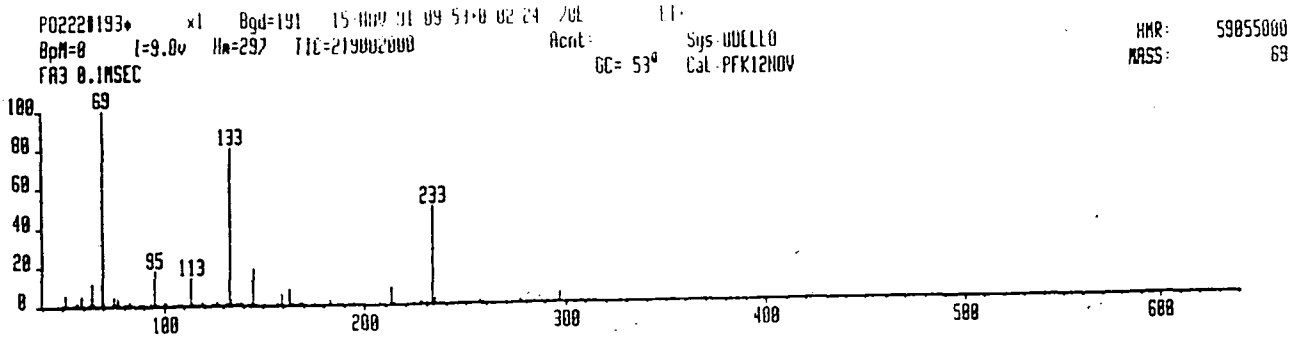


N°4 3,3,5,5,7,7,9,9-octahydro-2-trifluoromethylperfluorodecane (12).



50	0.62	104	0.06	159	1.63	213	7.36
51	6.08	105	0.01	160	0.29	214	0.37
52	0.15	106	0.10	161	0.05	215	0.09
53	0.19	107	0.22	162	0.09	216	0.02
54	0.04	108	3.64	163	4.88	217	0.75
55	0.08	109	9.93	164	0.33	218	0.07
56	0.22	110	0.44	165	0.25	219	0.06
57	2.33	111	0.05	166	0.02	220	0.01
58	0.44	112	0.42	167	0.04	221	0.24
59	14.64	113	32.95	168	0.05	222	0.02
60	7.71	114	1.09	169	0.68	223	0.55
61	0.27	115	0.32	170	0.08	224	0.05
62	0.08	116	0.02	171	0.19	225	0.04
63	1.01	117	0.04	172	0.58	226	0.02
64	36.71	118	0.03	173	1.06	227	0.73
65	3.96	119	0.90	174	0.08	228	12.24
66	0.10	120	0.09	175	0.32	229	0.79
67	0.05	121	0.41	176	0.31	230	0.03
68	1.16	122	0.05	177	16.67	231	0.08
69	50.27	123	0.25	178	0.94	232	0.79
70	0.62	124	0.11	179	0.06	233	50.68
71	0.18	125	0.23	180	0.01	234	2.53
72	0.08	126	0.43	181	0.14	235	0.08
73	0.06	127	2.16	182	0.04	236	0.07
74	0.10	128	9.67	183	0.83	237	0.07
75	1.69	129	0.96	184	0.05	238	0.05
76	0.40	130	0.05	185	0.01	239	0.12
77	4.67	131	0.23	186	0.01	240	7.53
78	0.33	132	1.69	187	0.09	241	0.55
79	0.09	133	100.00	188	0.03	242	0.03
80	0.02	134	3.13	189	1.01	243	0.05
81	0.15	135	0.13	190	0.09	244	0.01
82	0.41	136	0.03	191	0.32	245	0.30
83	1.73	137	0.39	192	12.41	246	0.03
84	0.19	138	0.06	193	0.88	247	0.01
85	0.13	139	0.94	194	0.10	248	0.04
86	0.03	140	0.13	195	0.50	249	0.02
87	0.08	141	0.10	196	0.65	250	0.15
88	0.64	142	0.03	197	51.03	251	0.02
89	2.93	143	0.09	198	2.55	252	0.03
90	0.53	144	0.38	199	0.08	253	1.08
91	0.09	145	15.58	200	0.03	254	0.60
92	0.02	146	0.67	201	0.10	255	0.03
93	0.53	147	0.30	202	0.01	256	0.60
94	0.58	148	0.02	203	0.20	257	0.19
95	12.50	149	0.18	204	0.13	258	7.02
96	0.44	150	0.25	205	0.03	259	0.53
97	0.06	151	0.09	206	0.01	260	0.03
98	0.05	152	2.08	207	0.61	261	0.01
99	0.09	153	0.15	208	0.08	262	0.04
100	0.57	154	0.03	209	0.54	263	0.01
101	0.94	155	0.04	210	0.05	264	0.05
102	0.23	156	1.06	211	0.04	265	0.01
103	0.39	157	0.26	212	0.11	266	0.02

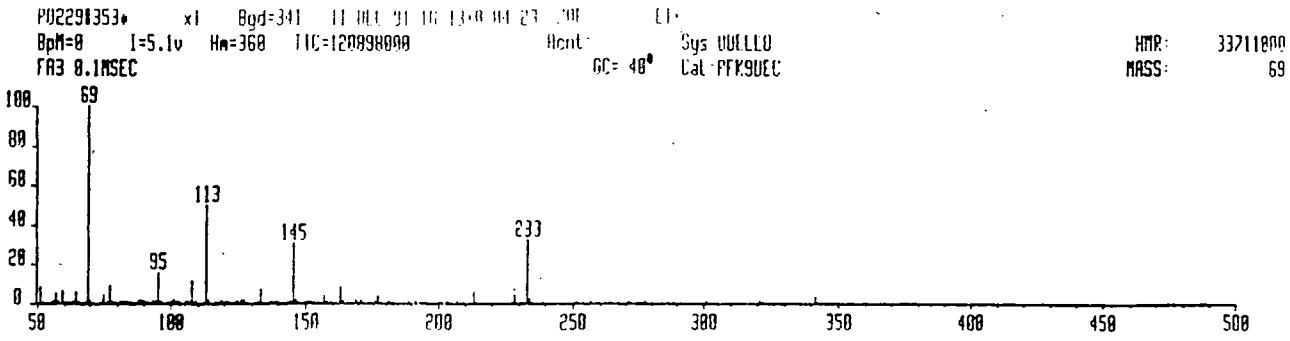
N°5 2,4,4-trihydro-5-trifluoromethylperfluorohex-1-ene (24).



P0222#193◆ ×1 Bgd=191 15-NOV-91 09:53+0.02.24 70E EI+
BpM=0 I=9.0v Hm=297 TIC=219082000 Acnt. Sys:0EE
FA3 0.1MSEC GC= 53 Cal:PFK

Mass	% Base	
49.98	0.54	
50.99	4.89	
55.99	0.32	
56.99	1.39	
59.01	4.56	
62.99	0.43	
63.99	11.07	
65.00	0.47	
68.97	100.00	
69.98	1.04	
74.97	3.61	
75.98	0.61	
76.99	3.23	
81.97	0.87	
82.98	1.01	
87.97	0.55	
88.98	0.64	
92.95	1.30	
93.96	0.68	
94.97	17.44	
95.97	0.52	
99.95	1.15	
100.96	0.58	
107.98	0.55	
112.96	13.69	
113.96	0.45	
118.95	1.60	
126.96	1.42	
131.90	0.87	F
132.94	79.35	F
133.95	2.67	
136.94	0.38	
138.95	0.66	
143.93	0.35	
144.94	17.93	
145.94	0.87	
156.93	0.64	
158.94	5.31	
162.92	7.60	
163.92	0.52	
168.91	0.71	
182.94	1.76	
206.89	0.51	
212.86	8.24	
213.89	0.40	
226.89	0.52	
227.90	0.37	
232.88	49.53	
233.89	2.65	
256.87	0.47	
276.86	1.30	
296.85	4.50	

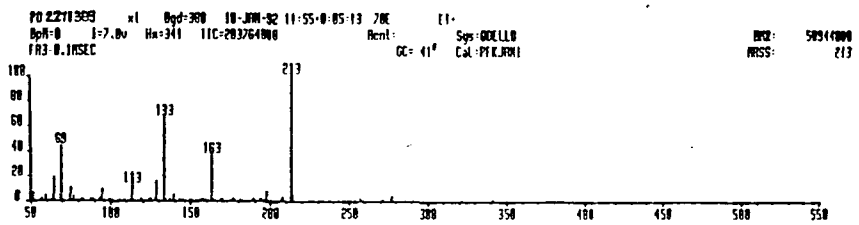
N°6 2,4,4,6,6-pentahydro-7-trifluoromethylperfluorooct-1-ene (13).



P0229#353+ x1 Bgd=341 11-DEC-91 16:13+0:04:23 70E EI+ 5
BpM=0 I=5.1v Hm=360 TIC=120898000 Acnt: Sys:ODELLO
FA3 0.1MSEC GC= 40 Cal:PFK9DEC

Mass	% Base	Mass	% Base
49.98	0.54	189.01	0.57
50.98	7.98	191.02	0.54
55.99	0.54	203.02	0.68
57.00	4.22	207.00	0.52
58.00	0.37	212.99	5.32
59.01	6.08	227.02	0.34
63.00	0.52	228.02	3.66
63.99	5.32	232.99	32.13
65.00	0.65	234.00	1.83
68.97	100.00	251.02	0.61
69.98	1.52	257.01	0.39
74.98	3.87	271.03	0.76
75.99	0.51	277.02	0.46
77.00	3.58	301.05	0.34
78.00	0.40	321.05	1.52
80.98	0.38	341.06	2.78
81.98	0.41	360.07	0.30
83.00	0.72		
87.99	1.57		
89.00	1.52		
90.02	0.33		
92.98	0.96		
93.98	0.79		
94.99	15.19		
96.00	0.47		
99.99	0.76		
101.00	1.93		
102.01	0.52		
103.02	0.41		
105.99	0.36		
107.00	0.53		
108.00	10.63		
109.01	0.62		
112.98	50.31		
113.98	1.60		
118.98	1.52		
121.01	0.67		
124.99	0.35		
125.99	1.21		
126.99	3.08		
130.99	0.31		
132.00	0.56		
132.99	6.10		
136.98	0.81		
139.00	0.95		
143.98	0.36		
144.99	30.38		
145.99	1.17		
151.00	0.91		
152.01	0.37		
156.99	3.38		
158.00	0.76		
162.98	7.75		
163.99	0.57		
168.97	1.52		
170.99	1.07		
175.99	0.50		
177.00	3.51		
180.99	0.35		
183.01	0.32		

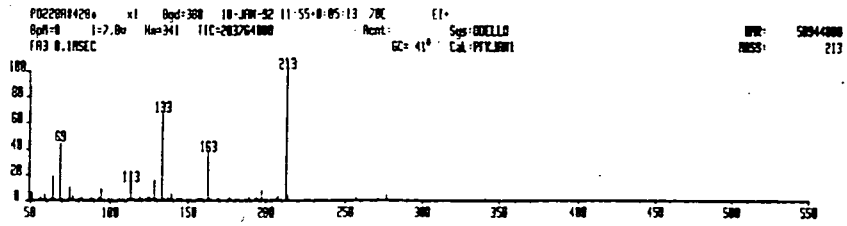
N°7 3-hydro-2-trifluoromethylperfluorobut-2-ene (7).



P0227#389* x1 Bgd=187 21-JAN-92 14:36+0:04:49 70E EI+ 4
BpM=0 I=242mv Hm=276 TIC=5960000 EN Acnt: Sys:ODELLC
FA3 0.1MSEC GC= 40 Cal:PFK21JA

Mass	% Base
51.00	4.90
57.02	1.26
59.03	3.77
64.01	17.54
68.99	40.85
75.00	13.07
77.02	2.89
82.98	0.88
89.03	1.01
93.00	1.26
95.00	8.55
113.01	16.09
119.01	2.26
125.00	1.76
128.02	16.09
133.00	65.05
134.00	2.39
139.02	5.03
142.98	1.07
162.99	38.91
163.99	1.57
168.97	1.01
169.03	0.88
176.99	2.01
189.01	1.63
193.98	1.26
197.01	5.72
207.00	2.01
208.01	2.33
212.98	100.00
213.99	6.29
257.00	2.01
277.00	3.27

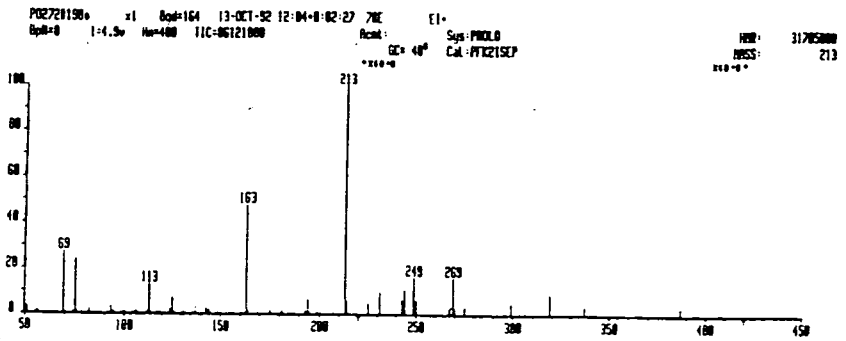
N°8 3,5,5-trihydro-2-trifluoromethylperfluorohex-2-ene (24a).



P0228A#420* x1 Bgd=388 10-JAN-92 11:55+0:05:13 70E EI+ 3.
BpM=0 I=7.8v Hm=341 TIC=203764000 Acnt: Sys:ODELLO
FA3 0.1MSEC GC= 41 Cal:PFKJAN1

Mass	% Base		Mass	% Base
50.00	0.51		256.99	1.61
51.00	5.67		271.03	0.50
56.00	0.58		277.00	4.02
57.01	1.66		341.06	0.50
59.02	4.02			
63.00	0.51			
64.00	18.23			
65.01	0.66			
68.97	43.72			
70.00	0.70			
73.99	0.33			
74.99	9.85			
76.00	0.53			
77.01	3.22			
81.99	1.01			
83.00	1.14			
88.00	1.01			
89.01	1.05			
92.98	2.01			
93.99	0.64			
95.00	8.46			
99.00	0.69			
101.01	0.56			
106.00	0.50			
108.02	0.62			
109.02	0.50			
112.00	0.50			
113.00	12.25			
114.01	0.50			
119.00	2.06			
123.98	1.01			
124.96	2.04			
127.01	0.50			
128.01	14.98			
129.02	0.58			
132.97	66.33			
133.99	1.60			
137.00	1.01			
139.01	4.52			
142.98	1.51			
143.99	0.71			
145.00	0.59			
157.00	1.01			
158.01	1.01			
159.01	0.50			
162.95	35.60	F		
163.96	1.51	F		
169.00	1.10			
176.99	1.76			
180.96	0.69			
187.00	0.31			
189.01	1.71			
192.97	1.01			
193.98	1.60			
196.99	6.84			
198.01	0.33			
206.99	2.06			
207.99	3.02			
212.93	100.00	F		
213.98	4.59	F		

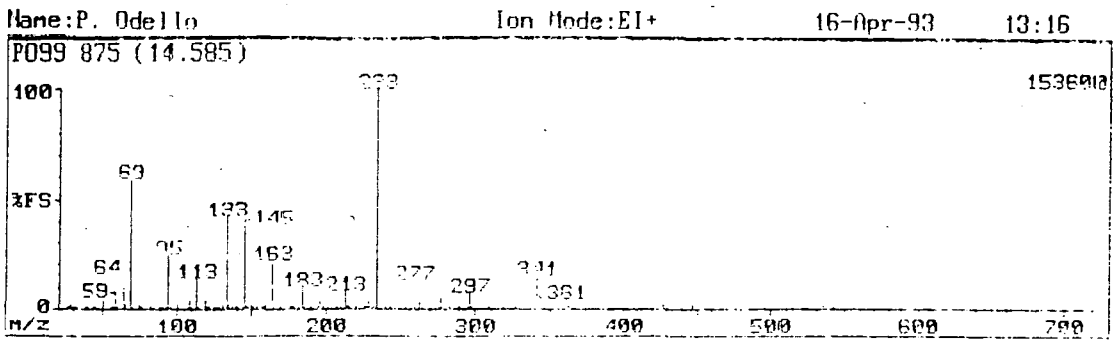
N°9 (Z,Z) 3,5-dihydro-2-trifluoromethylperfluorohex-2,4-di-ene (23a).



P0272#198# x1 Bgd=164 13-OCT-92 12:04+0:02:27 70E EI+
BpM=0 I=4.9v Hm=408 TIC=86121000 Acnt: Sys:PA0LO
GC= 40 Cal:PFK21SE

Mass	% Base
49.96	0.52
50.97	2.91
55.97	1.24
68.95	26.66
73.96	0.72
74.96	23.47
75.97	0.73
81.96	1.72
92.96	3.14
93.97	1.07
98.97	0.31
99.96	0.60
104.96	0.34
105.97	1.40
111.96	0.80
112.96	12.77
113.97	0.44
116.96	0.33
118.97	0.34
123.96	2.10
124.95	6.98
136.97	0.68
142.96	2.66
143.97	1.87
149.98	0.39
154.97	0.37
160.98	0.31
162.98	47.57
163.99	2.20
174.98	1.40
180.98	0.94
192.95	1.31
193.95	6.23
194.97	0.36
198.98	0.45
199.99	0.35
212.99	100.00
213.99	5.95
249.00	0.40
269.03	0.40

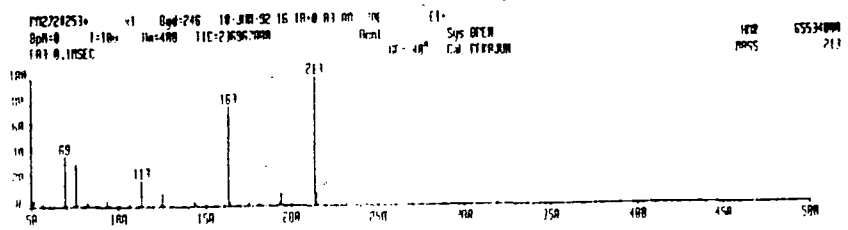
N°10 3,3,5,5,7,7,10,10,12,12,14,14-dodecahydro-2,15-bis(trifluoromethyl)perfluoro-hexadecane (19).



P099 875 (14.585) 153600

Mass	Rel Int	Mass	Rel Int	Mass	Rel Int	Mass	Rel Int
26	0.14	108	0.79	175	1.67	259	0.32
27	0.23	109	3.79	176	0.29	263	3.13
28	1.54	110	0.23	177	0.85	264	0.40
31	1.01	113	13.33	178	0.26	273	0.54
32	0.68	114	0.96	181	0.83	275	0.24
33	0.61	115	0.97	183	10.00	277	4.38
39	1.01	119	3.62	184	0.49	278	0.35
40	0.24	120	0.83	189	1.42	283	0.91
44	0.70	121	0.29	194	0.54	289	0.41
45	1.04	125	0.35	195	2.88	295	0.47
46	0.21	126	0.48	197	1.26	297	7.25
50	0.55	127	0.69	201	0.25	298	0.56
51	3.50	128	0.29	203	0.19	309	0.32
56	0.20	131	1.56	207	0.99	319	0.29
57	0.79	133	41.33	209	0.66	321	0.21
59	4.88	134	1.51	213	7.67	327	0.26
60	0.34	137	0.33	214	0.51	339	0.29
64	7.46	139	1.33	215	0.48	341	2.92
65	1.55	140	0.16	219	0.22	342	0.31
69	59.33	144	0.73	225	0.43	361	3.62
70	0.79	145	38.00	227	1.10	362	0.35
75	1.49	146	1.74	228	2.92	363	0.17
76	0.24	147	0.25	229	0.21	407	0.35
77	1.16	150	1.72	231	0.19	427	1.77
83	0.50	151	1.03	233	100.00	447	1.72
89	1.15	153	0.22	234	5.21	473	0.54
90	0.44	157	1.01	239	0.21	477	0.71
91	0.19	158	0.32	243	0.38	541	0.74
93	0.37	159	2.10	245	0.68	556	0.20
95	23.83	163	9.75	247	1.81	605	0.61
96	0.94	164	0.67	251	0.21		
100	1.86	165	0.80	253	0.32		
101	0.79	169	1.43	257	0.85		

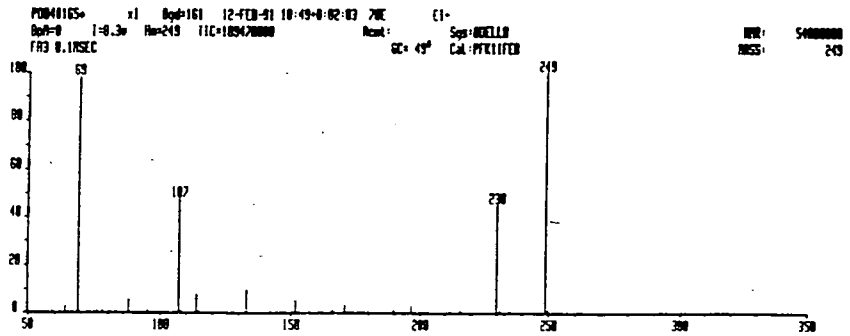
N°11 3,6-dihydro-2,7-bis(trifluoromethyl)perfluorooctadi-2,6-ene (22).



P0272#253# x1 Bgd=246 10-JUN-92 16:18+0:03:08 70E EI+
BpM=0 I=10v Hm=408 TIC=236967000 Acnt. Sys:OPEN
FA3 0.1MSEC GC= 40 Cal:PFK8JUN

Mass	% Base	
69.10	38.67	
75.12	32.03	
113.19	19.92	
125.20	9.78	F
163.25	77.35	
194.29	9.04	
213.37	100.00	FO
214.34	9.38	F
407.61	0.39	
408.59	0.03	

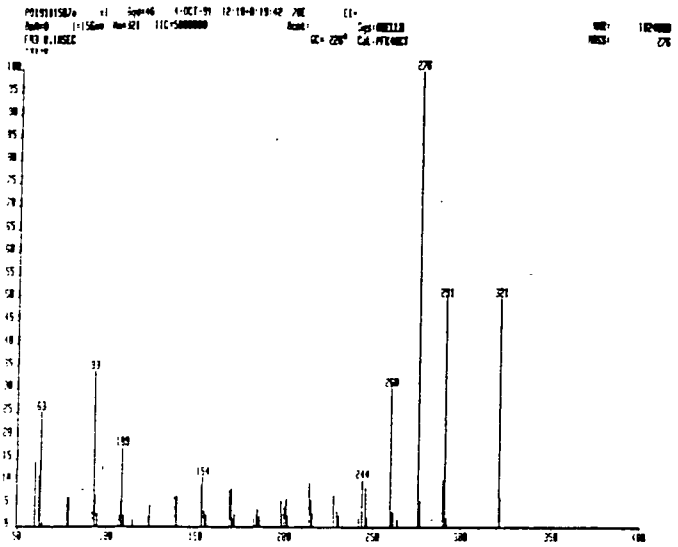
N°12 Hexafluorophosphazene (55).



P084#165* x1 Bgd=161 12-FEB-91 10:49+0:02:03 70E EI+
BpM=0 I=8.3v Hm=249 TIC=189470000 Acnt: Sys:ODELL
FA3 0.1MSEC GC= 49 Cal:PFK11

Mass	% Base
49.90	17.71
58.91	0.47
63.90	2.37
68.89	97.95
77.88	0.73
87.87	5.21
94.84	0.72
106.85	47.39
113.82	7.10
114.85	0.47
132.80	9.24
151.77	4.79
165.80	0.55
170.79	2.84
189.78	0.54
196.76	2.37
215.76	0.67
229.76	44.75
230.76	0.55
234.77	0.47
248.76	100.00
249.75	1.12

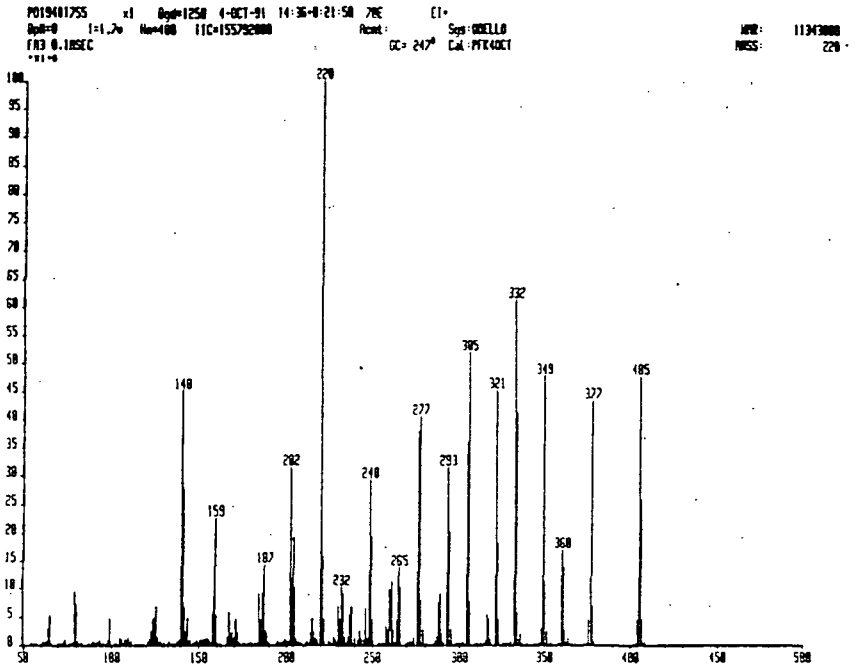
N°13 Hexakis(methoxy)cyclotriphosphazene (63).



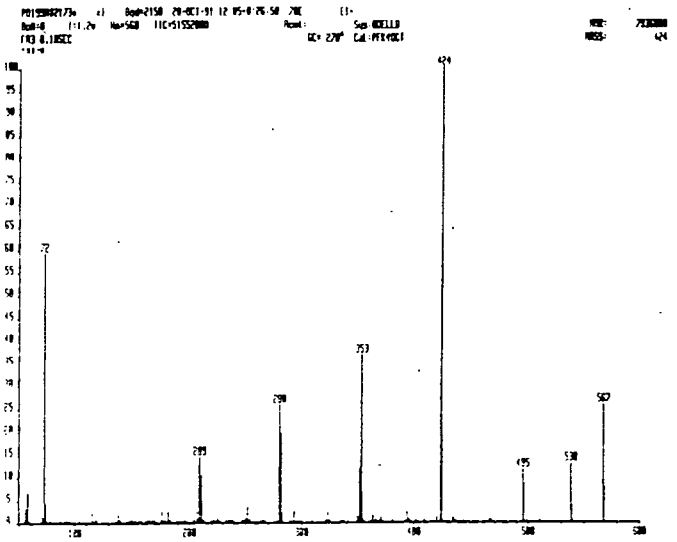
P0191#1587* x1 Bgd=46 4-OCT-91 12:10+0:19:42 70E EI+ 1.:
BpM=0 I=156mv mm=321 TIC=5800000 Acnt: Sys:ODELLO
FA3 0.1MSEC GC= 226 Cal:PFK40CT

Mass	% Base
59.98	14.36
61.98	11.33
62.98	25.00
63.98	1.17
77.98	6.35
78.97	6.45
91.95	3.42
92.99	33.98
93.98	6.93
94.97	2.73
106.96	2.34
107.97	5.86
108.97	17.48
109.93	2.54
109.99	1.86
114.93	1.37
123.94	2.25
124.93	4.69
137.97	6.64
138.95	6.54
139.95	6.54
152.96	9.28
153.94	11.13
154.93	3.32
155.91	2.64
168.93	8.11
169.95	8.40
170.91	2.05
171.94	2.64
182.95	2.05
183.91	2.64
184.96	4.00
185.98	2.15
197.89	5.66
198.90	2.73
199.94	4.30
200.95	6.15
201.90	2.34
213.88	9.67
214.92	6.05
215.90	2.93
227.87	5.93
229.90	3.42
230.87	2.44
242.27	1.36
243.88	10.45
245.90	3.59
246.86	2.05
259.89	30.37
260.93	3.32
261.88	3.13
263.89	1.56
275.90	100.00
276.90	5.76
289.92	10.25
290.91	50.00
291.92	1.36
320.93	50.00
321.93	6.25

N°14 Hexakis(ethoxy)cyclotriphosphazene (64).



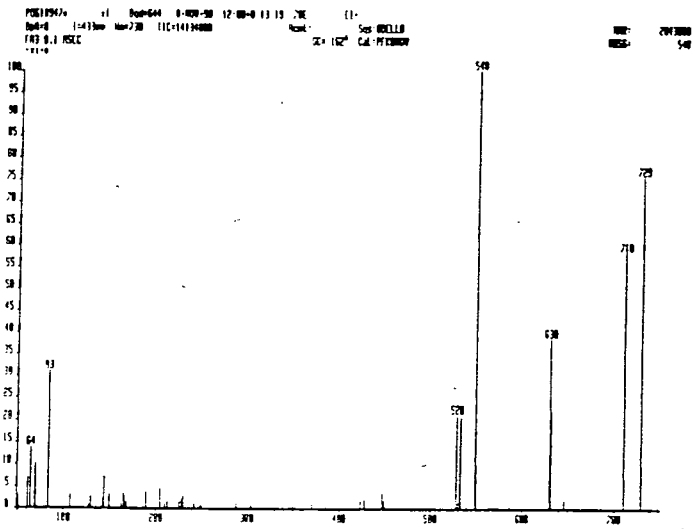
N°15 Hexakis(diethylamino)cyclotriphosphazene (66).



P0199A#2173• <1 Sqe=2150 29-OCT-91 12:05+0:26:58 70E EI+ 3.
BpM=0 I=1.2v Pm=568 TIC=51552000 Acnt: Sys:ODELLS
FA3 0.1MSEC GC= 270 Cal:PFK40CT

Mass	% Base		Mass	% Base	
55.99	3.24		277.90	1.27	
57.00	3.63		279.63	19.48	F
58.00	6.51		280.01	25.81	F
59.00	0.30		280.90	6.45	
69.98	1.44		281.90	19.53	
71.01	1.01		282.90	1.98	
72.00	59.21		290.76	0.30	
73.00	3.55		293.50	2.36	
74.00	4.06		297.08	0.30	
75.02	0.30		320.92	0.55	
87.00	0.40		322.94	2.15	
92.88	0.79		323.94	0.48	
103.95	0.59		324.94	0.68	
115.00	2.19		334.92	0.50	
118.95	0.77		348.95	1.42	
137.82	1.54		349.95	0.93	
139.84	0.71		350.96	11.79	F
146.90	0.33		351.95	13.53	F
148.89	0.74		352.75	26.54	F
150.87	0.32		353.07	36.73	F
152.78	0.55		353.99	6.45	F
161.92	0.42		354.99	0.55	
163.91	1.16		363.06	1.41	
165.89	0.32		365.67	0.37	
167.94	0.37		366.11	0.37	
174.96	1.03		370.03	0.33	
175.94	2.39		370.96	0.96	
176.49	0.54		392.08	0.39	
176.95	0.44		393.99	2.15	
179.81	0.54		395.00	0.66	
180.83	2.36		396.04	0.84	
181.88	0.30		409.05	0.37	
182.85	0.63		420.07	1.05	
194.77	0.33		422.93	30.56	F
203.43	0.44		423.79	56.55	F
204.48	0.82		424.16	100.00	F
204.92	0.40		425.14	19.92	F
206.82	2.39		434.20	0.83	
207.80	0.98		465.11	0.57	
208.70	12.90	F	467.15	0.91	
208.90	14.54	F	494.96	11.63	F
209.82	1.59		496.33	8.58	F
210.82	10.70	F	510.22	0.38	
211.58	4.17	F	538.19	13.03	F
212.46	0.76		539.24	3.97	F
219.93	0.34		540.25	0.64	
221.83	0.47		567.26	25.81	F
222.36	0.33		568.44	7.70	F
225.30	0.97				
232.96	0.38				
234.94	0.30				
235.85	0.63				
237.84	0.43				
247.00	0.57				
247.95	0.43				
249.85	0.98				
251.86	3.33				
252.86	0.63				
253.87	0.76				
265.92	0.66				

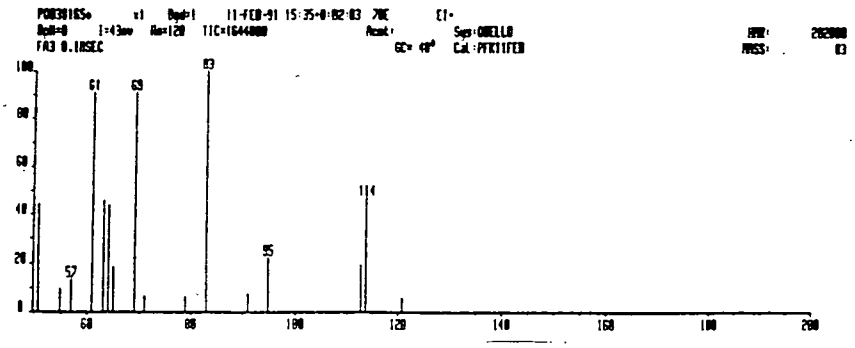
N°16 Hexakis(trifluoroethoxy)cyclotriphosphazene (50).



P0618947* x1 Bgd=644 9-NOV-90 12:08+0:13:19 70E EI+
BpM=0 I=433mv Hm=730 TIC=14134000 Acnt: Sys:00EL
FA3 0.1 MSEC GC= 162 Cal:PFKBN

Mass	% Base
50.93	2.92
60.97	6.68
63.99	13.58
68.98	9.88
93.02	30.95
106.99	2.85
127.00	0.74
128.99	1.30
129.98	2.53
142.02	1.97
144.01	6.93
149.99	2.99
163.03	0.95
165.01	3.13
165.99	2.39
167.99	1.30
189.00	3.59
205.01	4.47
210.01	0.98
212.98	1.55
225.04	1.09
225.99	1.58
227.99	2.15
228.97	1.69
229.98	2.85
241.99	0.88
249.01	0.67
288.02	1.06
304.10	0.74
350.02	0.91
370.05	1.02
424.09	1.69
428.04	1.76
448.07	3.27
450.10	1.62
528.07	21.00
530.09	1.37
532.08	20.44
533.14	1.69
548.07	100.00
549.11	9.85
550.12	2.43
630.09	38.62
631.10	22.19
632.16	1.76
646.15	1.72
710.14	58.71
711.18	6.82
729.15	76.15
730.18	9.74

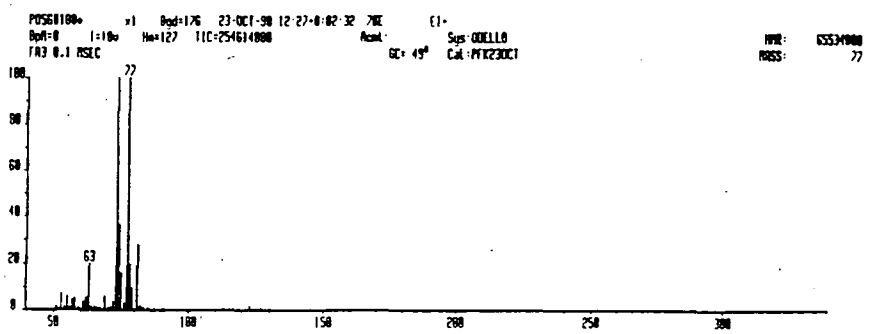
N°17 2,2,2-trifluoroethylmethylether (71)



P083#165* x1 Bgd=1 11-FEB-91 15:35+0:02:03 70E EI+
BpM=0 I=43mv Hm=120 TIC=1644000 Acnt: Sys:ODEL
FA3 0.1MSEC GC= 40 Cal:PFK1

Mass	% Base
49.88	9.57
50.89	43.97
54.93	9.22
56.95	13.12
60.88	90.78
62.89	45.39
63.88	43.97
64.88	18.09
68.85	90.78
70.93	6.03
78.83	5.67
78.86	6.03
82.83	100.00
90.87	7.09
94.84	21.99
112.79	19.15
113.80	46.81
120.89	5.32

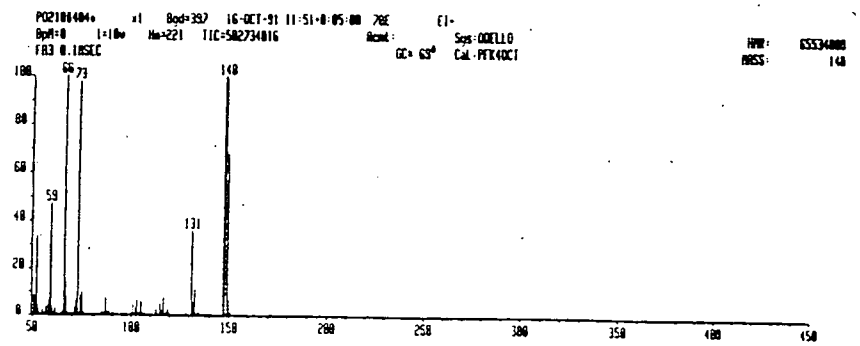
N°18 Trifluoromethyltrimethylsilane (78).



P056#180* x1 Bgd=176 23-OCT-90 12:27+0:02:32 70E EI+ 2.
BpM=0 I=10v Hm=127 TIC=254614000 Acnt: Sys:ODELLC
FA3 0.1 MSEC GC= 49 Cal:PFK230C

Mass	% Base	
50.98	1.31	
51.97	0.51	
52.98	6.83	
53.99	1.59	
54.99	5.56	
56.00	0.95	
57.01	4.17	
58.02	4.84	
59.02	0.72	
60.98	3.63	
61.99	5.32	
62.99	19.55	
63.99	1.56	
64.99	1.09	
65.97	0.65	
66.97	0.74	
68.98	5.78	
70.00	0.74	
71.01	1.06	
72.02	3.40	F
73.05	100.00	F0
74.03	36.33	
75.02	15.63	
75.99	2.97	F
77.03	100.00	F0
78.01	19.34	
79.01	9.25	
79.99	0.35	
80.98	27.58	
81.98	1.79	
82.98	0.87	
84.96	0.80	
90.98	0.37	
123.03	1.93	

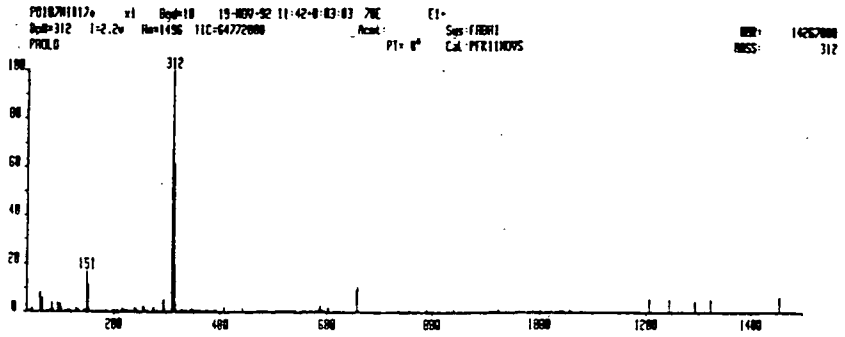
N°19 Pentafluoroethyltrimethylsilane (88).



P0210#404# x1 Bgd=397 16-OCT-91 11:51+0:05:00 70E EI+
BpM=0 I=10v Hm=221 TIC=502734000 Acnt: Sys:ODELL
FA3 0.1MSEC GC= 69 Cal:PFK40CT

Mass	% Base		Mass	% Base	
51.00	9.02		150.09	6.66	F
51.50	1.10	F	151.08	1.40	
52.01	33.73	F			
52.51	3.99				
53.00	2.89				
55.01	2.22				
56.01	0.62				
57.02	3.91				
58.02	5.97				
58.49	0.49	F			
59.03	46.89	F			
59.52	1.21				
60.04	3.56				
61.03	2.73				
65.01	1.06	F			
65.50	2.11	F			
66.03	100.00	F0			
66.53	15.37	F			
67.02	7.98				
67.53	0.71				
69.01	0.47				
70.02	0.78				
71.04	3.16				
72.04	6.52	F			
73.05	97.72	F			
73.54	0.78				
74.05	8.31				
75.03	9.50				
76.04	0.52				
83.03	0.40				
85.04	1.17				
85.98	0.97				
86.99	7.12				
87.98	1.37				
88.99	1.37				
91.01	0.35				
100.99	4.30				
102.00	3.00				
103.00	6.05				
104.01	0.91				
105.02	5.77				
106.02	0.78				
107.02	0.46				
113.03	2.40				
114.03	0.39				
115.01	4.72	F			
115.98	2.03	F			
117.02	7.68	F			
118.13	1.19	F			
119.04	2.45	F			
120.03	0.32				
129.06	0.44	F			
131.03	35.85	F			
132.03	5.47	F			
133.05	11.19	F			
134.05	1.56				
135.06	0.78				
147.17	100.00	F0			
148.08	100.00	F0			
149.08	67.65	F			

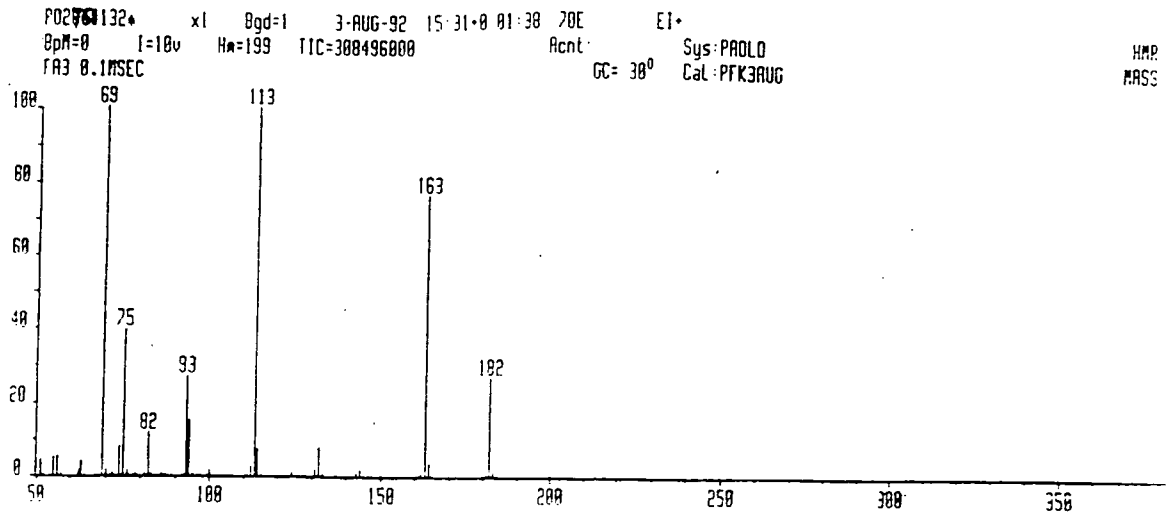
N°20 Hexakis(1,1-dichloro-2,2,2-trifluoroethoxy)cyclotriphosphazene (93).



P0107HI#18* x1 Bgd=10 19-NOV-92 11:42+0:03:12 70E EI+ 3..
BpM=312 I=1.9v Hm=1457 TIC=67940000 Acnt. Sys:FABHI
PA0L0 PT= 0 Cal:PFK11NOV

Mass	% Base		Mass	% Base	
41.07	0.37		355.58	0.45	
47.06	1.71		356.58	0.62	
50.07	1.18		361.01	0.80	
62.94	13.48		376.99	0.54	
64.93	4.16		392.83	0.93	
65.91	0.98		408.86	1.96	
68.96	7.73		427.78	0.77	
75.86	0.41		442.91	1.29	
81.85	0.92		471.27	0.43	
83.85	0.53		487.54	0.46	
84.89	6.75		489.55	0.42	
86.89	2.00		491.62	0.32	
91.87	0.31		587.67	3.99	F
96.94	3.57		603.46	2.52	F
100.86	4.06		641.55	2.51	F
102.86	2.64		655.55	10.49	F
104.85	0.50		657.89	18.10	F
110.80	0.46		659.83	19.12	F
115.87	0.66		661.37	13.78	F
116.83	0.62		737.60	0.69	
118.83	0.54		1206.85	7.39	F
131.87	1.07		1243.58	4.87	F
133.86	0.61		1293.77	4.54	F
145.79	1.32		1322.53	5.40	F
147.78	0.84		1456.04	4.77	F
150.83	28.23				
151.83	0.58				
152.83	17.75				
153.80	0.38				
154.82	3.02				
201.69	0.45				
215.69	1.44				
217.69	1.83				
219.67	0.86				
239.72	1.37				
241.71	1.10				
255.74	0.58				
257.78	0.55				
260.30	0.54				
262.70	0.42				
276.19	2.09				
282.68	0.36				
293.11	4.82	F			
295.63	5.36	F			
297.12	2.41	F			
309.07	65.89	F			
311.60	100.00	F			
313.61	61.12	F			
315.62	19.23	F			
317.15	3.27	F			
325.70	0.43				
327.74	0.84				
329.21	0.84				
334.63	0.49				
337.57	0.31				
339.56	0.32				
346.42	1.72				
350.60	0.88				
352.56	0.32				
354.56	0.47				

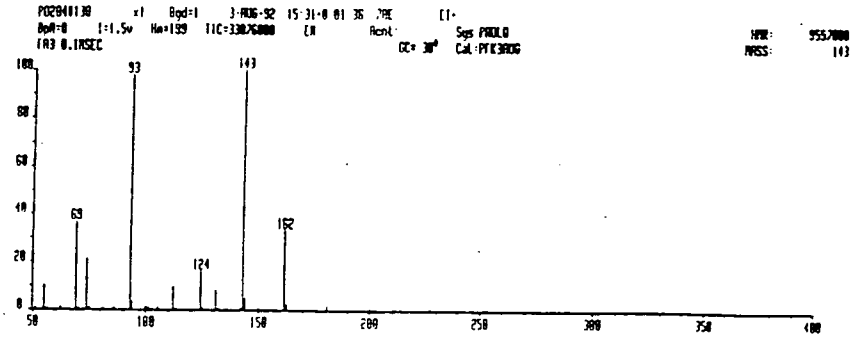
N°21 2-hydroperfluorobut-2-ene (109).



Hd=132♦ x1 Bgd=1 3-AUG-92 15:31+0 01:38 70E EI+ 1.1
I=10v Hm=199 TIC=308496000 Acnt Sys:PAOLO
1MSEC GC= 30 Cal:PFK3AUG

Mass	% Base	
49.97	9.32	
50.98	4.21	
54.97	4.82	
55.98	5.29	
61.97	1.20	
62.98	3.66	
68.97	100.00	0
69.97	1.48	
71.97	0.62	
73.96	7.96	
74.97	39.87	
75.98	1.29	
81.97	11.67	
92.96	26.99	
93.97	15.02	
94.98	0.51	
99.96	1.24	
111.97	2.34	F
112.99	100.00	F0
113.97	7.16	
123.95	0.78	
130.95	1.69	
131.96	7.39	
142.94	0.85	
143.95	1.85	
161.81	0.84	F
162.94	76.41	F
163.95	3.42	
180.92	0.49	F
181.93	27.17	F
182.94	1.17	

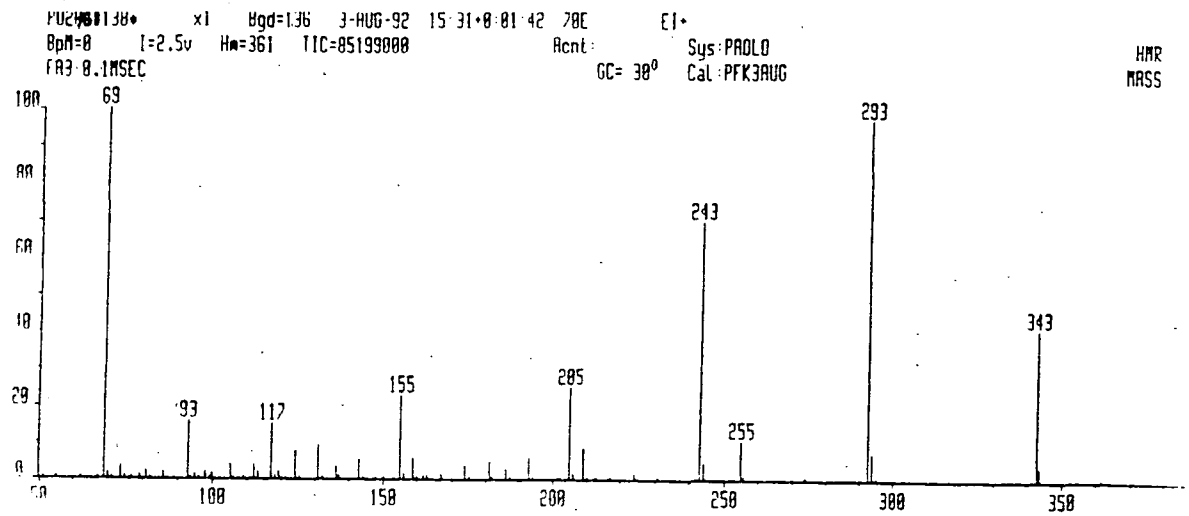
N°22 2,3-dihydroperfluorobut-2-ene (109).



P0284#130 x1 Bgd=1 3-AUG-92 15:31+0:01:36 70E EI+ 1.1
BpM=0 I=1.5v Hm=199 TIC=33876000 EN Acnt: Sys:PA0L0
FA3 0.1MSEC GC= 30 Cal:PFK3AUG

Mass	% Base	
49.97	4.41	
50.98	0.70	
54.97	9.66	M
61.97	1.08	
68.96	36.35	
69.96	0.39	
73.96	20.67	M
74.97	0.75	
85.96	0.85	
92.95	97.84	M
93.96	3.19	
99.96	1.06	
100.96	0.72	
104.96	0.73	
111.95	9.38	M
123.95	15.42	M
124.94	0.67	
130.94	7.54	
142.93	100.00	M
143.94	4.50	
149.93	0.45	
161.92	32.85	M
162.92	1.90	
180.91	1.38	
199.89	0.65	

N°23 5-hydroperfluoro-3,4-bis(trifluoromethyl)hexadi-2,4-ene (110a).



x1 Bgd=136 3-AUG-92 15:31+0:01:42 70E EI+ 2 1
I=2.5v Hm=361 TIC=85199000 Acnt Sys:PAOL0
1MSEC GC= 30 Cal:PFK3AUG

Mass	% Base
49.97	1.60
50.98	0.31
54.98	0.81
68.95	100.00
69.96	1.28
70.96	0.40
73.96	3.09
74.97	0.75
76.98	0.37
78.96	1.01
80.96	1.97
85.96	1.70
92.96	15.45
93.96	0.48
94.97	0.86
97.96	1.82
99.96	1.28
104.96	3.86
108.93	0.31
111.95	3.43
112.96	1.80
116.95	14.84
117.95	0.83
118.94	1.74
123.95	7.34
124.96	0.49
130.94	8.91
131.95	0.31
135.94	3.09
136.93	0.53
142.93	5.15
147.92	0.45
149.93	0.38
154.92	22.76
155.93	1.30
158.92	5.48
159.92	0.30
161.92	0.79
162.94	0.99
166.93	0.96
173.92	3.28
180.91	4.38
181.93	0.33
185.91	2.34
192.90	5.35
193.91	0.42
201.40	0.36
204.89	25.06
205.90	1.49
208.88	8.13
212.90	0.33
216.89	0.32
223.90	1.54
230.90	0.50
242.88	69.70
243.88	4.27
254.88	10.21
255.89	0.77

Mass	% Base
293.86	6.98
342.83	41.15
343.84	3.58
361.80	0.51

APPENDIX 4

The Board of Studies in Chemistry requires that each postgraduate research thesis contains an appendix listing:-

(1) all research colloquia, seminars and lectures arranged by the Department of Chemistry during the period of the author's residence as a postgraduate student;

(2) lectures organised by Durham University Chemical Society;

(3) all research conferences attended and papers presented by the author during the period when research for the thesis was carried out;

(4) details of the postgraduate induction course.

COLLOQUIA, LECTURES AND SEMINARS GIVEN BY INVITED SPEAKERS.

January 1990 - December 1992

24.1.90 **Dr. R.N. Perutz** (York University)
Plotting the Course of C-H Activations with Organometallics

31.1.90 **Dr. U. Dyer** (Glaxo)
Synthesis and Conformation of C-Glycosides

1.2.90 **Prof. J.H. Holloway** (Leicester University)
Noble Gas Chemistry

7.2.90 **Dr. D.P. Thompson** (Newcastle University)
The role of Nitrogen in Extending Silicate Crystal Chemistry

8.2.90 **Rev. R. Lancaster** (Kimbolton Fireworks)
Fireworks - Principles and Practice

12.2.90 **Prof. L. Lunazzi** (University of Bologna)
Application of Dynamic NMR to the Study of Conformational Isomerism

14.2.90 **Prof. D. Sutton** (Simon Fraser University, Vancouver B.C.)
Synthesis and Applications of Dinitrogen and Diazo Compounds of Rhenium and Iridium

15.2.90 **Prof. L. Crombie** (Nottingham University)
The Chemistry of Cannabis and Khat

21.2.90 **Dr. C. Bleasdale** (Newcastle University)
The Mode of Action of some Anti-tumour Agents

22.2.90 **Prof. D.T. Clark** (ICI Wilton)
Spatially Resolved Chemistry using Nature's Paradigm in the Advanced Materials Area

28.2.90 **Dr. R.K. Thomas** (Oxford University)
Neutron Reflectometry from Surfaces

1.3.90 **Dr. J.F. Stoddart** (Sheffield University)
Molecular Lego

8.3.90 **Dr. A.K. Cheetham** (Oxford University)
Chemistry of Zeolite Cages

21.3.90 **Dr. I. Powis** (Nottingham University)
Spinning off in a huff: Photodissociation of Methyl Iodide

23.3.90 **Prof. J.M. Bowman** (Emory University)
Fitting Experiment with Theory in Ar-OH

9.7.90 **Prof. L.S. German** (USSR Academy of Sciences - Moscow)
New Syntheses in Fluoroaliphatic Chemistry: Recent Advances in the Chemistry of Fluorinated Oxiranes

9.7.90 **Prof. V.E. Platonov** (USSR Academy of Sciences - Novosibirsk)
Polyfluoroindanes: Synthesis and Transformation

9.7.90 **Prof. I.N. Rozhkov** (USSR Academy of Sciences - Moscow)
Reactivity of Perfluoroalkyl Bromides

11.10.90 **Dr. W.A. MacDonald** (ICI Wilton)
Materials for the Space Age

24.10.90 **Dr. M. Bochmann** (U.E.A.)
Synthesis, Reactions and Catalytic Activity of Cationic Titanium Alkyls

26.10.90 **Prof. R. Soulen** (South Western University, Texas)
Chemistry of some Fluorinated Cyclobutenes

31.10.90 **Dr. R. Jackson** (Newcastle University)
New Synthetic Methods: a-aminoacids and Small Rings

1.11.90 **Dr. N. Logan** (Nottingham University)
Rocket Propellants

6.11.90 **Dr. P. Kocovsky** (Uppsala University)
Stereo-controlled Reactions Mediated by Transition and Non-Transition Metals

7.11.90 **Dr. D. Gerrard** (B.P.)
Raman Spectroscopy for Industrial Analysis

7.11.90 **Dr. W. Dolbier** (Gainsville, Florida)
Rearrangements of bis CF_3 Vinyl Aromatics: a Route to 1,3,5-Hexatrienes

8.11.91 **Dr. S.K. Scott** (Leeds University)
Clocks, Oscillations and Chaos

14.11.90 **Prof. T. Bell** (SUNY, Stony Brook , U.S.A)
Functional Molecular Architecture and Molecular Recognition

21.11.90 **Prof. J. Pritchard** (Queen Mary and Westfield College, London)
Copper Surfaces and Catalysts

28.11.90 **Dr. B.J. Whitaker** (Leeds University)

Two-dimensional Velocity Imaging of State-selected Reaction Products

29.11.90 **Prof. D. Crout** (Warwick University)
Enzymes in Organic Synthesis

5.12.90 **Dr. P.G. Pringle** (Bristol University)
Metal Complexes with Functionalised Phosphines

13.12.90 **Prof. A.H. Cowley** (University of Texas)
New Organometallic Routes to Electronic Materials

15.1.91 **Dr. B.J. Alder** (Lawrence Livermore Labs., California)
Hydrogen in all its Glory

17.1.91 **Dr. P. Sarre** (Nottingham University)
Comet Chemistry

23.1.91 **Prof. J.S. Higgins** (Imperial College, London)
Rheology and Molecular Structure of Ionomer Solutions

24.1.91 **Dr. P.J. Sadler** (Birkbeck College, London)
Design of Inorganic Drugs: Precious Metals, Hypertension and HIV

30.1.91 **Prof. E. Sinn** (Hull University)
Coupling of Little Electrons in Big Molecules. Implications for the active Sitee of Macromolecules

31.1.91 **Dr. D. Lacey** (Hull University)
Liquid Crystals

6.2.91 **Dr. R. Bushby** (Leeds University)
Biradicals and Organic Magnets

14.2.91 **Dr. M.C. Petty** (Durham University)
Molecular Electronics

20.2.91 **Prof. B.L. Shaw** (Leeds University)
Synthesis with Coordinated, Unsaturated Phosphine Ligands

28.2.91 **Dr. J. Brown** (Oxford University)
Can Chemistry Provide Catalysts Superior to Enzymes?

6.3.91 **Dr. C.M. Dobson** (Oxford University)
NMR Studies of Dynamics in Molecular Crystals

7.3.91 **Dr. J. Markam** (ICI Pharmaceuticals)
DNA Fingerprinting

24.4.91 **Prof. R.R. Schrock** (MIT)
Metal-ligand Multiple Bonds and Metathesis Initiators

25.4.91 **Prof. T. Hudlicky** (Virginia Polytechnic Institute)
Biocatalysis and Symmetry Based Approaches to the Efficient Synthesis of Complex Natural Products

20.6.91 **Prof. M.S. Brookhart** (University of North Carolina)
Olefin Polymerisations, Oligomerisations and Dimerisations Using Electrophilic Late Transition Metal Catalysts

29.7.91	**Dr. M.A. Brimble** (Massey University, New Zealand) *Synthetic Studies Towards the Antibiotic Griseusin-A*
3.10.91	**Dr. R. Keeley** (Metropolitan Police) *Modern Forensic Scinece*
17.10.91	**Dr. J. A. Salthouse** (Manchester University) *Son et Lumiere*
6.11.91	**Prof. B. F. G. Johnson** (Edinburgh University) *Cluster-Surface Analogies*
7.11.91	**Dr. A. R. Butler** (St. Andrews University) *Traditional Chinese Herbal Drugs*
13.11.91	**Prof. D. Gani** (St. Andrews University) *The Chemistry of PLP Dependant Enzymes*
20.11.91	**Dr. R. More O'Ferrall** (Dublin) *Some Acid-Catalysed Rearrangements in Organic Chemistry*
28.11.91	**Prof. I. M. Ward** (Leeds University) *The Science & Technology of Orientated Polymers*
4.12.91	**Prof. R. Grigg** (Leeds University) *Palladium Catalysed Cyclisation and Ion Capture Processes*
5. 12.91	**Prof. A. L. Smith** (ex Unilever) *Soap Detergents and Black Puddings*
11.12.91	**Dr. W. A. Cooper** (Shell Research) *Colloid Science, Theory, and Practice*
16.1.92	**Dr. N. J. Long** (Exeter University) *Metallocenophanes-Chemical sugar-tongs*
22.1.92	**Dr. K. D. M. Harris** (St. Andrews University) *Understanding the Prperties of Solid Inclusion Compounds*
29.1.92	**Dr. A. Holmés** (Cambridge University) *Cycloaddition Reactions in the Service of the Synthesis of Piperidine and ndolizidine Natural Products*
12.2.92	**Dr. D. E. Fenton** (Sheffield University) *Polynuclear Complexes of Molucular Clefts as Models for Copper Biosites*
19.2.92	**Prof. E. J. Thomas** (Manchester University) *Application of Organo-Stannanes to Organic Synthesis*
25.2.92	**Prof. J. F. Nixon** (University of Sussex) *Phosphoalkylenes, New Building Blocks in Inorganic and Organometallic Chemistry*
26.2.92	**Prof. M. L. Hitchman** (Stratheclyde University) *Chemical Vapour Deposition*
11.3.92	**Dr. S. E. Thomas** (Imperial College)

Recent Advances in Organoiron Chemistry

18.3.92 **Dr. H. Maskill** (Newcastle University)
Mechanistic Studies of Organic Group Transfer Reactions

13.5.92 **Dr. J-C. Gehret** Ciba Geigy, Basel
Some aspects of industrial agrochemical research

4.11.92 **Dr. T. Kee** University of Leeds
Synthesis and coordination chemistry of silylated phosphites

5.11.92 **Dr. C. J. Ludman** University of Durham
Explosions. A demonstration lecture

11.11.92 **Prof. D. Robins** Glasgow University
Pyrrolizidine alkaloids: biological activity, biosynthesis and benefits

12.11.92 **Prof. M. R. Truter** University College London
Luck and logic in host - guest chemistry

25.11.92 **Prof.Y.Vallee** University of Caen France
Reactive thiocarbonyl compounds

25.11.92 **Prof. L. D. Quin** University of Massachusetts, Amherst
Fragmentation of phosphorus etherocycles as a route to phosphoryl species with uncommon bonding

26.11.92 **Dr. D. Humber** Glaxo Greenford
Aids - the development of a novel series of inhibitors of HIV

2.12.92 **Prof. A. F. Hegarty** University College Dublin
Highly reactive enols stabilised by steric protection

Research Conferences Attended

7.3.90	SCI Graduate Symposium, York University.
2.4.90	North East Graduate Symposium, Newcastle University.
Sept 91	13th International Symposium on Fluorine Chemistry, Ruhr Universität, Bochum, Germany.
Sept 92	European Symposium on Fluorine Chemistry, Padova, Italy.
Jan 93	11th ACS Fluorine Winter Conference St. Petersburg Florida
March 93	SmithklineBeecham Symposium: Metals in Organic Synthesis, Cambridge.

FIRST YEAR INDUCTION COURSE

This course consists of a series of one hour lectures on the services available in the department.

Departmental Organisation - Dr. E.J.F. Ross
Safety Matters - Dr. M.R. Crampton
Electrical Appliances - Mr. B.T. Barker
Chromatography and Microanalysis - Mr. T.F. Holmes
Atomic Absorptiometry and Inorganic Analysis - Mr. R. Coult
Library Facilities - Mr. R.B. Woodward
Mass Spectroscopy - Dr. M. Jones
Nuclear Magnetic Resonance Spectroscopy - Dr. R.S. Matthews
Glass-blowing Techniques - Mr. R. Hart and Mr. G. Haswell