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UNIVERSITY OF DURHAM

A THESIS

entitled

SOME HIGHLY FLUORINATED CARBOCATIONS

submitted by

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(ST. AIDAN'S COLLEGE)

A candidate for the degree of Doctor of Philosophy
1973



ACKNOWLEDGEMENTS

The author wishes to thank Dr. R.D. Chambers for his continual encouragement and advice during the supervision of the work presented in this thesis, Professor W.K.R. Musgrave for his interest and Dr. R.S. Matthews for his invaluable assistance in the interpretation of N.M.R. spectra. Thanks are also due to Mrs. E. Duddy for her skill and patience in the typing of this manuscript, to the technical staff of the Chemistry Department of the University of Durham for their cheerful co-operation, and to the Science Research Council for financial support.

TO TONY AND MY PARENTS

MEMORANDUM

The work described in this thesis was carried out in the University of Durham between October 1969 and September 1972. This work has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

SUMMARY

Reactions have been carried out between a variety of fluorinated olefins and the strong acid systems antimony pentafluoride in sulphur dioxide and antimony pentafluoride/fluorosulphonic acid, with the intention of generating some highly fluorinated allyl cations. The cations were analysed by means of their N.M.R. spectra and by the products obtained on quenching the ionic solutions.

Initial experiments were carried out with highly fluorinated propenes, substituted at the 1- or 2-positions by electron donating groups. Reaction of 1-p-anisylpentafluoropropene with antimony pentafluoride in sulphur dioxide at -30° resulted in removal of fluoride ion from the $-CF_3$ group and generation of the 1,1,2,3-tetrafluoro-3-p-anisylallyl cation. A detailed study of the N.M.R. spectrum of this cation has yielded a great deal of information about the structure of the allyl cation itself and the manner in which the charge is stabilized by the fluorine atoms.

Reaction also occurred between 1-methoxypentafluoropropene and antimony pentafluoride in sulphur dioxide, apparently with removal of fluoride ion, but a simple allyl cation was not formed. Similarly 1-phenyl- and 1-methyl-pentafluoropropene did not yield simple allyl cations.

Reactions of 2-phenyl- and 2-p-anisyl-pentafluoropropene with antimony pentafluoride in sulphur dioxide also did not produce the expected allyl cations, and 2-p-anisylpentafluoropropene reacted with antimony pentafluoride/fluorosulphonic acid to form an addition product.

Hexafluoropropene itself reacted with antimony pentafluoride at room temperature to produce the hydrogen fluoride addition product and a dimer which could possibly have been formed from an intermediate allyl cation.

The work was extended into the field of cyclobutenes, and allyl cations were produced on reaction of 1,2-dimethyl- and 1,2-dimethoxy-tetrafluorocyclobutenes with antimony pentafluoride in sulphur dioxide. Conclusive evidence could not be found for the presence of allyl cations in the reactions of 1-methoxypentafluorocyclobutene and 1,3,3-trimethoxy-2,4,4-trifluorocyclobutene with this acid system.

Further extension of the work into the field of highly fluorinated cyclopentenyl and cyclohexenyl cations was attempted, but it was found that neither 1,2-dimethylhexafluorocyclopentene nor 1,2-dimethyloctafluorocyclohexene yielded simple allyl cations with the strong acid systems used.

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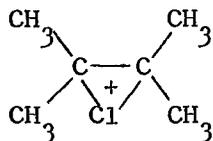
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Notes on Ion Numbering System

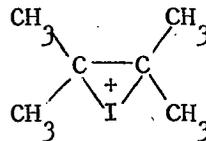
A large number of different ions are discussed in Chapters 1 and 2 of this thesis, and in an attempt to simplify the numbering system, these have been divided into classes.

For example, all ethylene halonium ions carry the class number 19, and individual ions in this series are characterised by the small letters a, b, c etc. The type of halogen atom is represented by small Roman numerals; (i) = F, (ii) = Cl, (iii) = Br etc.

Thus the tetramethyl-ethylene chloronium and tetramethyl-ethylene iodonium ions are represented by numbers 19e(ii) and 19e(iv) respectively:



19e(ii)

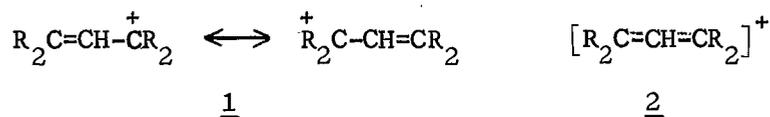


19e(iv)

CHAPTER 1

The Allyl Cation

The existence of the allyl cation as an intermediate in organic reactions has been the subject of extensive discussion.



Its existence as a delocalized cation 2 was generally accepted as giving an explanation for allylic rearrangements long before spectroscopic evidence was available to confirm this structure.¹

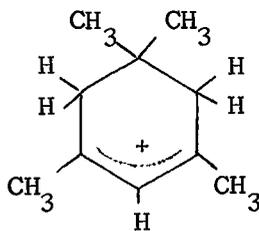
1.1. Methods of Identification.

A. Ultraviolet Data.

A great deal of information has been obtained from the U.V. spectra of these ions. As might be expected, extinction coefficients are high²⁻⁵ (of the order of 10^4) and the solutions often highly coloured as a result of charge delocalization. Values of λ_{max} have been interpreted in terms of the electronic structures of the ions.⁵ However, these results can often be misleading, as the presence of very small quantities of impurities can lead to highly coloured solutions, even when no ionization has occurred.

B. Infra-Red Data.

Infra-red measurements have also been of great value, especially in differentiating between structures 1 and 2. For example, in the ion 8a,² only one band was observed between $2,850 \text{ cm.}^{-1}$ and $1,450 \text{ cm.}^{-1}$



8a



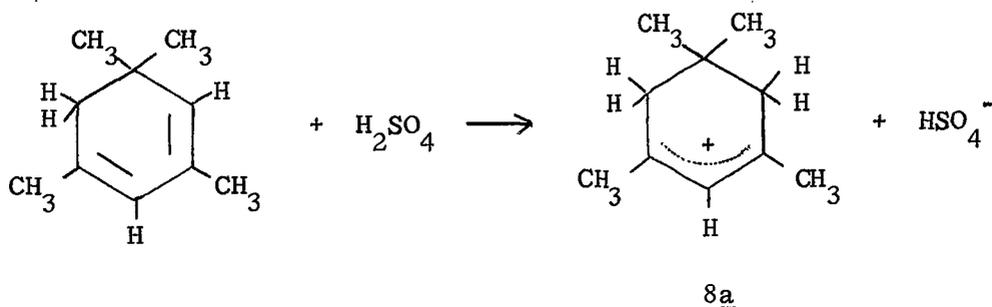
and this occurred at 1533 cm.^{-1} , i.e. intermediate in frequency between ordinary carbon-carbon single and double bond absorptions. Its extinction, however, was ten-times as great as the average extinction of two carbon-carbon double bond stretching absorptions in the I.R. spectrum of the diene. Signals of similar frequencies and extinctions have also been observed in several other related systems.⁵

C. Nuclear Magnetic Resonance Data.

N.M.R. spectroscopy has proved a particularly useful tool in the investigation of these ions. Chemical shifts give excellent information about the extent and the nature of the ionization, and coupling constants reveal a great deal about the state of hybridization. This is one of the major means of analysing these organic cations and the extent of its usefulness will be revealed in subsequent discussions.

D. Freezing Point Depression Measurements.

Despite the wealth of spectroscopic evidence now available about allyl cations, the most important piece of evidence to support their existence as discreet species is that of freezing point depression. This was first demonstrated in the protonation of 1,3,5,5-tetramethylcyclohexadiene using sulphuric acid,² when a two-fold depression was observed. The establishment



of the alkenyl cation in this way, coupled with the observation that different acid systems could be used to produce the same ions⁶ has been instrumental in the identification of many new alkenyl systems.

1.2. Types of Allylic Cations.

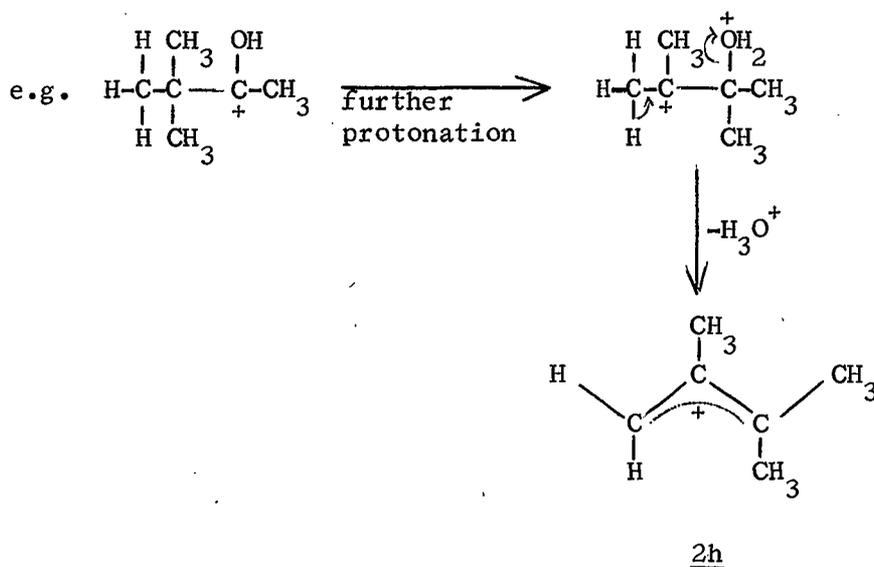
A. Propenyl Cations.

The concept of propenyl cations existing as intermediates in a number of chemical reactions (e.g. solvolysis of allyl halides⁷) is not a new one. They have now been generated by a variety of routes, and have been studied extensively, especially by means of their N.M.R. spectra.⁸

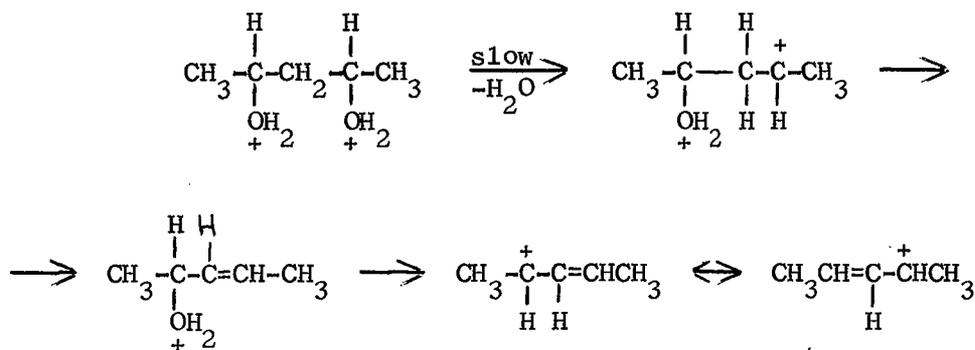
1. General Methods of Preparation.

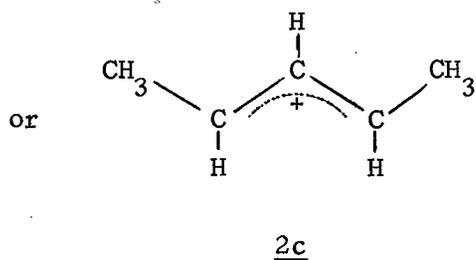
(a) Dehydration of Protonated Ketones.

This provides a useful synthesis of several different allyl cations:⁹⁻¹¹



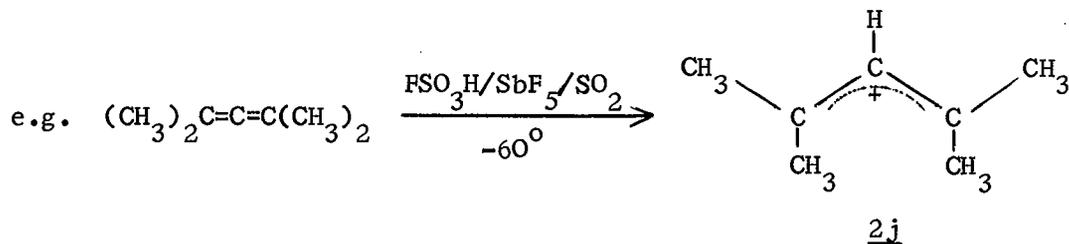
A similar type of reaction has been observed in the dehydration of a diprotonated aliphatic glycol:¹²



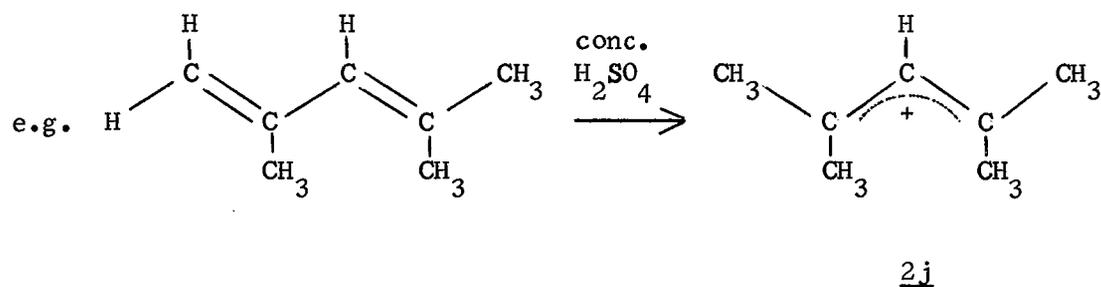


(b) Protonation of Olefins.

Such reactions have included protonation of allenes^{13a}



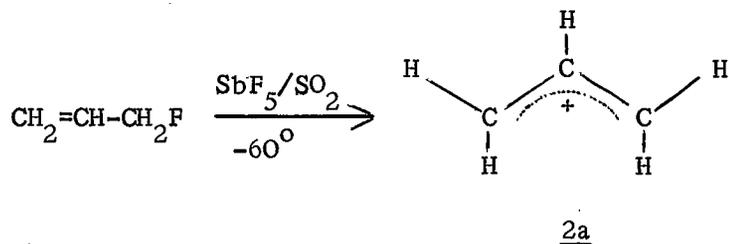
and dienes¹⁴

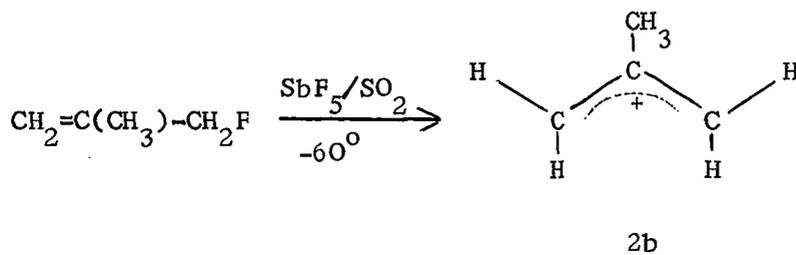


(c) Halogen Abstraction.

1. From Allyl Fluorides.

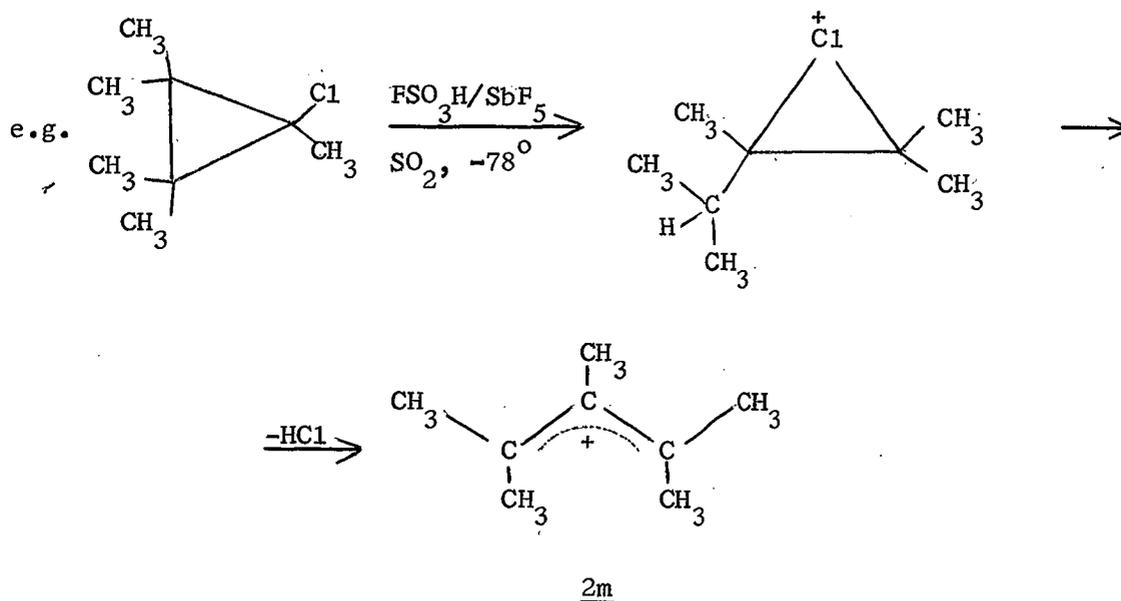
A useful synthesis of the simple allyl cation 2a and 2-methyl allyl cation 2b was provided by the reaction of the corresponding allyl fluorides with antimony pentafluoride in sulphur dioxide.¹⁵





2. Cleavage Reactions of Halogenated Cyclopropanes.

Allyl cations have been reported in a number of solvolytic reactions of cyclopropyl compounds.¹⁶⁻¹⁸ A series of ions has now been produced by the action of the strong acid system antimony pentafluoride/fluorosulphonic acid/sulphur dioxide on cyclopropyl halides.¹³ Reaction products were found to be dependant on the temperature and solvent system used, but in general breakdown eventually occurred to produce propenyl cations. The authors favour a mechanism involving protonation, forming an intermediate chloronium ion, followed by loss of HCl,



This series of reactions was later extended to also include a number of halogenated systems¹⁹ and activation parameters have been calculated for these ions for rotation about the double bond. The results will be reported in a later section.

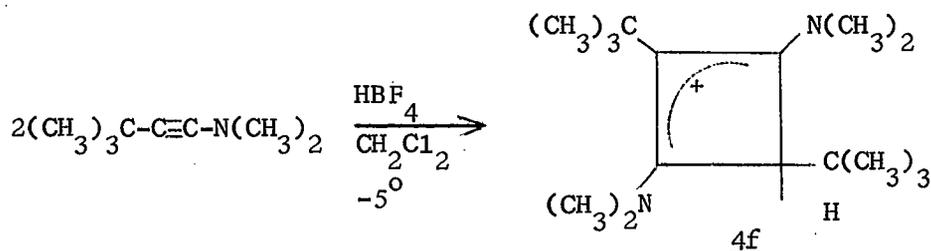
B. Cyclobutenyl Cations.

1. Monocations.

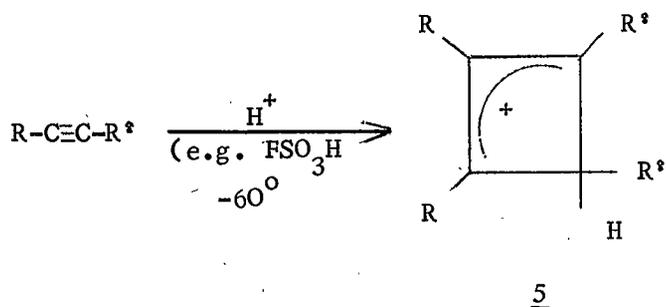
(a) General Methods of Preparation.

1. Reactions of Substituted Acetylenes with Acids.

The formation of substituted cyclobutenyl ions by this method was noticed by Viehe²⁰ in a series of reactions of alkynylamines.



This was later extended to the field of aryl substituted cyclobutenes.^{21,22}

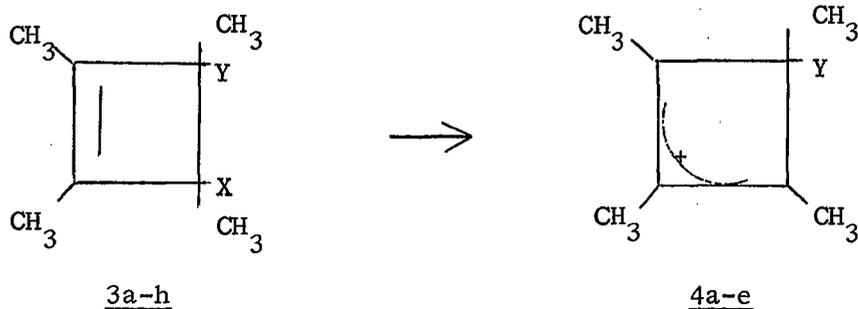


R = aryl

or other isomers, depending on the substituents present.

2. From Substituted Cyclobutenes.

A number of allyl cations have now been generated from substituted cyclobutenes using strong Lewis acids. The majority of this work has been carried out in recent years by Katz and Gold^{5,6,23} who have succeeded in producing a series of cyclobutenyl ions which have been investigated by means of N.M.R., U.V. and I.R.

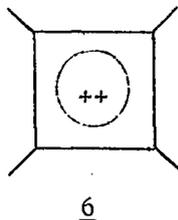


- | | | | | | |
|--------------------|------------------------------|-----------|---|-----------|---------------------|
| <u>3a</u> | Y = CH ₃ , X = Cl | <u>e</u> | Y = H, X = H | <u>4a</u> | Y = Cl |
| <u>b</u> | Y = CH ₃ , X = Br | <u>f</u> | Y = CH ₃ , X = CH ₃ | <u>b</u> | Y = CH ₃ |
| <u>c</u> | Y = H, X = Cl | <u>g</u> | Y = Br, X = Br | <u>c</u> | Y = H |
| <u>d</u> | Y = Cl, X = Cl | | | <u>d</u> | Y = Br |
| And in later work: | <u>h</u> | Y = X = I | | <u>e</u> | Y = I ⁶ |

These ions were prepared using silver hexafluoroantimonate in sulphur dioxide at -60° , and aluminium trichloride in methylene chloride at room temperature.

2. Dications.

Cyclobutenyl cations were initially generated in experiments which were designed to produce the aromatic cyclobutadiene dication 6 - a 2π electron system.



This according to Hückel theory, should be a stable system, obeying the $(4n + 2)\pi$ electron rule. However, in the case of the methyl-substituted cyclobutenes only the monocations have been observed.

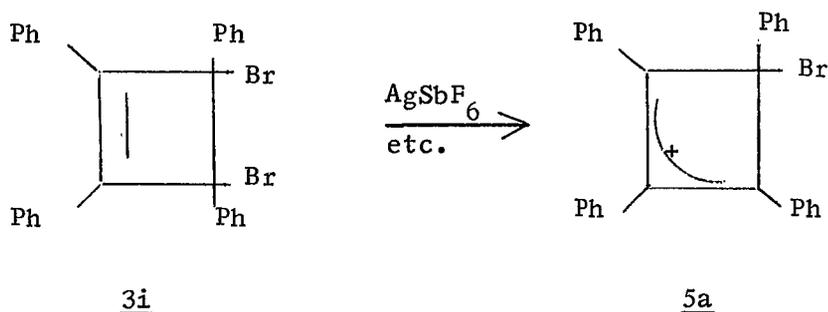
Katz²³ et al. have attributed the stability of the monocations to the favourable interaction of non-adjacent carbon 2p orbitals in the cyclobutenyl system.

(a) General Methods of Preparation.

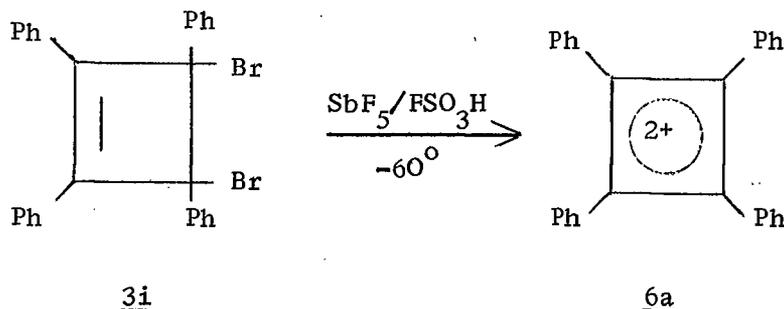
The presence of phenyl groups seems to be essential for the formation of the cyclobutadiene dication. This observation is in sharp contrast to the case of the cyclopropyl cation, where alkyl groups have a greater stabilizing effect than phenyl groups.²⁴⁻²⁶ This is perhaps an indication that the π -system of the cyclobutadiene dication is more capable of receiving electronic charge than that of the cyclopropyl cation.

1. From Dihalogenated Aryl Cyclobutenes.

Although the formation of a dication was claimed in the reaction of 3,4-dibromo-1,2,3,4-tetraphenylcyclobutene with silver perchlorate, -hexafluoroantimonate and -tetrafluoroborate,²⁷ the evidence for this was mainly chemical (precipitation of two moles of silver bromide). In subsequent crystallographic investigations²⁸ it was found that, certainly in the solid state, only the monocation was formed.

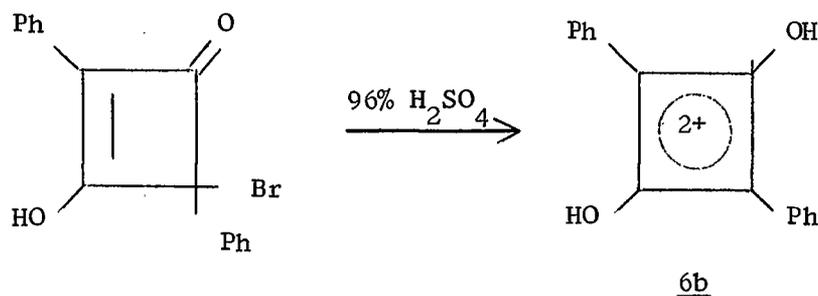


In later work, the same authors presented evidence, again chemical, of the generation of the dication from the dibromo-olefin by the use of silver tetrafluoroborate.²⁹ However, again the presence of a monocation could not be completely eliminated, and it was not until 1970 that Olah³⁰ and co-workers succeeded in obtaining direct N.M.R. evidence of the dication from the dibromocyclobutene 3i by the use of antimony pentafluoride/fluorosulphonic acid.



2. α -Bromoketones.

The stable 1,3-dihydroxy-2,4-diphenylcyclobutadiene dication has recently been formed³¹ by ionization of an α -bromoketone.



Its structure was proven by N.M.R. observations, and precipitation of an α -hydroxyketone on dilution by ice-water. No evidence was found in the N.M.R. spectrum for the presence of protonated ions. It was notable in this investigation that a dication could not be generated from 2-bromo-3-hydroxy-2,4-dimethylcyclobutenone, which was in fact completely resistant to solvolysis.

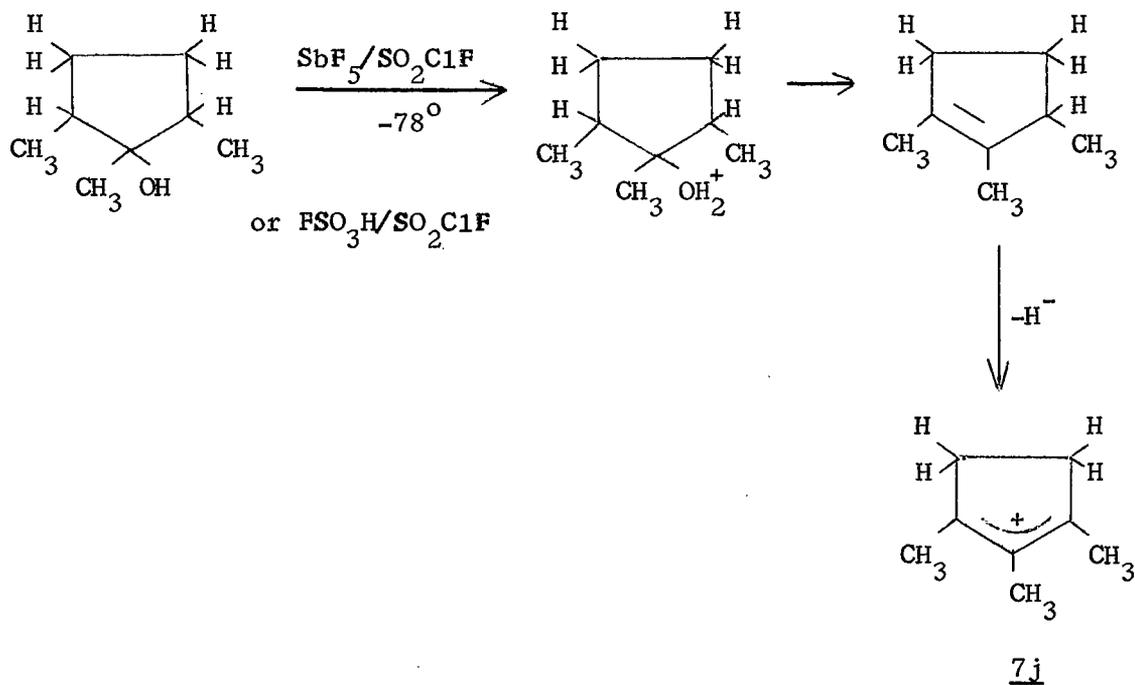
C. Cyclopentenyl and Cyclohexenyl Cations.

These are probably the best documented allyl systems. Investigations have been carried out into their stability and susceptibility to hydrogen-deuterium exchange.³²

1. General Methods of Preparation.

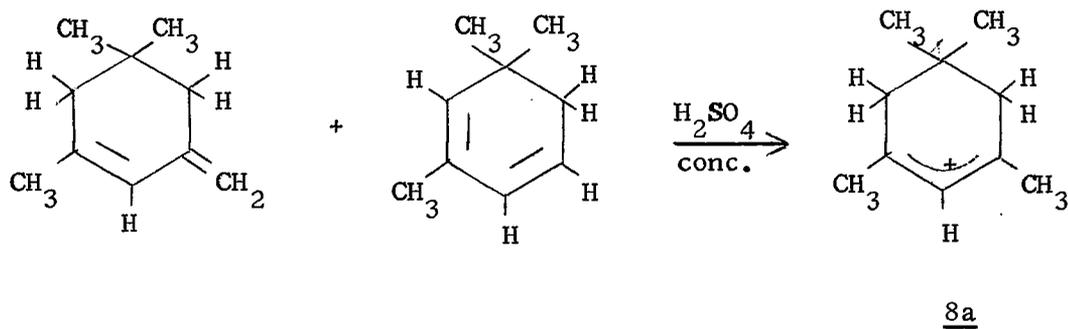
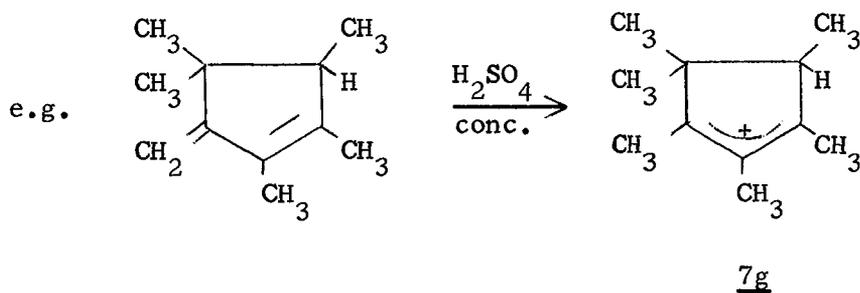
(a) Dehydration of Protonated Alcohols.

An example of this is seen in the case of 1,2,5-trimethylcyclopentan-2-ol.³³

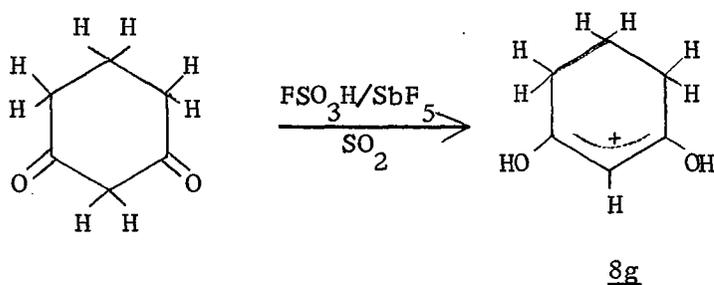
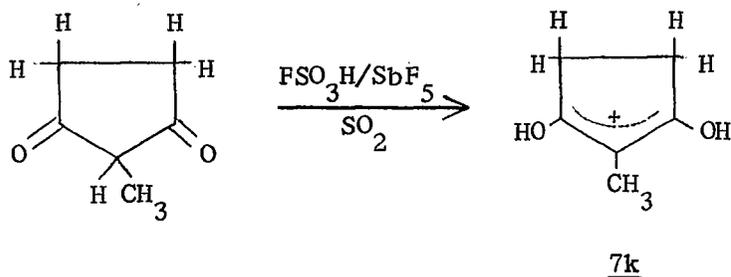


(b) Protonation Reactions.

The majority of the cyclopentenyl and -hexenyl ions which have been studied have been prepared by protonation of cyclopentadienes and cyclohexadienes.^{2,4,14,32}

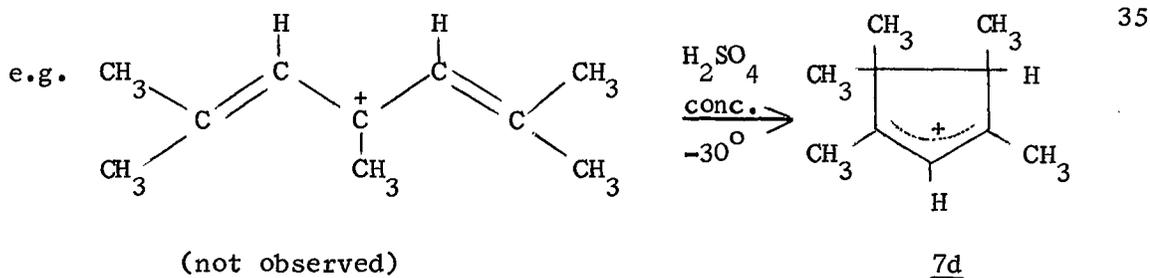


Protonation of cyclic diketones in low acid concentrations has been found to result in hydroxy allylic ketones.³⁴



(c) Cyclization Reactions.

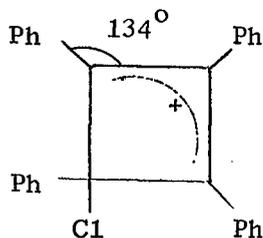
Cyclopentenyl ions have been produced in a number of cyclization reactions of pentadienyl and heptatrienyl cations.³⁵⁻³⁷



1.3. Structure of Allyl Cations.

A. Bond Angles.

Generally, bond angles around the trigonal carbons in the allyl cation are presumed to be 120° , although there is no direct experimental evidence to verify this.¹ However, in the case of cyclobutenyl cations, the ring size makes it unlikely that such bond angles could be observed, and in fact crystallographic measurements on the 4-chloro-1,2,3,4-tetraphenylcyclobutenyl cation²⁸ show external bond angles of $134^\circ \pm 7^\circ$.

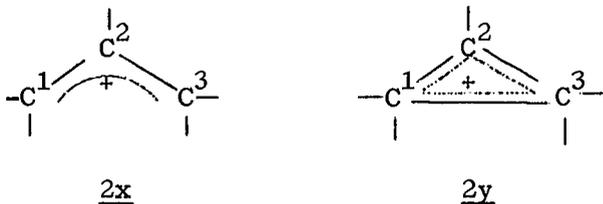


5a

B. Electronic Charge Distribution.

1. Charge Calculations.

The question of charge distribution in the allyl cation is one which has aroused extensive discussion. Molecular orbital calculations³⁸ reveal a structure in which the charge is located on the terminal carbons, and bond overlap between these centres is negligible (i.e. 2x). (If anything this bond order is slightly antibonding.) A structure such as 2y is completely ruled out.



However valence bond calculations,³⁹ allowing for a certain amount of 1,3-interaction, have produced results which are in good agreement with experimental observations.

2. Spectroscopic Evidence.

(a) Ultraviolet Data.

The normal λ_{\max} , characteristic of cyclohexenyl and linear alkenyl cations, occurs at 300-320 $m\mu$.^{1,4} As ring size decreases, a shift of λ_{\max} to lower wavelengths is observed, the limiting size being of course the cyclopropyl cation, for which λ_{\max} is below 185 $m\mu$.

The size of λ_{\max} has thus been attributed to the amount of homocyclopropenyl character the ion possesses. Low values have been noticed

particularly for cyclobutenyl ions,^{4,21,22} where stereochemical factors would also favour 1,3-interaction.

However, U.V. measurements are not always completely reliable, as impurities present even in very low concentrations can lead to erroneous results, and therefore these observations are not conclusive.

(b) Nuclear Magnetic Resonance Data.

A very large amount of information about charge distribution has been acquired from N.M.R. studies. The relationship between chemical shifts and π electron densities is now fairly well established.⁴⁰ Although discrepancies have been observed, reasonable linear relationships have been reported between proton and C^{13} magnetic resonance shifts with electronic charge.⁴¹⁻⁴⁶ Thus if a graph is plotted of C^{13} shift against the theoretically calculated electron density in one system, it is possible, from a knowledge of C^{13} shift in a second system, to obtain, from the graph, the electron density in the second system.

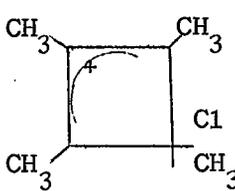
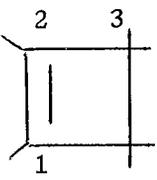
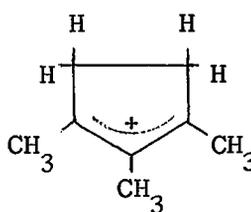
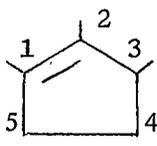
However, while it is possible to draw good correlations between molecules of the same type, comparisons between molecules of different types have frequently proved misleading. For example, the relative downfield shift for a carbon atom per unit electronic charge in an aromatic system^{45,46} is completely different from that observed for a simple alkyl cation.^{42,43} This is hardly surprising, as other factors than π -electron distribution affect the chemical shift.⁴⁷ Thus while C^{13} measurements can be used quite adequately to calculate electron distribution in similar systems, great care must be taken in drawing comparisons between unrelated systems.

1. C^{13} N.M.R. Measurements.

Recently C^{13} work has been carried out on some simple allyl cations.³³ The results are presented below in Table 1.

TABLE 1

C^{13} Chemical Shifts of Allyl Cations and Reference Olefins in SO_2ClF at -70°

Cation	Ion No.	$^{13}C^a$		Reference Olefin	$\delta^{13}C_R^b$	$\Delta\delta C_2^c$
		$C_1 C_3$	C_2			
$\begin{array}{c} 1 \quad 2 \quad 3 \\ (CH_3)_2 C=C^+-C(CH_3)_2 \\ \\ CH_3 \end{array}$	<u>2m</u>	-31.3	+41.3	$\begin{array}{c} 1 \quad 2 \quad 3 \\ (CH_3)_2 C=C(CH_3)CH(CH_3)_2 \end{array}$	+54.4	-13.1
$\begin{array}{c} (CH_3)_2 C=C^+-C(CH_3)_2 \\ \\ H \end{array}$	<u>2j</u>	-41.0	+51.6	$(CH_3)_2 C=CHCH(CH_3)_2$	+61.4	-9.8
$\begin{array}{c} CH_3 CH=C^+-CHCH_3 \\ \\ CH_3 \end{array}$	<u>2f,g,i</u>	-36.0	+33.2	$CH_3 CH=C(CH_3)CH_2 CH_3$	+56.8	-23.6
$\begin{array}{c} CH_3 CH=C^+-CHCH_3 \\ \\ H \end{array}$	<u>2c-e</u>	-46.6	+41.9	$CH_3 CH=CHCH_2 CH_3$	+59.5	-17.6
$\begin{array}{c} CH_3 CH=C^+-CHCH_3 \\ \\ C_6H_5 \end{array}$	<u>2n</u>	-42.7	+31.8	$CH_3 CH=C(C_6H_5)CH_2 CH_3$	+48.5	-16.7
	<u>4a</u>	-1.6	+16.9		+51.1	-34.2
	<u>7j</u>	-54.3	+37.4		+53.0	-15.6

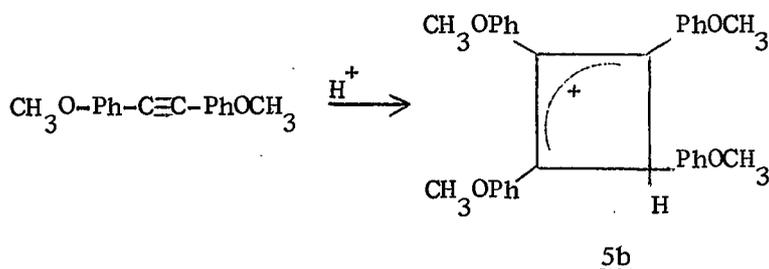
^a In p.p.m. from CS_2 .

^b $\delta^{13}C_R$ is chemical shift of C_2 in reference olefin in p.p.m. from CS_2 .

^c $\Delta\delta$ is difference in chemical shift of C_2 in the allyl cations and $\delta^{13}C_R$.

It was found that for open allyl cations (i.e. propenyl cations) and a cyclopentenyl cation, C_2 was shifted downfield by between 9 and 24 p.p.m. However C_2 for a cyclobutenyl cation was shifted downfield by 34 p.p.m. The authors interpret this as indicating that 1,3-interaction is possible in the cyclobutene ring, where steric factors encourage it, but is not likely in the open allyl system.

C^{13} N.M.R. measurements have also been carried out on a number of tetra-p-anisyl cyclobutenyl cations,²² generated from acetylenes, (Section 1.2.B1(a)1).



π -electron densities were calculated from the chemical shifts⁴⁰ and compared with those calculated by S.C.F. methods. The best agreement between experimental and theoretical calculations was obtained when some allowance was made for 1,3-interaction in the S.C.F. treatment.

2. 1H N.M.R. Measurements.

Proton magnetic resonance spectra have provided a very useful means of examining allyl cations.

(i) Propenyl Cations.

Table 2 presents the information obtained for a series of propenyl cations. The chemical shift of the hydrogen or methyl group at the 2-position should give some indication of the amount of charge localized on this position (i.e. the extent of 1,3-interaction taking place). For ions 2c-m variations in the chemical shifts of the 2-substituents are small. However for simple allyl cation 2a¹⁵ and the 2-methyl allyl cation 2b,¹⁵

TABLE 2
N.M.R. Data on Propenyl Cations.^a

Cation	Ion. No.	C ₁ ^b CH ₃ [H] ^c	C ₂ CH ₃ [H]	C ₃ CH ₃ [H]	Ref. No.
	2a	[8.97]	[9.64]	[8.97]	15
	2b	[8.95]	3.85	[8.95]	15
	2c	3.38 [9.88]	[8.24]	3.38 [9.88]	19
	2d	3.58 [10.00]	[8.30]	3.58 [10.00]	19
	2e	3.46 [9.97]	[8.31]	3.46 [10.61]	19
	2f	3.26 [9.73]	2.49	3.26 [9.73]	19
	2g	3.37 [9.73]	2.69	3.37 [9.73]	19
	2h	3.54, 3.41	2.38	[8.27] [7.72]	19
	2i	3.26 [9.73]	2.59	3.26 [10.46]	19
	2j	2.91	[7.83]	2.91	13
	2k	3.31, 3.22	2.37	2.97	19
	2l	3.15, 1.72	[8.10]	3.15	13
	2m	3.10, 2.94	3.30	3.10, 2.94	19

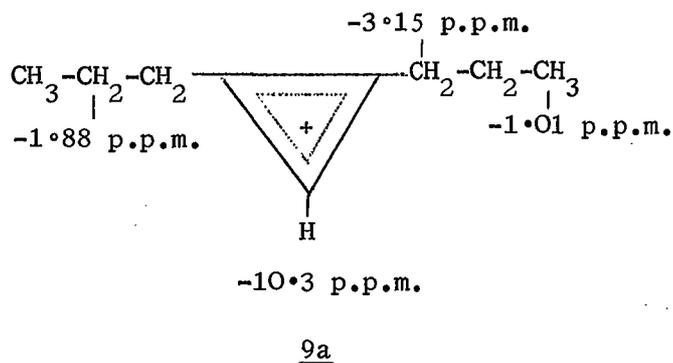
^a Chemical shifts in p.p.m. downfield from T.M.S.

^b C₁ substituent on carbon atom at position 1; as indicated in the allylic cation.

^c Figures in brackets are for hydrogen at this position.

the 2-substituents appear substantially further downfield than those in the rest of the series.

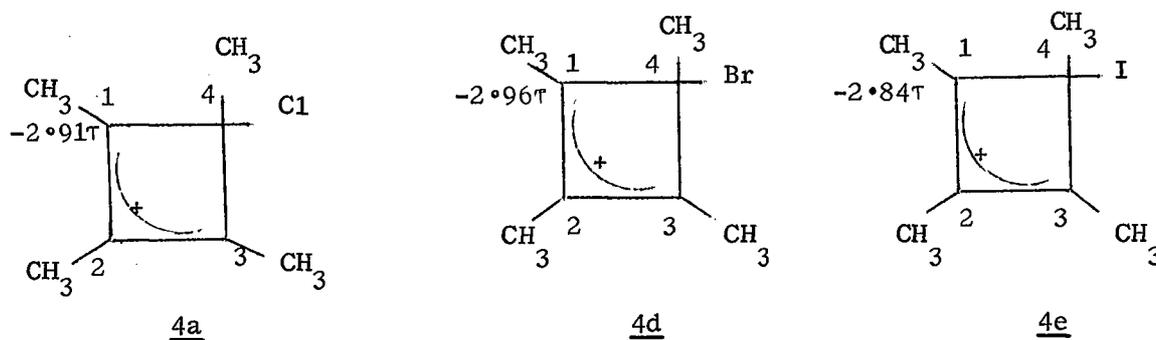
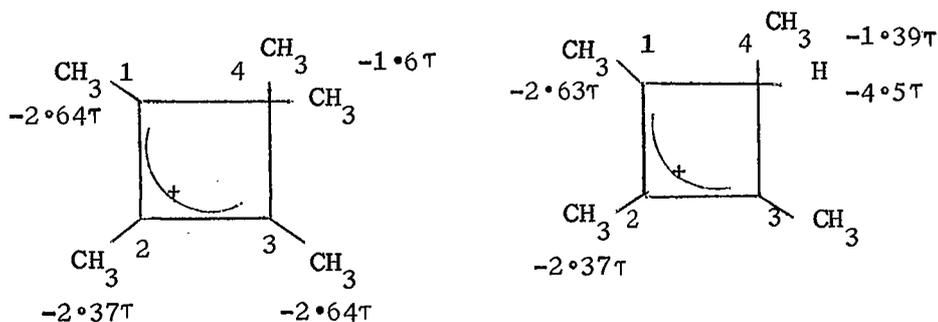
In fact the hydrogen at the 2-position in the allyl cation 2a has been compared to the single hydrogen in the cyclopropenium ion 9a^{24,26}



which also appears at very low field. This would seem to indicate that ion 2a possesses cyclopropenium character.

(ii) Cyclobutenyl Cations.

The alkyl substituted cyclobutenyl cations which have been prepared are shown below. In the cases of ions 4a, d and e, the authors have not distinguished between the methyl groups at the 2 and 4-positions.



(Chemical shifts in p.p.m. downfield from T.M.S.).

The positions of these signals are in the same regions as those observed for the open propenyl cations, although in the cyclobutenes the methyl groups at the 1 and 3 positions appear slightly further upfield.

(iii) Cyclopentenyl and Hexenyl Cations.

The N.M.R. data available on cyclopentenyl and hexenyl cations is presented in Table 3. Again it can be seen that absorptions occur in the regions observed for other allyl cations. However, in particular two interesting points do arise:

1. The substituents at the 2-position show little sensitivity to alkyl substitution or to the type of cation (i.e. cyclopentenyl or cyclohexenyl). The position of the 2-hydrogen varies only from -7.5 to -7.7 p.p.m. and the 2-methyl from -2.12 p.p.m. to -2.15 p.p.m.
2. The positions of the hydrogen atoms α to the allylic system also vary only slightly from cyclopentenyl to cyclohexenyl ions, occurring in the range -2.7 to -3.6τ .

These observations imply that the hydrogen atoms in these positions contribute little to the charge delocalization.

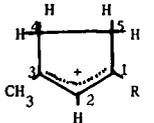
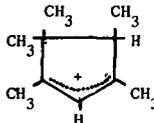
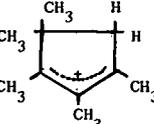
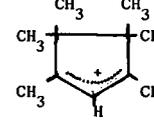
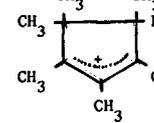
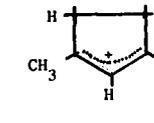
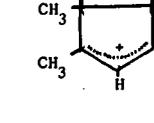
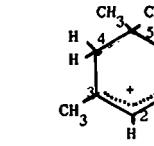
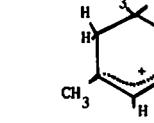
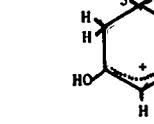
Thus while the large amount of p.m.r. data now available on allyl cations is extremely useful in identifying new allylic systems and, to a certain extent, in distinguishing between them, it cannot really be used to draw definite conclusions about the electronic structure of these species.

3. Chemical Evidence.

Kinetic results have also been used as evidence for and against 1,3-interaction in transition states. Secondary deuterium isotope effects have been investigated in solvolysis reactions of some allyl and β -aryl allyl tosylates,⁴⁸ and the results have shown that in the

TABLE 3
N.M.R. Spectra of Cyclopentenyl and Cyclohexenyl
Cations.¹⁴

(Chemical Shifts in p.p.m. downfield from T.M.S.)

Cation	Ion No.	H on C ₂	H on C ₄ and C ₅	CH ₃ on C ₃ (and C ₁ when present)	CH ₃ on C ₂	CH ₃ of ethyl or isopropyl group	CH ₃ on C ₄ and C ₅
	R = methyl a	<u>7a</u>	7.64	3.55	2.98		
	ethyl b	<u>b</u>	7.65	3.51(3.4)	3.00	1.42	
	isopropyl c	<u>c</u>	7.68	3.54(3.4)	2.99	1.43	
		<u>7d</u>	7.62	3.37	2.93		1.37
		<u>7e</u>		3.30	2.87 2.78	2.15	1.39
		<u>7f</u>	7.49		2.90		1.33
		<u>7g</u>		3.2	2.81	2.15	1.34 1.38 1.28
		<u>7h</u>	6.81	3.33	2.63		
		<u>7i</u>	6.65		2.52		1.32 1.25
	R = methyl a	<u>8a</u>	7.62	3.06	2.84		1.10
	ethyl b	<u>b</u>	7.63	3.09	2.84	1.36	1.10
	isopropyl c	<u>c</u>	7.61	3.09	2.84	1.35	1.10
	phenyl d	<u>d</u>	7.59 → 8.38	3.42 2.93	2.76		1.16
		<u>8e</u>	6.78	2.83 2.71	2.45		1.12
		<u>8f</u>	6.20	2.71			1.10

intermediate allyl cation negligible positive charge is centred on the 2-position.

However rate enhancement in the solvolysis of 1-methyl cyclobutenyl bromide⁴⁹ has been interpreted as evidence for 1,3-interaction in the delocalized transition state.

Clearly, a great deal more information is required from all areas before investigations can be closed.

CHAPTER 2

Halogenated Carbocations

This chapter is concerned in general with the chemistry and formation of halogenated carbocations. However special attention will be drawn to fluorinated species, which have provided particularly interesting information and are especially relevant to the original work presented in this thesis.

2.1. Introduction.

The effect of a substituent on the electron density of a molecule is generally described⁵⁰ in terms of

(a) its inductive effect



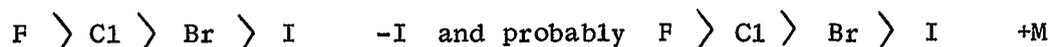
i.e. its tendency to attract or repel electrons according to its electronegativity, without changing the arrangement of the electron pairs in the molecule, and

(b) its mesomeric effect

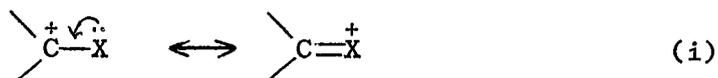


i.e. its tendency to extend the conjugation path by rearrangement of the electron pairs in an unsaturated molecule.

A consideration of the physical and chemical properties of the ground states of halogenated molecules shows the halogens to have a -I effect and a +M effect, and the magnitudes of these effects are in the order



Thus a halogen atom directly attached to a positively charged centre might be expected to stabilize that centre by back donation of its lone pair electrons (i.e. +M effect)

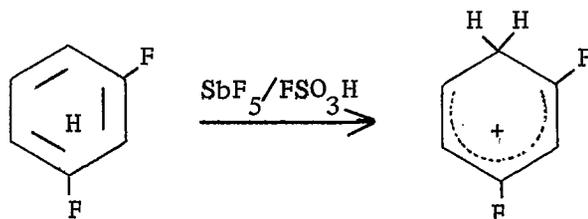
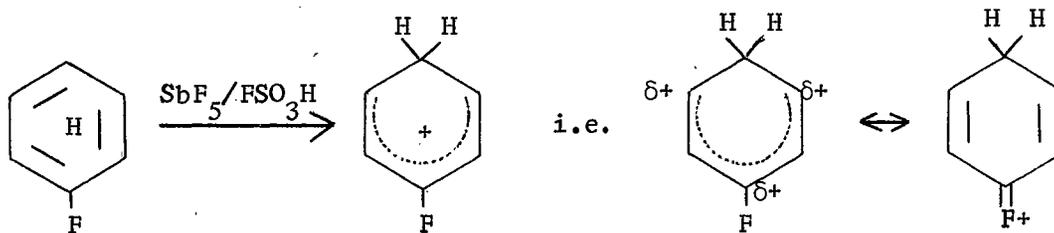


while one which is adjacent to a positively charged centre will have a destabilizing -I effect, i.e.

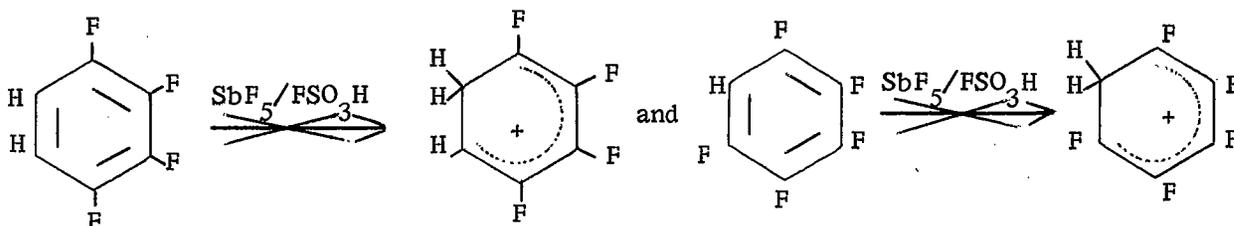


If the orders of magnitudes quoted above are correct it can be seen that both of these effects should be greatest for fluorine. Indeed, examples of the ability of the fluorine atom to exert a stabilizing effect in situations represented by (i) and a destabilizing effect in situations represented by (ii) are numerous.

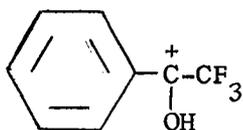
Protonation of fluorobenzenes⁵¹ occurs preferentially ortho or para to the fluorine atom, e.g.



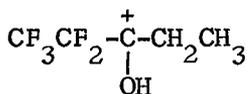
and the presence of a meta fluorine can prevent the protonation occurring:



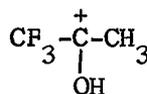
Another example of the destabilizing effect of a fluorine atom adjacent to a positively charged centre can be found in the series of protonated ketones 10a-c⁵² in which it was found that only ketones with



10a



10b



10c

up to three α -fluorine atoms could be protonated by $\text{SbF}_5/\text{FSO}_3\text{H}$.

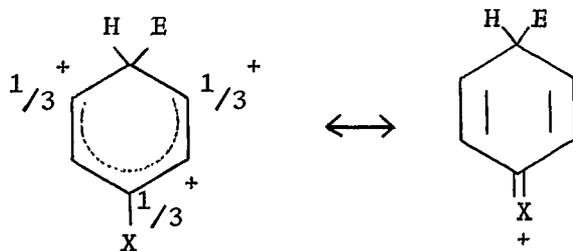
1,1,3,3-Tetrafluoroacetone and hexafluoroacetone with four and six α -fluorines respectively could not be protonated under the same conditions.

In the remainder of this chapter, an attempt will be made to draw attention to more examples of the effects of the fluorine atom in similar situations.

A. Experimental Evidence for the Electronic Effects of Halogen Atoms.

1. Electrophilic Aromatic Substitution.

Whilst the halogens generally deactivate the aromatic ring towards electrophilic aromatic substitution, they do direct substitution into the ortho- and para-positions.⁵³ Such an orientating effect cannot be explained in terms of the -I effect, but it is accounted for by conjugative interaction of the type:



where E = electrophile, X = halogen.

It can be seen from Table 4 that the magnitude of this effect is in the order $\text{F} > \text{Cl} > \text{Br}$. The preference of fluorobenzene for para

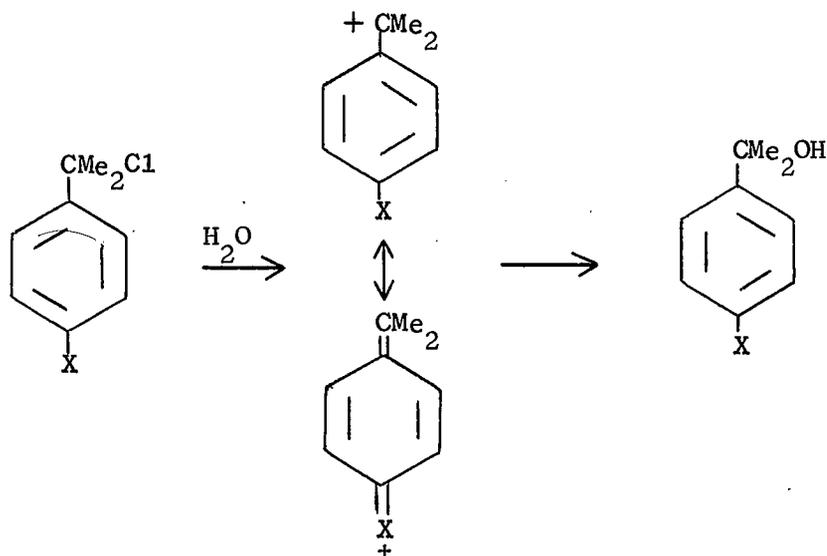
TABLE 4
Nitration of the Halobenzenes⁵³

Substituent	Relative Reaction Rate ^a	% Orientation		
		ortho	meta	para
F	0.15	12.4	87.6	
Cl	0.033	29.6	0.9	69.5
Br	0.030	36.5	1.2	62.4

^a Relative to benzene.

rather than ortho substitution indicates that the inductive effect of the fluorine is felt most strongly at the ortho-position.^{53,54}

In fact in chlorination reactions it has been found that fluorine actually activates the ring towards electrophilic attack.⁵³ This activating effect was also observed when Brown calculated σ^+ values for substituent effects in the reaction⁵⁵ in which the transition state



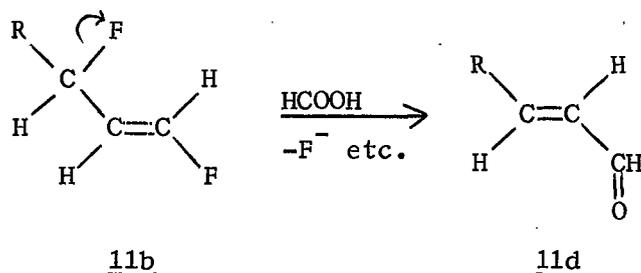
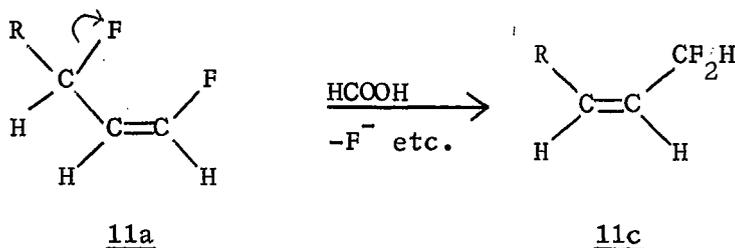
closely resembles the transition state in electrophilic aromatic substitution.

It was found that σ^+ para for fluorine had a negative (i.e. activating) value, in sharp contrast to the positive value for the other halogens. This is a clear indication that its +M effect out-weighs its -I effect in these circumstances.

The stabilizing influence of a para-fluorine has also been observed in calculations of the basicity of the triphenyl carbo-cation.⁵⁶ It was found that the electron supplying ability of the aromatic ring in such species decreased in the order 4-fluorophenyl > phenyl > 3-fluorophenyl.

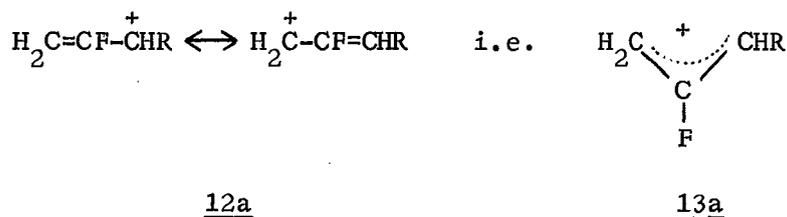
2. Solvolysis Reactions.

While the solvolysis of the cis- and trans-olefins 11a and 11b yielded 11c and 11d respectively,⁵⁷ their isomer $RCHFCF=CH_2$ 11e

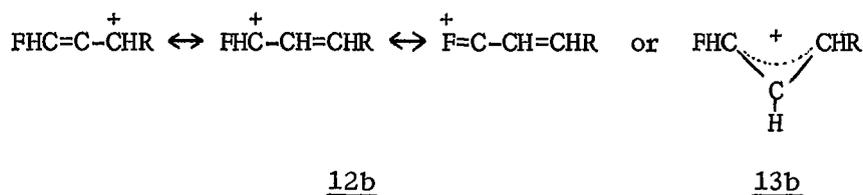


(where $R = \text{CF}_3\text{CH}_2\text{CHFCH}_2-$)

was completely unreactive. This low reactivity was attributed to the high energy requirements for an ion of the type



in which the fluorine atom is in a destabilizing position β to the positive charge, as opposed to ions

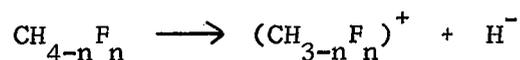


in which the positive charge is α to the fluorine atom.

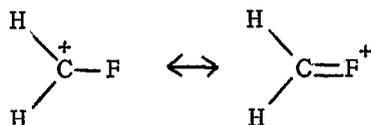
3. Physical Measurements.

(a) Molecular Orbital Calculations.

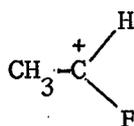
M.O. calculations by Baird and Datta have shown that the stability of fluoromethyl cations is increased with increasing fluorine substitution.⁵⁸ This is in opposition to the results previously obtained by Martin and Taft⁵⁹ from Appearance Potential measurements. However it seems likely that the latter results illustrated the increased stability of the neutral molecules to hydride abstraction rather than the decreasing stability of the cations.



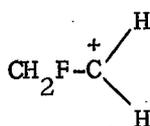
The calculations also indicated a short carbon-fluorine bond length in the ions, suggesting resonance structures of the type



Other M.O. calculations⁶⁰ have indicated that the 1-fluoroethyl cation 14d(i) is more stable than the ethyl cation itself and than the 2-fluoroethyl cation 14e(i).

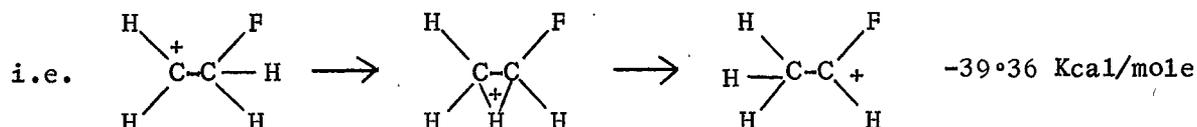


14d(i)



14e(i)

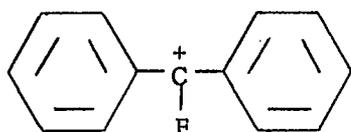
This has been attributed to fluorine's +M effect. It was also shown⁶¹ that 14e(i) could be converted to 14d(i) without an activation barrier via a bridged protonated fluoroethylene which was calculated to be 12.10 Kcal/mole more stable than 14e(i).



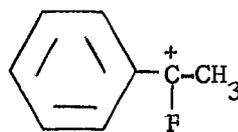
(b) F¹⁹ N.M.R. Measurements.

The deshielding of the proton N.M.R. signal by a positive charge was described in Chapter 1. The F¹⁹ N.M.R. resonance is affected in a similar way by a cationic centre. However the range over which the fluorine nucleus resonates is much greater than that for the proton, and hence F¹⁹ N.M.R. measurements provide a more sensitive means of measuring the extent of charge delocalization onto the fluorine atom.

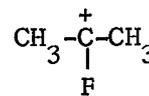
This is illustrated in the series of ions 16b(i), 15a(i) and 14b(i),⁶²



16b(i)



15a(i)



14b(i)

Chemical shift
of fluorine
(from CFCl₃)

-11.26 p.p.m.

-51.48 p.p.m.

-181.91 p.p.m.

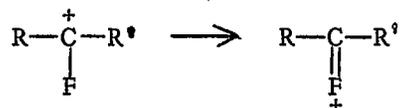
Deshielding
from precursor

-100.87 p.p.m.

-140.17 p.p.m.

-266.84 p.p.m.

in which the fluorine resonance moves further downfield as the delocalizing ability of the other substituents decreases and the contributions of resonance structures such as



(i.e. via +M effect) increases.

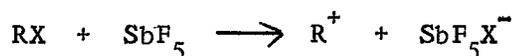
The major part of this chapter deals with the N.M.R. spectra of fluorinated cations, and from these spectra can be seen quite clearly the manner in which the charged species are affected by substituent fluorine atoms.

2.2. The Strong Acid Systems Antimony Pentafluoride in Sulphur Dioxide and Fluorosulphonic Acid/Antimony Pentafluoride.

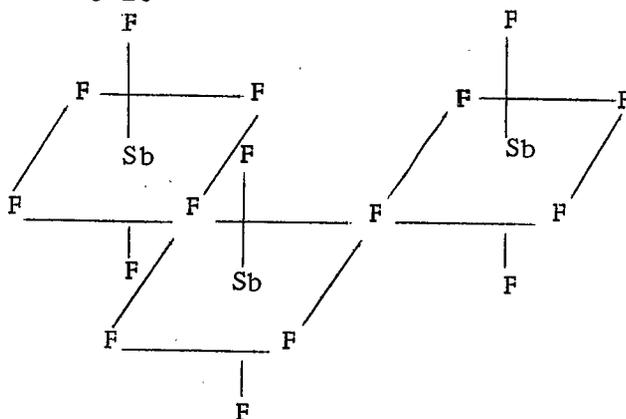
In recent years antimony pentafluoride has been used to an increasing extent as a Lewis Acid. A full survey of the reactions in which it has been involved is beyond the scope of this text, although numerous examples will be quoted in this chapter alone.⁶³ The use of SO₂ enables temperatures of -60° to be reached, and the systems can be cooled even further by using the solvent SO₂FCl (m.pt. -124.7°).

The acid strength of SbF₅/FSO₃H is second only to HF/SbF₅.⁶⁴⁻⁶⁶ Hammett acidity functions^{67,68} have not yet been calculated accurately but are estimated at ~ -17 (cf. H₀ for H₂SO₄ = -11, and for HSO₃F itself = -12.8).

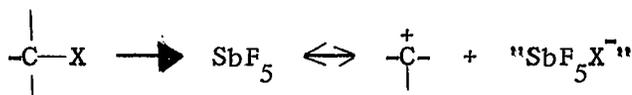
The simplest representation of the reaction between antimony pentafluoride and a neutral halide is abstraction of the halide ion to form the SbF₅X⁻ anion.



However, the situation is by no means as straightforward as this, as is evident from the fact that excess antimony pentafluoride is required to stabilize the systems. In fact, in the solvent systems used, polyanions $\text{Sb}_n\text{F}_{5n+1}$ (where $n \ll 4$) can exist^{69,70} and have been studied by their F^{19} N.M.R. spectra. These ions appear to have cis fluorine bridged polymeric structures, e.g. the $\text{Sb}_3\text{F}_{16}^-$ anion.



In some cases also it has proved extremely difficult to distinguish between donor-acceptor complexes and discrete ions.

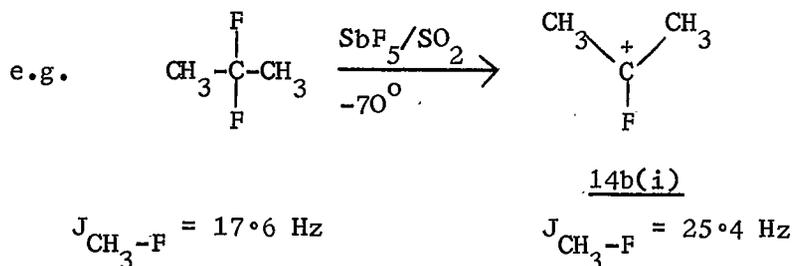


For example, in the reaction between alkyl fluorides and SbF_5 , species were formed in which the protons were not as deshielded as expected for alkyl cation formation, but in which proton-fluorine couplings had disappeared.^{71,72} However a detailed study of the F^{19} N.M.R. spectra of the polyanions showed that rapidly exchanging donor-acceptor complexes existed even at very low temperatures.⁷³

2.3. Halogenated Carbocations with Alkyl and Aryl Substituents.

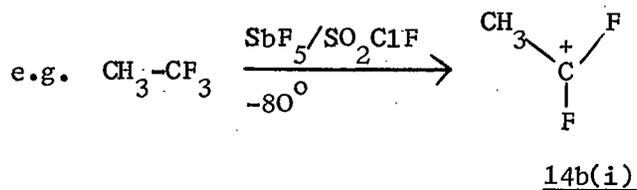
The ability of a fluorine atom to stabilize an adjacent positive charge is illustrated particularly well in this series of cations. The extent to which the fluorine atoms are deshielded is related directly to the amount of charge delocalized on them. In addition, the increased

coupling constants on ionization are strong evidence for a change in hybridization of sp^3 to sp^2 .

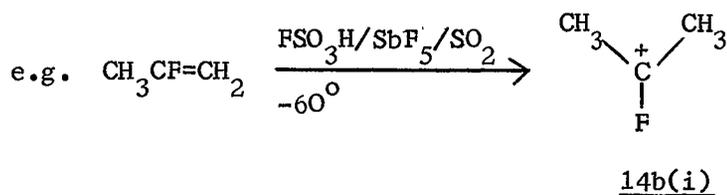


A. Halo-Alkyl Cations.

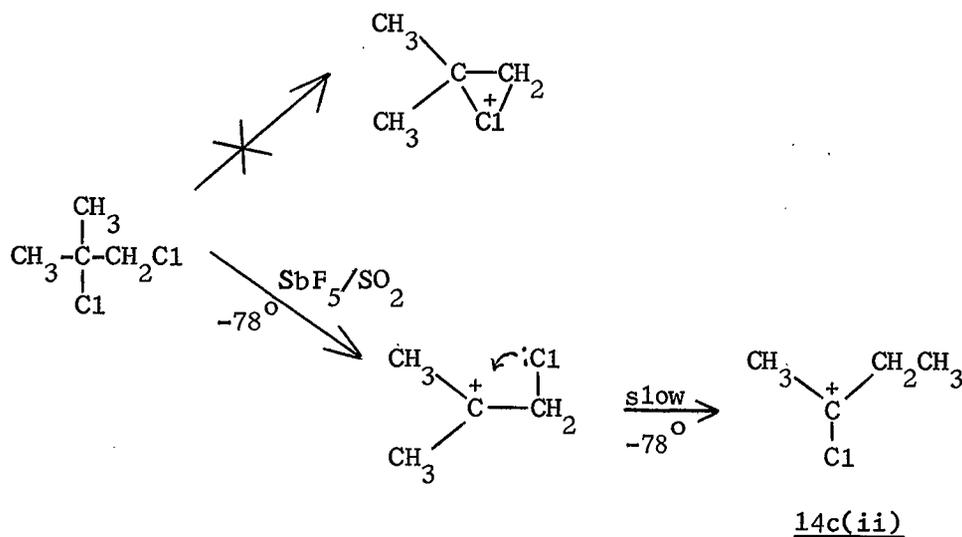
In general these systems are produced by either ionization of the appropriate haloalkane,^{62,74-77}



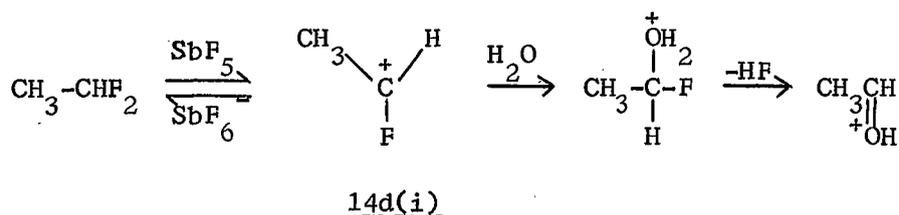
or protonation of the appropriate olefin⁷⁶



The 2-fluoro and 2-chloro-s-butyl cations were obtained in reactions intended to generate bridged halonium ions⁷⁸ (Section 2.4.).



It has not proved possible to observe directly any less substituted halo-alkyl cations. Attempts to observe the 1-fluoroethyl cation were unsuccessful.⁷⁵ Ionization of 1,1-difluoroethane with $\text{SbF}_5/\text{SO}_2\text{ClF}$ at -80° ⁷⁶ gave a species in which the p.m.r. showed a doublet at -4.32τ and a quartet at -10.47τ . Both of these signals are too shielded to belong to ion 14d(i) and from the absence of a fluorine signal (other than the solvent) and fluorine-proton coupling, it was concluded that exchange was occurring.



In the presence of water, protonated acetaldehyde was the sole product observed.

The N.M.R. data which is available on halo-alkyl cations is presented in Table 5. A comparison of the chemical shifts of the fluorine atoms

TABLE 5
N.M.R. Data^a of Halo-Alkyl Carbo-Cations

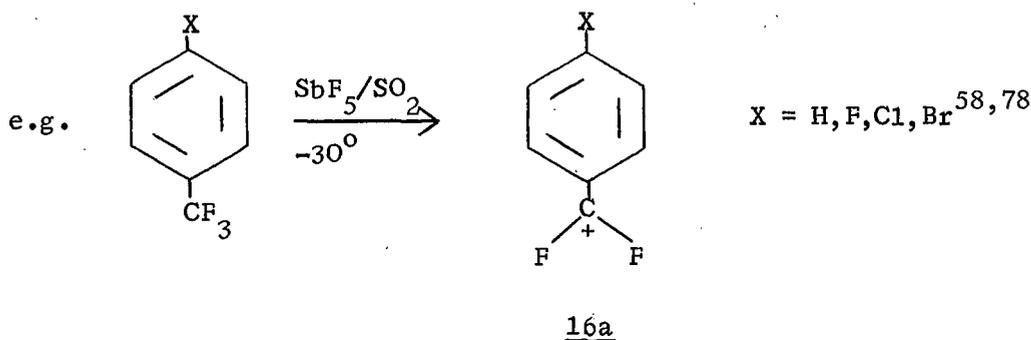
Ion	Ion No.	Saturated Precursor			Ion CH_2	Ref. No.
		X	CH_3	^{19}F		
$\text{CH}_3-\overset{+}{\text{C}}(\text{X})_2$	<u>14a(i)</u>	F	-2.0	62.0^b	-4.50	-96.4^c 74
	<u>14a(ii)</u>	Cl	-3.10		-4.60	74
$\text{CH}_3-\overset{+}{\text{C}}(\text{CH}_3)(\text{X})$	<u>14b(i)</u>	F	-1.30	84.93^d	-3.83	-181.91^e 62,75
	<u>14b(ii)</u>	Cl	-1.89		-4.06	62
	<u>14b(iii)</u>	Br	-2.38		-3.82	62
$\text{CH}_3-\text{CH}_2-\overset{+}{\text{C}}(\text{CH}_3)(\text{X})$	<u>14c(i)</u>	F			-3.88	4.49 78
	<u>14c(ii)</u>	Cl			-4.38	6.26 78

^a Chemical shifts quoted from references T.M.S. or CFC1_3 ; ^b $J_{\text{H-F}} = 14$ Hz;
^c $J_{\text{H-F}} = 17$ Hz; ^d $J_{\text{H-F}} = 17.6$ Hz; ^e $J_{\text{H-F}} = 25.4$ Hz.

in ions 14a(i) and 14b(i) shows the importance of fluorine in stabilizing these systems. Replacement of a fluorine in 14a(i) by a methyl group results in an ion 14b(i) in which the chemical shift of the remaining fluorine is 85.5 p.p.m. more deshielded than that of the 1,1-difluoroethyl cation 14a(i). This gives a good indication of the extent to which the single fluorine is stabilizing the cation by back donation of its lone pair electrons.

B. Halo-Alkyl/Aryl and -Aryl Cations.

These ions are generally prepared by the action of a Lewis Acid on the saturated parent halide^{62,79} or alcohol;⁵²



However one unusual method reported involves transfer of Cl^+ from antimony pentachloride to an olefin.⁸⁰

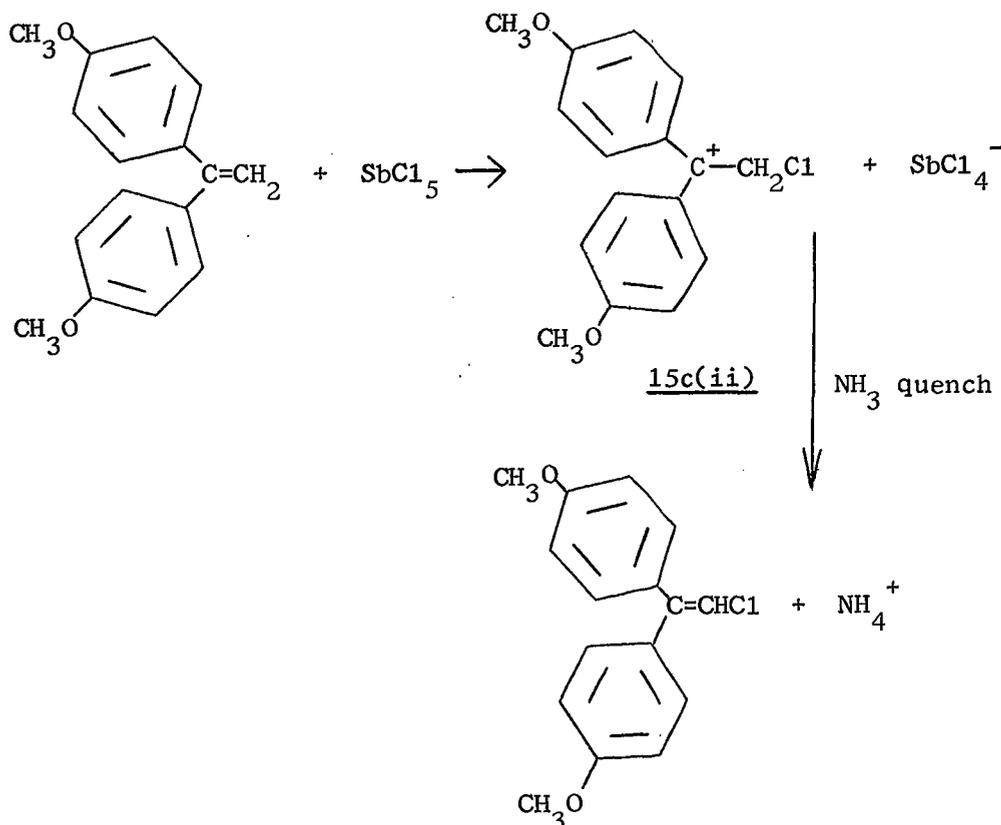
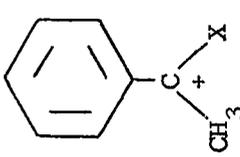
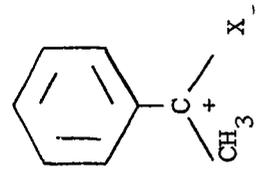


TABLE 6

N.M.R. Data^a of Halo-Phenyl Methyl Cations

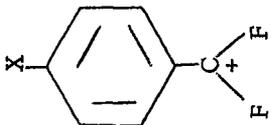
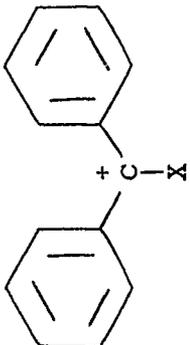
Ion	Ion No.	Precursor						Ion			Ref. No.			
		X	o	m	p	CH ₃	F	o ^s	m	p		CH ₃	F	
	<u>15a(i)</u>	F	-7.19	-7.19	-7.19	-1.62	+88.69 ^b	-8.83	-8.67	-7.90	-8.58	-3.46	-51.48 ^c	62
	<u>15a(ii)</u>	Cl	-8.50	-8.16	-8.16	-2.30	-8.81	-8.90	-7.87	-8.57	-3.72			62
	<u>15a(iii)</u>	Br	-7.47	-7.02	-7.02	-2.71	-8.80	-8.80	-7.83	-8.64	-3.82			62
	<u>15b(i)</u>	CF ₃		-7.12 ^d		-1.31	+81.1 ^e		-8.30 ^d		-3.30	+56.3 ^e	52	

^a Chemical shifts quoted in p.p.m. from T.M.S. or CFC1₃; ^b $J_{\text{CH}_3-\text{F}} = 17.8 \text{ Hz}$; ^c $J_{\text{CH}_3-\text{F}} = 22.8 \text{ Hz}$;

^d Average of signals quoted; ^e CF₃ group.

TABLE 7

N.M.R. Data^a of Halo-Aryl Carbo-Cations

Ion	Ion No.	Precursor				Ion				Ref. No.	
		X	O	m	p	CF ₃ [F] ^b	O	m	p		CF ₂ [F] ^b
	<u>16a</u>	H	-7.31	-7.15	-7.15	+63.63	-8.88	-8.04	-8.84	-11.99	62
	<u>16a(i)</u>	F	-7.36	-6.87 ^c	+108.52 ^d	+62.92 ^{c,d}	-9.00 ^e	-8.96	+40.41 ^f	-6.77 ^{e,f}	62,79
	<u>16a(ii)</u>	C1	-7.26	-7.15		+63.49	-8.80	-8.06		-8.61	62
	<u>16a(iii)</u>	Br	-7.23	-7.31		+63.54	-8.64	-8.23		-8.78	62
	<u>16b(i)</u>	F		↔	↔	+ [89.61]	-8.41	-7.86	-8.34	[-11.26]	62,79
	<u>16b(ii)</u>	C1		↔	↔		-8.17	-7.78	-8.27		62
	<u>16c</u>	Ph		-7.09 ^h		+74.1		-8.01 ^h		+66.5 ⁱ	52
	<u>16d</u>			-7.18 ^h		+78.4		-7.85 ^h		+69.3 ⁱ	52

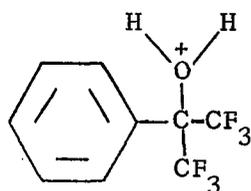
^a Chemical shifts in p.p.m. from T.M.S. or CFC1₃; ^b Figures in brackets represent single fluorine at this position;

^c J_{CF₃-o-H} = 0.5 Hz; ^d J_{CF₃-F} = 1.8 Hz; ^e J_{CF₂-o-H} = 1.1 Hz; ^f J_{CF₂-F} = 19.8 Hz; ^g No information given;

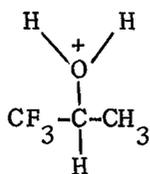
^h Average of signals quoted; ⁱ -CF₃ group.

The ion 15c(ii) was analysed by means of its U.V. and N.M.R. spectra, and by the product formed on quenching with ammonia.

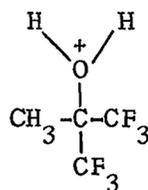
The N.M.R. data for a series of these ions is presented in Tables 6 and 7. Increased substitution by groups which can delocalize the charge results in more stable ions. This is particularly evident in the ions 15b(i), 16c and 16d⁵² which were generated from their parent alcohols by $\text{SbF}_5/\text{FSO}_3\text{H}$ in SO_2 , despite the presence of destabilizing trifluoromethyl groups. However, the presence of a second trifluoromethyl group, or absence of conjugative stabilization resulted in the formation of the protonated alcohols, 17a-c.



17a



17b



17c

C. Perfluorophenyl Cations.

The reaction of SbF_5 and $\text{SbF}_5/\text{FSO}_3\text{H}$ with a series of phenyl halides and carbinols has resulted in the preparation of an extremely interesting series of perfluorinated aryl cations,^{62,81-83} the N.M.R. data of which is presented in Table 8.

The large deshielding effects of the ortho- and para-fluorines show the high degree of charge delocalization at these positions and thus present strong evidence for the presence of resonance structures of the type:

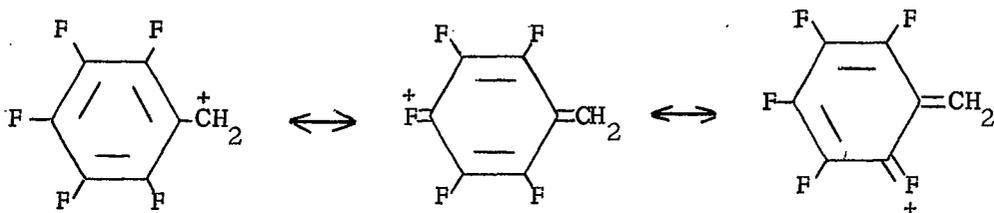
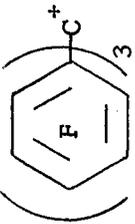
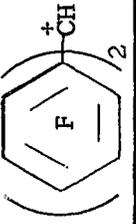
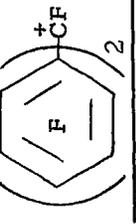


TABLE 8

 ^{19}F N.M.R. Data^a of Perfluoroaryl Cations

Ion	Ion No.	-CH	Precursor			CH ₂	o	ION	m	p	+ CF or CF ₂	Ref. No.
	<u>18a</u>		+140.98	+161.54	+152.22		+126.25	+154.29		+112.12		62 81 82
	<u>18b</u>	-3.67	+144.17	+162.28	+153.69	-10.10	+111.61	+153.86		+100.36		62 82
	<u>18c</u>	-5.47	+143.57	+162.53	+152.27	-9.60	+103.18	+151.53		+74.89		62 82
	<u>18d</u>								b ↔	-63	-202	83
	<u>18e</u>								b ↔	-84	-203	83

^a Chemical shifts in p.p.m. from CCl₄; ^b Shifts for precursors not quoted.

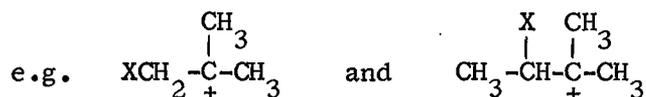
It is also noticeable that the deshielding of the ortho- and para-fluorines increases substantially as the number of pentafluorophenyl groups is reduced, in the series 18a-c. Only in the less substituted ions does the deshielding of the ortho- and para-fluorines approach that observed in benzenium ions (Section 2.5.B.).

2.4. Bridged Halonium Ions.

The electrophilic attack of bromine on olefins is generally considered to proceed by a bromonium ion intermediate. Such a mechanism has been used to explain the stereospecificity of the addition.

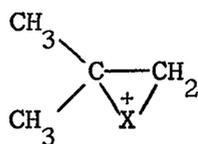
Halonium ions were also postulated in solvolysis reactions to account for the halogen shifts observed.⁸⁴⁻⁸⁸ However in none of these reactions were the intermediate ions isolated or observed directly. Thus the recent identification of a series of such ions has been greeted with a great deal of enthusiasm and has stimulated extensive investigation into their structure and reactivity.

The ions have been analysed by N.M.R. spectroscopy which has proved extremely successful in differentiating between the bridged ions and rapidly equilibrating open chain structures by examination of the couplings involved.⁷⁸ In open chain ions,



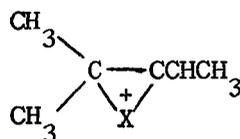
X = Cl, Br, I

long range methyl coupling through the sp^2 hybridized cationic carbon atoms should be observed, as in the t-amyl cation⁷⁷ whereas bridged ions, such as 19c and 19d should show no (or a very small) methyl coupling as in cyclopropyl compounds.^{78a}



19c

and

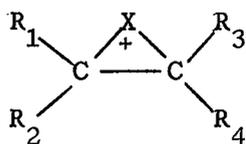


19d

X = Br, I

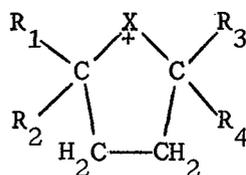
A, Types of Ion.

Ring size is an important factor in the stability of bridged halonium ions. A series of three^{78,89,90} and five^{91,92} membered ring ions have been prepared and studied.



19

- | | | | |
|---------|-----------------------------------|----------------|----------|
| where a | $R_1 = R_2 = R_3 = R_4 = H$ | } X = (iii) Br | |
| b | $R_1 = CH_3, R_2 = R_3 = R_4 = H$ | | (iv) I |
| c | $R_1 = R_2 = CH_3, R_3 = R_4 = H$ | | |
| d | $R_1 = R_2 = R_4 = CH_3, R_3 = H$ | } X = (ii) Cl | |
| e | $R_1 = R_2 = R_3 = R_4 = CH_3$ | | (iii) Br |
| | | | (iv) I |



20

- | | | | |
|---------|-----------------------------------|---------------|----------|
| where a | $R_1 = R_2 = R_3 = R_4 = H$ | } X = (ii) Cl | |
| b | $R_1 = CH_3, R_2 = R_3 = R_4 = H$ | | (iii) Br |
| c | $R_1 = R_3 = CH_3, R_2 = R_4 = H$ | | (iv) I |
| d | $R_1 = R_2 = CH_3, R_3 = R_4 = H$ | | |

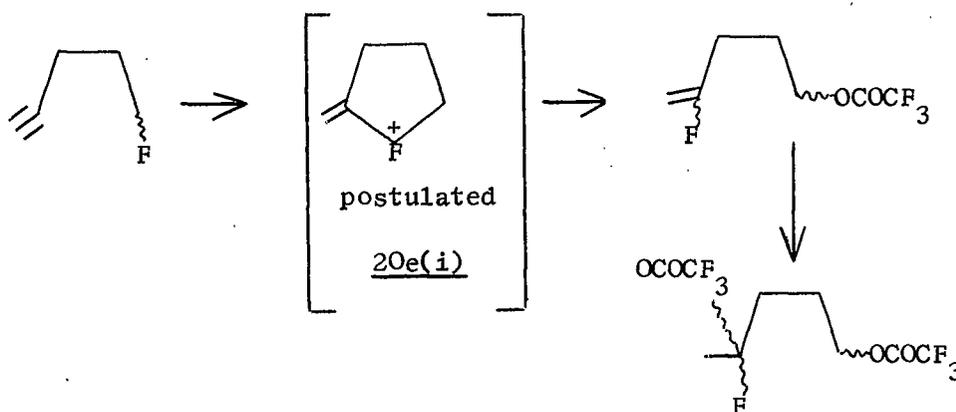
For the ethylene halonium ions 19a-e the $>CH_2$ groups experience downfield shifts in the region of two p.p.m., while the methyl substituents are deshielded by about one p.p.m. Similar results are obtained for the tetramethylene halonium ions.

Attempts to prepare four membered ring halonium ions have been unsuccessful,⁹³ resulting in three or five membered ring species.

B. Bridging Ability of the Halogen Atoms.

The ability of the halogen atoms to bridge follows the trend expected from their relative sizes and polarizability etc., i.e. $I > Br > Cl > F$. In fact it has proved impossible to prepare stable three membered ring chloronium ions with less than three methyl substituents (as can be seen in the series of ions presented in Section 2.4.A.).

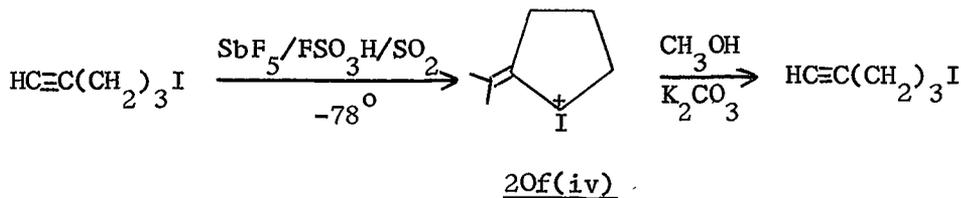
There is no direct experimental evidence available for the existence of fluorine bridged species, although a fluoronium ion intermediate has been postulated to explain the 1,4-fluorine shift in the reaction of 5-fluoro-1-pentyne with trifluoroacetic acid:⁸⁵



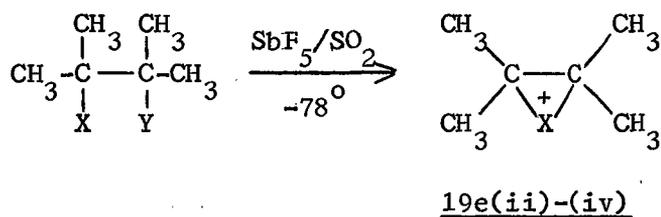
In fact the saturated product was obtained. However this was not considered surprising as a separate experiment showed that 2-fluoropropene is 200 times more reactive to trifluoroacetic acid than 2-chloropropene.

However a later attempt by Olah and co-workers to generate this ion by the reaction of 5-fluoro-1-pentyne with SbF_5/FSO_3H ⁹² was unsuccessful, producing, even under the most controlled reaction conditions, uninterpretable N.M.R. spectra.

However the corresponding iodo alkyne did produce the expected iodonium ion,⁹² although starting material was obtained on quenching with methanol.



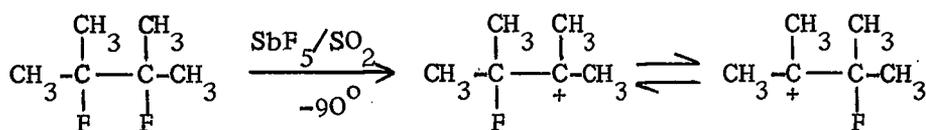
Similarly whilst a series of tetramethyl-ethylene chloronium, bromonium and iodonium ions have been prepared⁹⁰ the corresponding



X = Cl, Br, I

Y = F, Cl, Br

2,3-difluoro-2,3-dimethylbutane is reported to give equilibrating open chain ions, even at -90° :

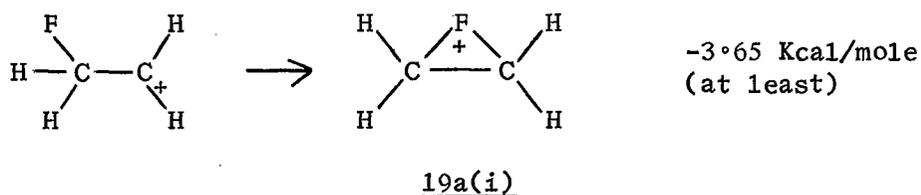


This analysis is based on two major observations:

- (a) The downfield shifts of the methyl groups (-1.76 p.p.m.) is almost twice that observed for the chloronium ion (0.95 p.p.m.) and much greater than that expected on the basis of electronegativity. It is in fact more comparable to the deshielding observed in open chain rapidly equilibrating alkyl cations.
- (b) A downfield shift of only 31 p.p.m. is observed for the single fluorine. This is more consistent with a β -fluorocarbo-

cation than a bridged species in which a substantial amount of charge would be located on the bridging fluorine.

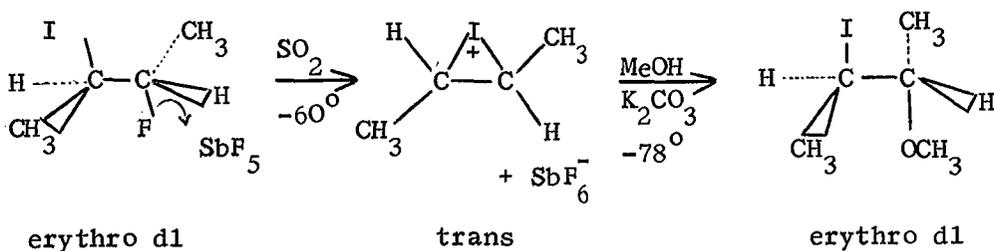
However, although there is no direct experimental evidence for fluoronium ion intermediates, M.O. calculations⁹⁴ predict that the bridged ethylene fluoronium ion should be more stable than the 2-fluoroethyl cation.



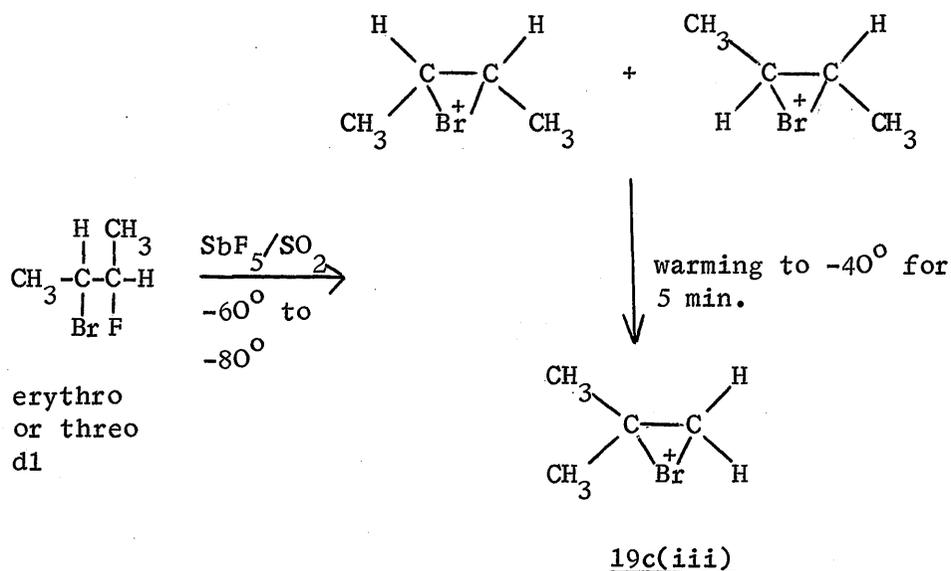
It is hoped that measurements of molecular core binding energies might help to distinguish between the two possibilities.

C. Synthesis and Uses.

In general these ions have been generated by ionization of haloalkanes, -alkenes, or -alkynes, although protonation of alkenes⁹² and cyclopropyl halides^{13,93} also has generated bridged halonium ions. Some examples of these ionizations have already been mentioned. They can be stereospecific, as in the case of 2-iodo-3-fluorobutane:⁸⁹

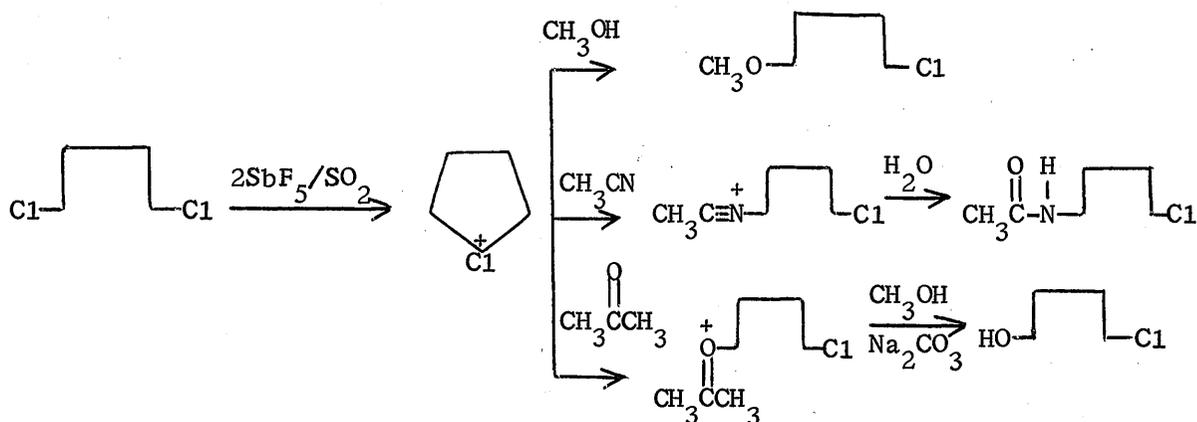


or non-stereospecific as in the case of 2-bromo-3-fluorobutane.⁸⁹



In both cases, the loss of fluorine rather than bromine or iodine is particularly interesting, as the ease of ionization of alkyl halides usually occurs in the order $\text{I} > \text{Br} > \text{Cl} > \text{F}$. Clearly this is an indication of the relative instability of a bridged fluoronium ion.

Tetramethylene halonium ions have been studied with respect to their utility as alkylating agents,⁹⁵ e.g.



This is an area in which further development seems likely in the future.

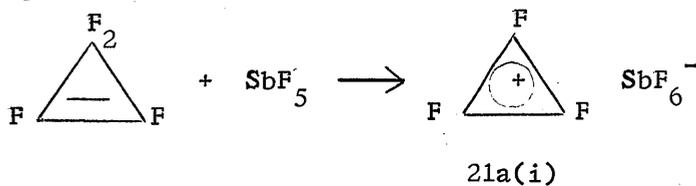
2.5. Halo-Arenium Ions.

A. Cyclopropenium Ions.

The formulation by Hückel of the $(4n + 2)$ π -electron rule for aromaticity sparked off numerous investigations into previously unprepared systems which theoretically obeyed this rule.⁹⁶ The first member ($n = 0$) of this series is the cyclopropenium ion. Predictions regarding the stability of this system were confirmed initially by the synthesis of cyclopropenium salts⁹⁷ and later by N.M.R. investigations.²⁴⁻²⁶ Recently the field has been extended into the halogenated cations.

1. The Trifluorocyclopropenium Cation.

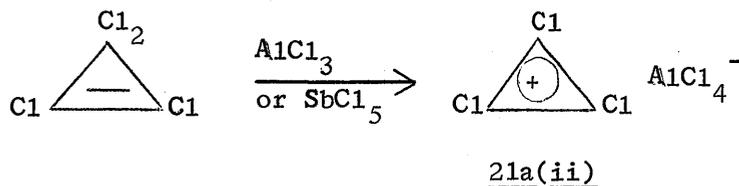
This cation was generated by the reaction of perfluorocyclopropene with antimony pentafluoride:⁹⁸



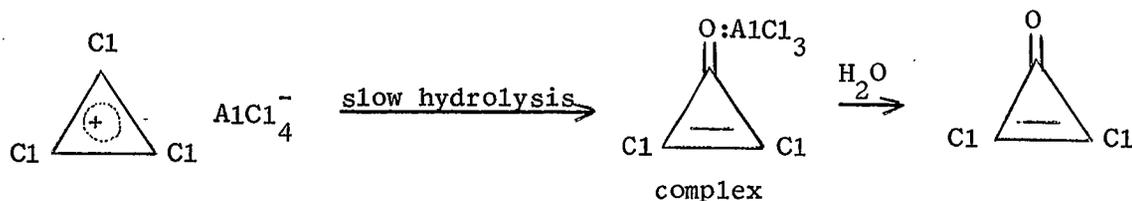
The ion was isolated as a white crystalline salt and its F^{19} N.M.R. spectrum showed a single peak at $+63.1$ p.p.m. from CFCl_3 , substantially deshielded from the signals of the starting olefin at $+96.7$ p.p.m. (CF_2 -) and $+145$ p.p.m. (vinyl fluorines).

2. The trichlorocyclopropenium Cation.

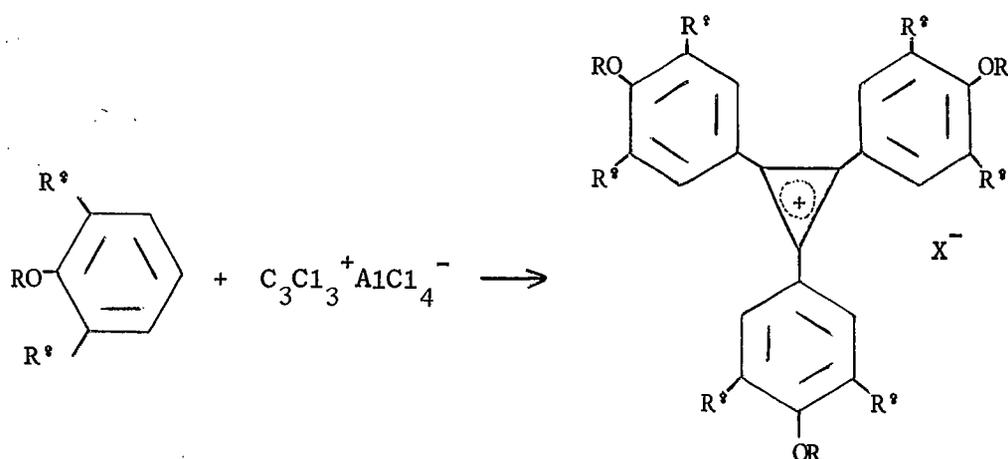
This was the first of this series of ions to be isolated as a crystalline salt,⁹⁹ in the reaction between a Lewis Acid and tetrachlorocyclopropene.¹⁰⁰⁻¹⁰²



Its physical¹⁰³ and chemical¹⁰⁴ properties have been fully investigated. Hydrolysis with water occurs via attack on the AlCl_4^- ion (See Section 2.6.A.1.(b).2.) and yields the dangerously unstable dichlorocyclopropenone.¹⁰⁵



An extremely useful reaction of the trichlorocyclopropenium ion is its Friedel Crafts-type condensation with aromatic compounds¹⁰⁶ leading to mono-, di- or tri-aryl cyclopropenium ions, the final substitution only occurring with an activated aromatic compound.



a $\text{R} = \text{Me}$, $\text{R}^* = \text{H}$ d $\text{R} = \text{H}$, $\text{R}^* = i\text{-Pr}$

b $\text{R} = \text{H}$, $\text{R}^* = \text{H}$ e $\text{R} = \text{H}$, $\text{R}^* = t\text{-Bu}$

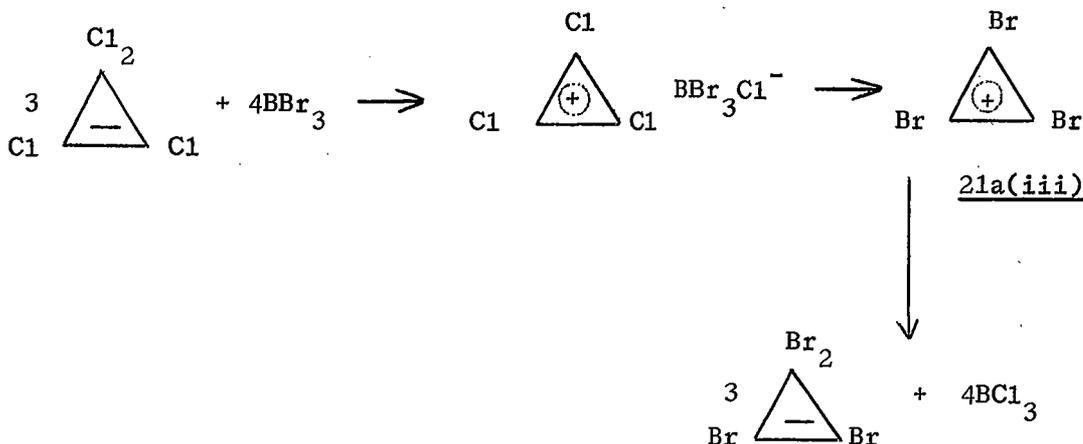
c $\text{R} = \text{H}$, $\text{R}^* = \text{Me}$

$\text{X} = \text{Cl}$, Br or ClO_4

3. The Tribromocyclopropenium Ion.

The trichlorocyclopropenium ion reacts vigorously with BBr_3 to produce tetrabromocyclopropene quantitatively.^{99,102} The reaction is presumed to go via the tribromocyclopropenium ion 21a(iii), although no

salt precipitates out.



Treatment of tetrabromocyclopropene with aluminium tribromide gives salts of the C_3Br_3^+ ion, whose chemistry has not yet been investigated.

B. Benzenium Ions.

From a consideration of the deactivating effects of halogen atoms on electrophilic substitution in aromatic rings, one would anticipate difficulty in generating stable benzenium ions. However partially and totally halogenated ions have now been observed by N.M.R. spectroscopy.

1. Protonated Halo- and Halo-methyl Benzenes.

The protonation of halobenzenes can be carried out in the strong acid systems antimony pentafluoride/hydrogen fluoride^{107,108} and antimony pentafluoride/fluorosulphonic acid^{51,109} at temperatures ranging from -60° to -10°C . In general the position of protonation is governed by the halogen atom which directs electrophilic attack to positions ortho and para to itself. The presence of a para-substituent (halogen or methyl) has an especially stabilizing effect on the protonated species.

Protonation is not usually observed at ring positions which are already substituted. (The one exception to this rule will be discussed in context). Protonation at a ring site already substituted by a halogen

TABLE 6
 ^{19}F N.M.R. Data on Fluorobenzenium and Methylfluorobenzenium Ions

Ion No.	Benzenium Ion	Chemical Shift of Parent Fluorobenzene p.p.m.	Chemical Shift of Fluorobenzenium Ion, p.p.m.			Ref. No.
			o-F	m-F	p-F	
23a(1)		+100.3		+11.2	51	
23b(1)		+104.8	+8.3	+3.7	51	
23c(1)		+113.2	+1.7 ^b	+100	51	
23e(1)		+101.0	+21.2	-5.4	51	
23f(1)		+108.8 +125.2 +133.8	+17.7	+118.2	-0.07	51
23g(1)		+107.6 +124.4 +156.3	+50	+143.0	+14.2	51
24a(1)		+110.0		+15.7	109	
24c(1)		+107.8		+19.3	109	
24e(1)		+111.7	+14.2		109	
24f(1)		+107.0 +107.9	+12.2	+2.87	109	
24g(1)		+117.0 +113.5	+15.1	+103.8	109	
24h(1)		+130.1 +140.6	+54.6	+122.2	109	
24a(1)		+119.5		+111.2	109	
24b(1)		+115.0		+103.7	109	
24k(1)		+114.3	+35.8	+1.8	109	

^a Chemical shifts in p.p.m. from CFCl_3 .

^b Misquoted as p-fluorine.

atom would lead to loss of conjugative interaction between the halogen atom and the aromatic π -electrons,¹⁰⁷ and in no case is this observed.

Where a choice of sites is available for protonation, a mixture of isomeric ions is often formed. These can generally be separately identified by means of N.M.R., as the chemical shifts of the ring, methylene and methyl protons are usually sufficiently different to give well separated resonance signals.

The proton magnetic resonance data is presented in Tables 10, 11 and 12. Deshielding effects on the ring and methyl protons follow the expected pattern. These effects are emphasised in the F^{19} N.M.R. spectra of the fluorinated benzenes (Table 9) in which it can be seen that a fluorine atom in a position meta to the positive charge is deshielded by only up to about 20 p.p.m., while the deshielding effect on fluorines in the ortho- and para-positions is in the order of 100 p.p.m., being slightly greater for the para-fluorine.

This is a clear example of the amount of back donation of charge which occurs when fluorine is directly attached to a positive centre, as mentioned in Section 2.1.A.3.(b).

(a) Mesitylenes.

The p.m.r. spectra of the halomesitylenium ions is presented in Table 10. Despite the deactivating effect of the meta-halogens, protonation usually occurs at an unsubstituted ring site. The one exception to this is trifluoromesitylene, in which the ion 22c(i) is formed:¹⁰⁹

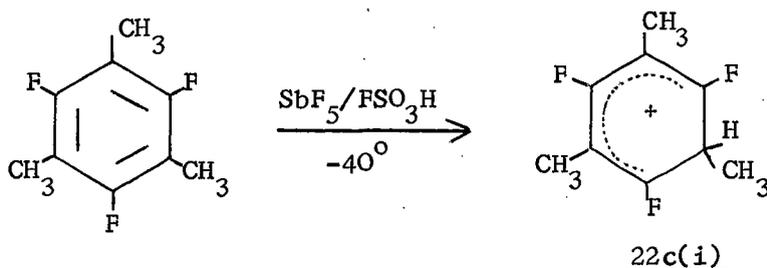
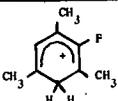
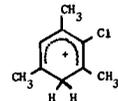
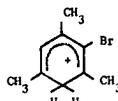
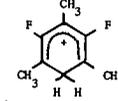
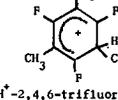
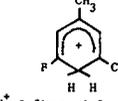
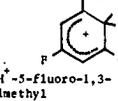
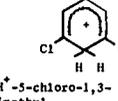
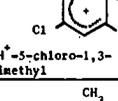
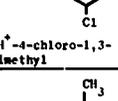
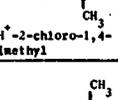
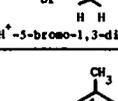
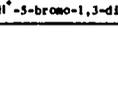
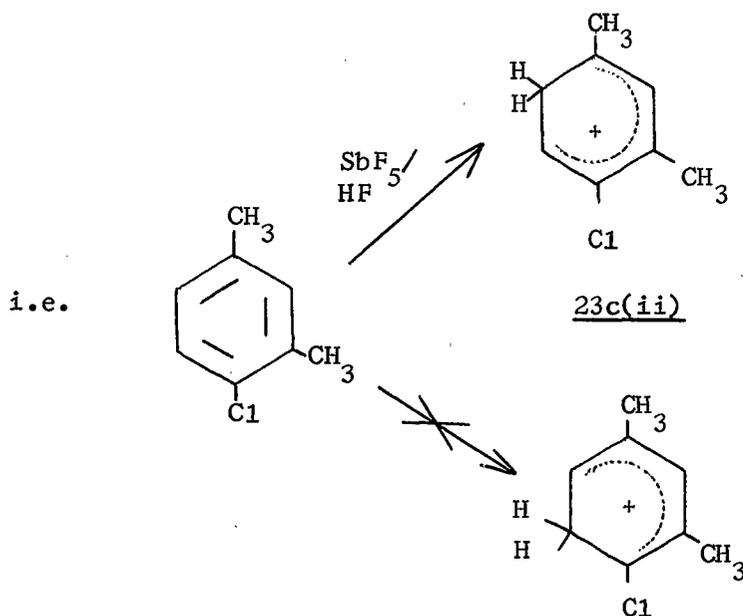


TABLE 10
P.M.R. Spectra of Halo-Mesitylenium and Xylenium Ions

Ion No.	Benzenium Ion	Chemical Shift in p.p.m. from T.M.S.						Ref. No.	
		o-H	m-H	CH ₂ or H ^{CH₃}	p-CH ₃	o-CH ₃	m-CH ₃		
22a(1)	 4H ⁺ -2-fluoro-1,3,5-trimethyl		-7.71	-4.78	-2.90	(3) -2.69 (5) -2.81	107		
22a(11)	 4H ⁺ -2-chloro-1,3,5-trimethyl		-7.77	-4.80	-3.03	(3) -2.83 (5) -2.81	107		
22a(111)	 4H ⁺ -2-bromo-1,3,5-trimethyl		-7.77	-4.83	-3.06	(3) -2.86 (5) -2.78	107		
22b(1)	 4H ⁺ -2,6-difluoro-1,3,5-trimethyl			-5.38	-3.33	-3.20	109		
22c(1)	 3H ⁺ -2,4,6-trifluoro-1,3,5-trimethyl			CH ₃ = -2.42 H = -4.88		2.70	109		
23a(1)	 4H ⁺ -5-fluoro-1,3-dimethyl	(2) -7.67 (6) -7.34		-4.59	-3.01	-2.78	107		
23b(1)	 2H ⁺ -5-fluoro-1,3-dimethyl		-7.44	-4.69		-2.85	107		
23a(11)	 4H ⁺ -5-chloro-1,3-dimethyl	(2) -7.73 (6) -7.77		-4.73	-2.96	-2.80	107		
23b(11)	 2H ⁺ -5-chloro-1,3-dimethyl		-7.80	-4.62		-2.80	107		
23c(11)	 4H ⁺ -4-chloro-1,3-dimethyl		-8.63	-8.03	-4.95	-3.04	-2.92	107	
23d(11)	 3H ⁺ -2-chloro-1,4-dimethyl		-8.67	-8.00	-4.78		-2.87	-2.57	107
23e(11)	 4H ⁺ -5-bromo-1,3-dimethyl	(2) -7.73 (6) -8.02		-4.68	-2.89	-2.78	107		
23b(111)	 2H ⁺ -5-bromo-1,3-dimethyl		-7.80	-4.62		-2.73	107		

(b) Xylenes.

The p.m.r. spectra of the halo-xylum ions are also presented in Table 10. Protonation of xylenes occurs generally to produce ions in which the halogen is ortho- or para- to the position of substitution, except in the case of 4-chloro-1,3-dimethylbenzene when the position of protonation is governed by the methyl groups:



(c) Toluenes.

The p.m.r. spectra of the halo-toluenium ions are presented in Table 11. In the case of the 3-halo-toluenes, three isomeric ions are formed. However the major components in this ionic mixture are those ions in which either a halogen or methyl group is para to the position of protonation, e.g.

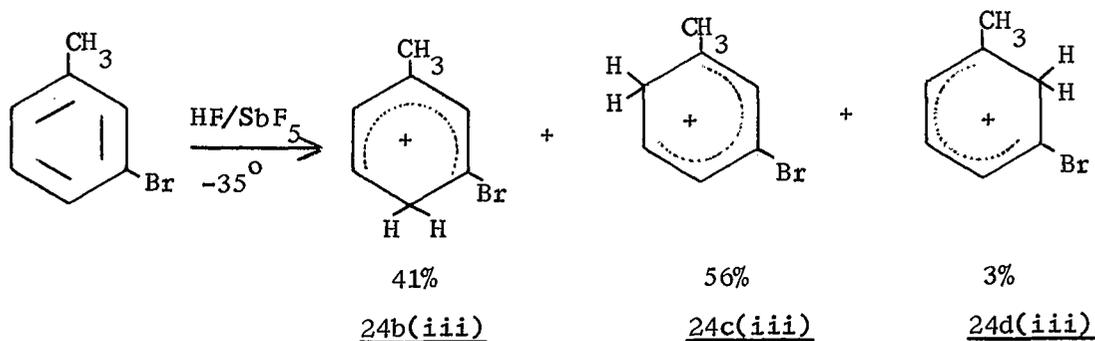
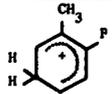
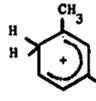
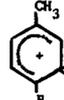
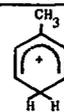
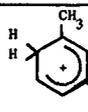
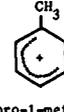
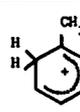
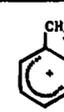
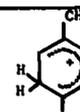
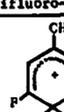
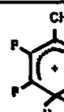


TABLE 11
P.M.R. Spectra of Halo-Toluenium Ions

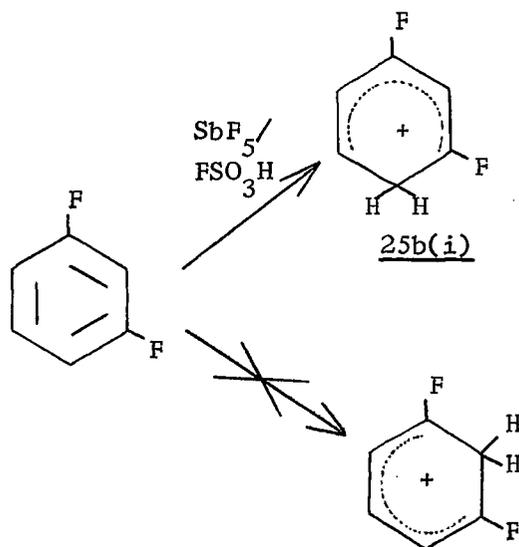
Ion No.	Benzenium Ion	Chemical Shift in P.P.M. from T.M.S.							Ref. No.
		o-H	m-H	p-H	CH ₂	o-CH ₃	m-CH ₃	p-CH ₃	
24a(1)		-9.76	-8.46		-5.44		-2.84		109
	5H ⁺ -2-fluoro-1-methyl								
24b(1)		^a	(2) ^a (6) -7.87		-4.6		-3.13	108 109	
	4H ⁺ -3-fluoro-1-methyl								
24c(1)		-9.06	(2) -7.60 (4) -7.70		-4.87	-3.00		108	
	6H ⁺ -3-fluoro-1-methyl								
24e(1)		-8.96	-8.24	9.94	-5.40		-2.84	109	
	3H ⁺ -4-fluoro-1-methyl								
24b(11)		-8.72	(2) -8.07 (6) -7.95		-4.89		-3.08	108	
	4H ⁺ -3-chloro-1-methyl								
24c(11)		-8.78	(2) -8.07 (4) -7.95		-4.80	-2.94		108	
	6H ⁺ -3-chloro-1-methyl								
24d(11)			^a	^a	-5.06	^a		108	
	2H ⁺ -3-chloro-1-methyl								
24b(111)		-8.85	(2) -8.23 (6) -7.94		-4.80		-2.99	108	
	4H ⁺ -3-bromo-1-methyl								
24c(111)		-8.63	(2) -8.23 (4) -8.16		-4.41	-2.85		108	
	6H ⁺ -3-bromo-1-methyl								
24d(111)			^a	^a	-4.97	^a		108	
	2H ⁺ -3-bromo-1-methyl								
24f(1)		-9.03	-7.97		-5.40		-2.84	109	
	5H ⁺ -2,4-difluoro-1-methyl								
24g(1)		-8.3	-8.3		-5.40		-3.53	109	
	4H ⁺ -2,5-difluoro-1-methyl								
24h(1)					-5.60		-3.50	109	
	4H ⁺ -2,3,5,6-tetrafluoro-1-methyl								

^a Cannot be identified with certainty.

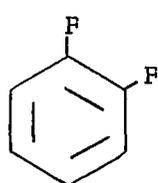
In the other ions in this series, the directing effect of the halogen is generally dominant.

(d) Benzenes.

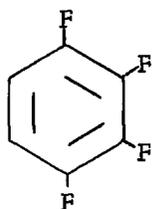
The p.m.r. spectra of the halobenzenium ions are presented in Table 12. Especially noticeable in the fluorobenzenes (and toluenes) is the preferential formation of ions containing a para-fluorine, e.g.



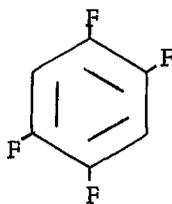
The deactivating effect of a halogen meta to a positive centre is also particularly obvious in the benzenes, in which other stabilizing groups are absent. This is illustrated by the lack of success in protonating the benzenes 26a(i)-e(i).



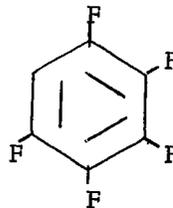
26a(i)



26b(i)



26c(i)

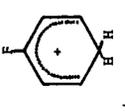
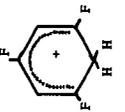
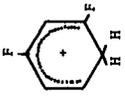
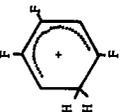
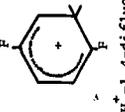
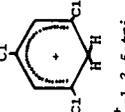
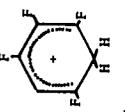
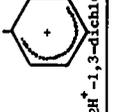


26d(i)



26e(i)

TABLE 12
P.M.R. Spectra of Halo-Benzenium Ions

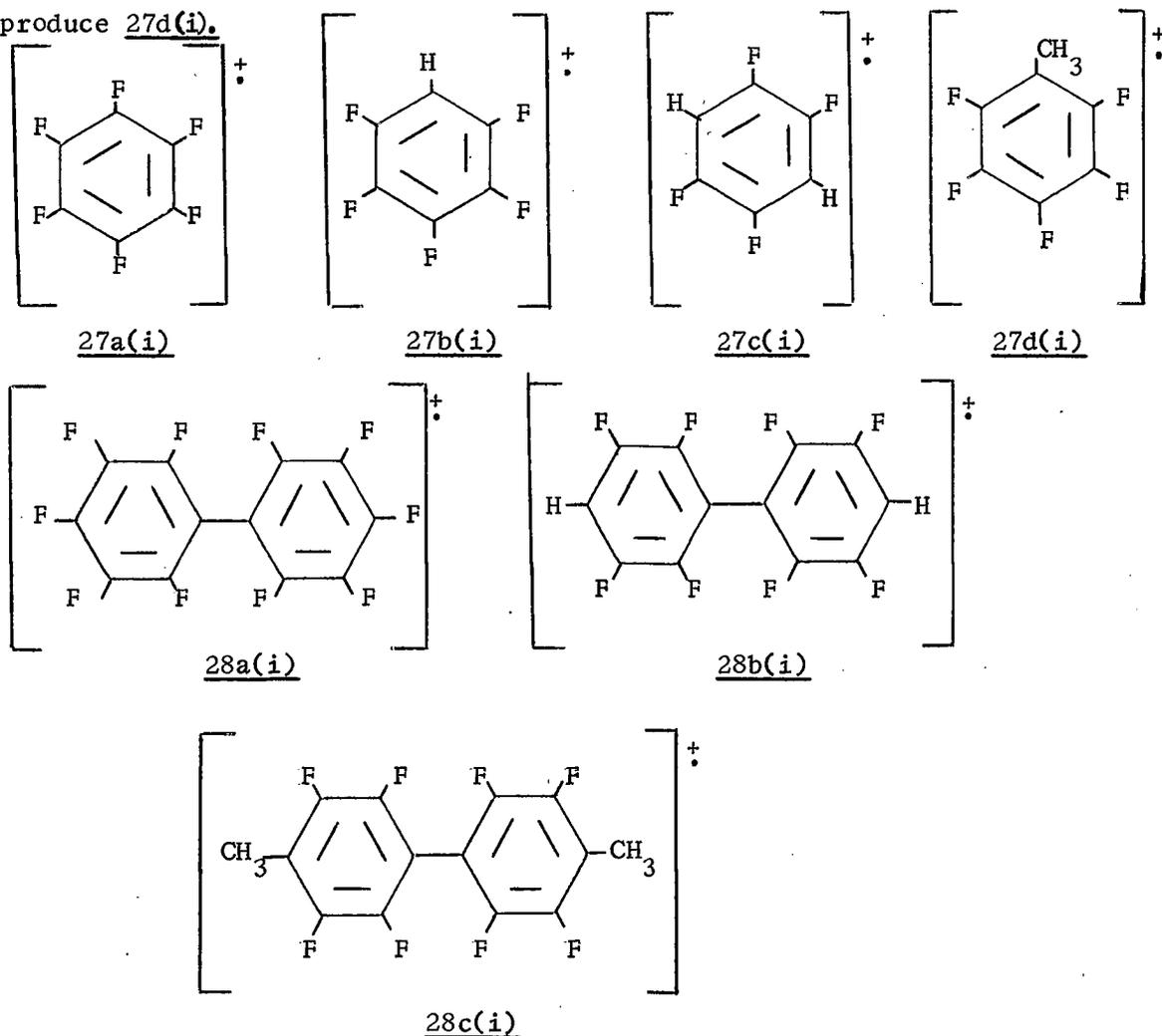
Ion No.	Benzenium Ion	Chemical Shift in P.P.M. from T.M.S. o-H m-H CH ₂	Ref. No.	Ion No.	Benzenium Ion	Chemical Shift in P.P.M. from T.M.S. o-H m-H CH ₂	Ref. No.
25a(i)	 4H ⁺ -1-fluoro-	-10.00 -8.40 -5.90	51	25e(i)	 4H ⁺ -1,3,5-trifluoro-	-7.8 -5.35	51
25b(i)	 4H ⁺ -1,3-difluoro-	-8.94 -7.64 -5.32	51	25f(i)	 5H ⁺ -1,2,4-trifluoro-	-8.94 -8.20 -5.09	51
25c(i)	 3H ⁺ -1,4-difluoro-	b -9 -5	51	25e(ii)	 4H ⁺ -1,3,5-trichloro-	-8.00 -4.98	51
25b(ii)	 4H ⁺ -1,3-dichloro-	(2) -8.16 -4.93 -8.78 (6) -7.98	108	25k(i)	 4H ⁺ -1,2,3,5-tetrafluoro-	-7.2 -5.0	108
25c(ii)	 2H ⁺ -1,3-dichloro-	a -5.11	108				

^a Cannot be identified with certainty.

^b Not quoted.

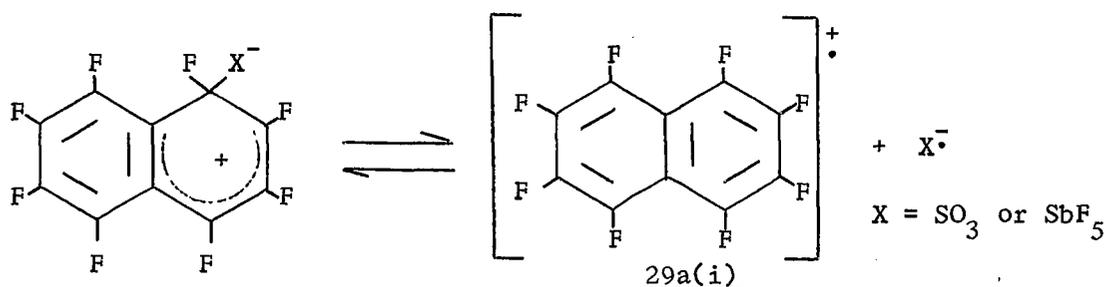
2. Polyfluoroaromatic Cation Radicals.

The unreactivity of some fluorobenzenes towards protonation described in the previous section has also been observed by Russian workers, who found that radical cations were produced on reaction of these fluorobenzenes with very strong acid systems. Reaction of antimony pentafluoride/fluoro-sulphonic acid with hexafluorobenzene, pentafluorobenzene and 1,2,4,6-tetrafluorobenzene produced the radical cations 27a-c,¹¹⁰ and with decafluorobiphenyl, 4,4'-dihydro-octafluorobiphenyl and 4,4'-dimethyl-octafluorobiphenyl produced radical cations, 28a-c.¹¹⁰ Pentafluoro toluene was reacted with antimony pentafluoride in sulphur dioxide to produce 27d(i).



The ions were analysed by E.S.R.

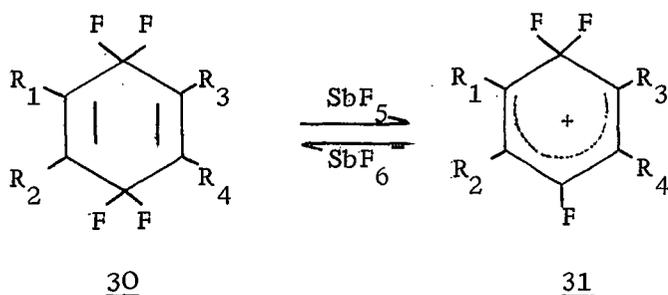
Similar cation radicals were also observed in the reaction between octafluoronaphthalene and sulphur trioxide, antimony pentafluoride¹¹¹ and antimony pentachloride/sulphur dioxide.¹¹² An equilibrium between radical cation and a σ -complex was postulated.¹¹¹



Similar results for a series of fluorinated naphthalenes were obtained by other workers in this field.^{113,114}

3. Polyfluoroaromatic Cations.

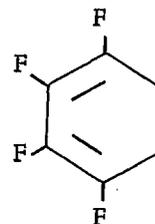
These have been reported in reactions of perhalodienes with antimony pentafluoride in sulphur dioxide.^{115,116}



where a $R_1 = R_2 = R_3 = R_4 = \text{F}$

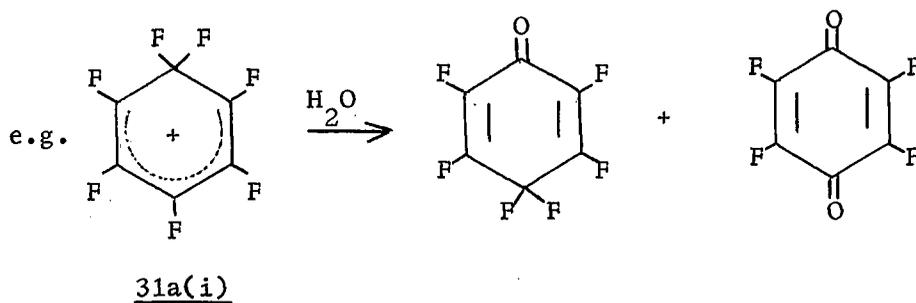
b $R_1 = R_2 = R_3 = R_4 = \text{Cl}$

c $R_1, R_2 =$

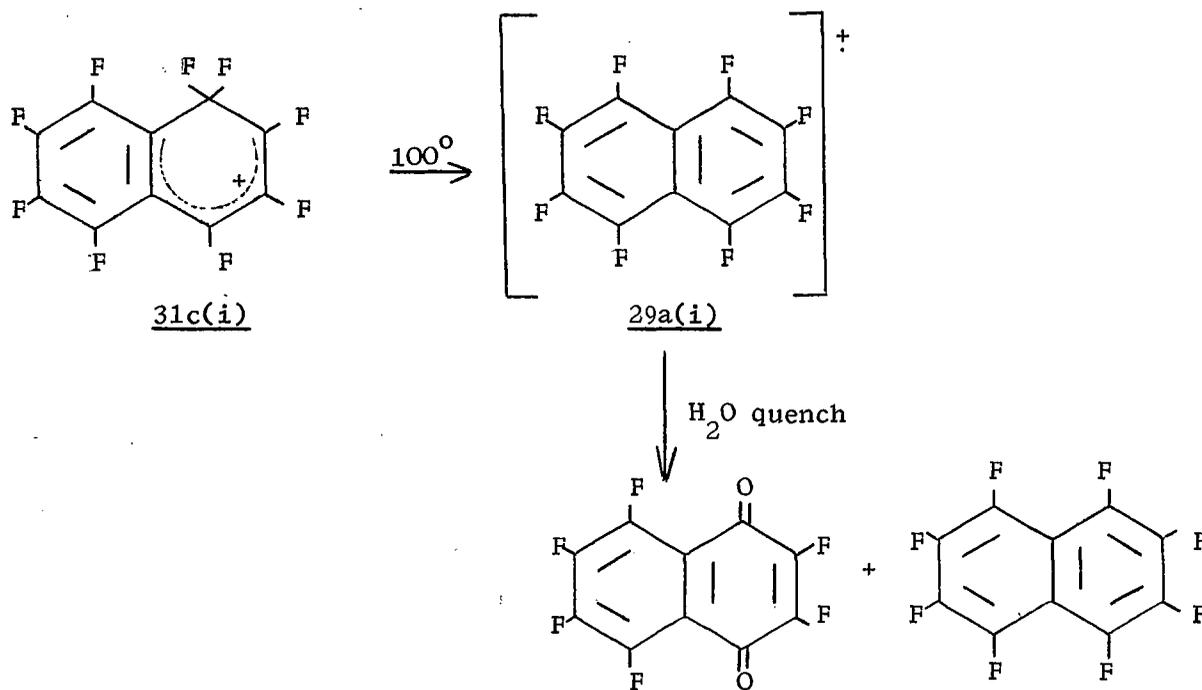


$R_3 = R_4 = \text{F}$

The deshielding of the fluorines in these systems is consistent with those observed for the protonated benzenes,^{51,109} and quenching in water yielded mixtures of halogenated cyclohexadienones and quinones.

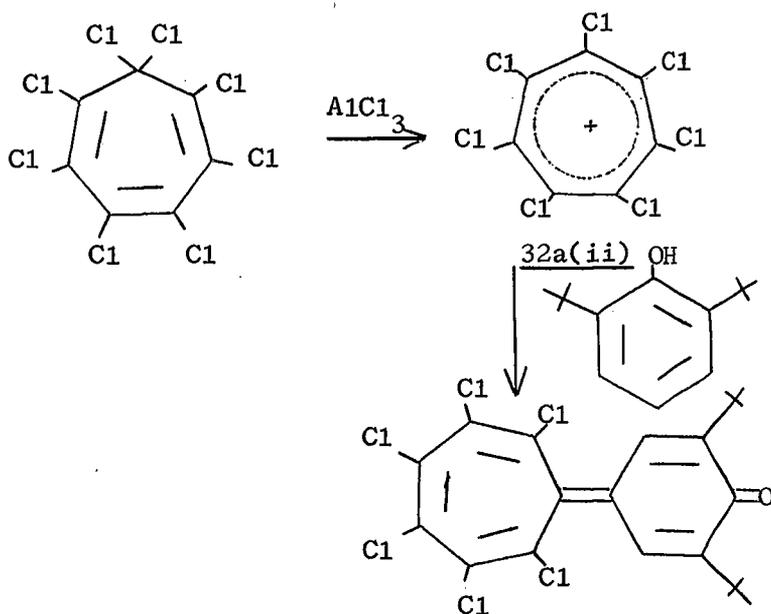


Heating the perfluorobenzenium and naphthalenium ions up to 100° produced the radical cations 27a(i) and 29a(i) respectively, identified by their intense green colours and E.S.R. spectra. On quenching these solutions with water, a mixture of starting material and quinone was recovered. This supports the concept of an equilibrium between the radical cation and a σ -complex.

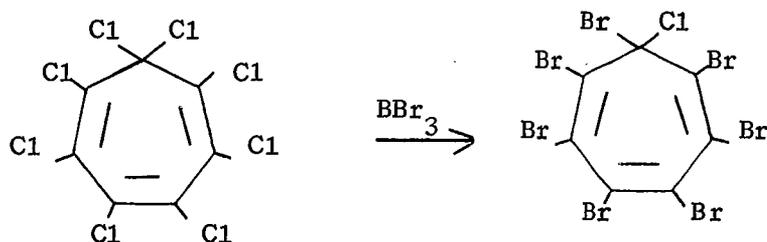


C. Tropylium Ions.

The tropylium ion, C_7H_7^+ , is a well known 6π electron aromatic system.¹¹⁷ The heptachlorotropylium ion has been isolated, as a salt in the reaction between a Lewis Acid and octachlorocycloheptatriene.¹¹⁸



Its geometry is unknown, but its stability and its chemistry resemble those of the trichlorocyclopropenium cation, e.g. arylation takes place with aromatic hydrocarbons, and with phenols is accompanied by loss of a proton to give 'quintropones'.¹⁰⁴ Halogen exchange between octachlorocycloheptatriene and BBr_3 also takes place (presumably via 32a(ii)) with replacement of seven of the eight halogens.¹⁰⁴



2.6. Reactions Involving Halo-Allyl Cations.

Whilst the chemistry of the hydrocarbon allyl cation has been extensively studied, that of the halogenated ions has not been developed in much detail. The original work to be presented in the next chapters of this thesis is concerned with the chemistry of fluorinated allyl cations, about which little information is presently available in the literature.

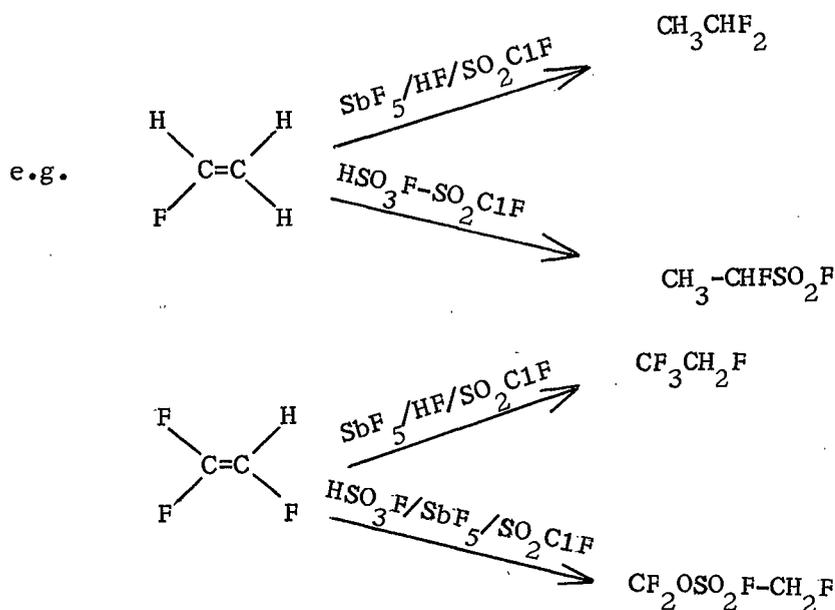
A. Generation.

1. Reactions of Lewis Acids with Halo-olefins.

The electronegativity of halogen atoms renders the olefinic double bond particularly susceptible to attack by nucleophiles. Electrophilic attack is less common, but has been observed in a number of systems.^{119,120} In the presence of strong Lewis acids however, halo-olefins have been reported to react via electrophilic attack to form addition compounds⁷⁴ and also, in the case of the propenes, via loss of halide ion from the $-CX_3$ group to form halo-allyl cations.

(a) Electrophilic Addition to Fluoro-olefins by Strong Lewis Acids.

A series of fluoro-olefins were studied in the super acid systems $SbF_5-HF-SO_2ClF$, $SbF_5-HSO_3F-SO_2ClF$ and HSO_3F at low temperatures.⁷⁴ While the intermediate fluorocarbenium ions were not observed, the covalent fluorides and fluorosulphates produced indicated that electrophilic attack had occurred.

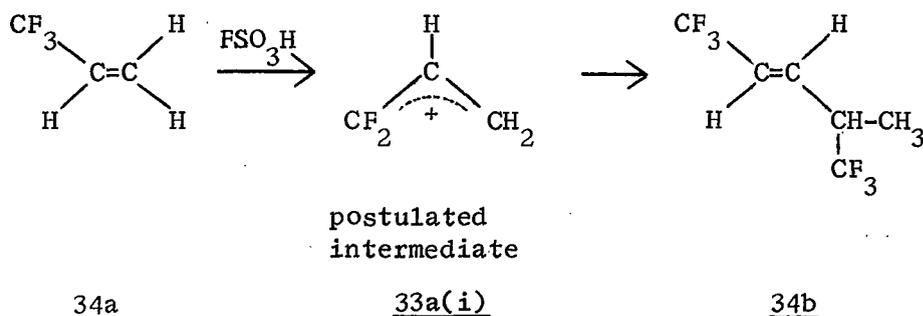


However the olefins tetrafluoroethylene and hexafluoropropene did not react at this temperature.

(b) Formation of Allyl Cations.

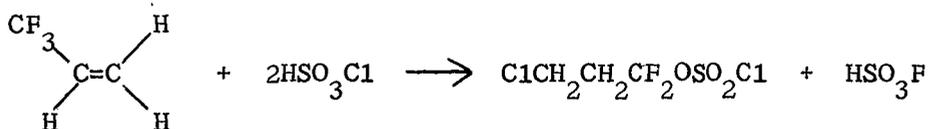
1. Reactions of Fluoropropenes with Lewis Acids.

The intermediate existence of the 1,1-difluoroallyl cation 33a(i) has been postulated in the reaction between 3,3,3-trifluoropropene and the strong acid systems FSO_3H , ClSO_3H , HCl-AlCl_3 and HBr-AlBr_3 .^{121,122} It was discovered initially that this olefin underwent dimerization in reactions with fluorosulphonic acid instead of the expected electrophilic addition of the acid. The dimerization rates showed marked acid catalysis, but no transfer of solvent protons to the olefinic carbons of the reactant was observed.



The authors suggested a reaction scheme involving initial formation of the ion 33a(i) which then participated in electrophilic attack on the olefin. Recapture of a fluoride ion from the solvent molecule on quenching with methanol would generate the dimer, 34b.

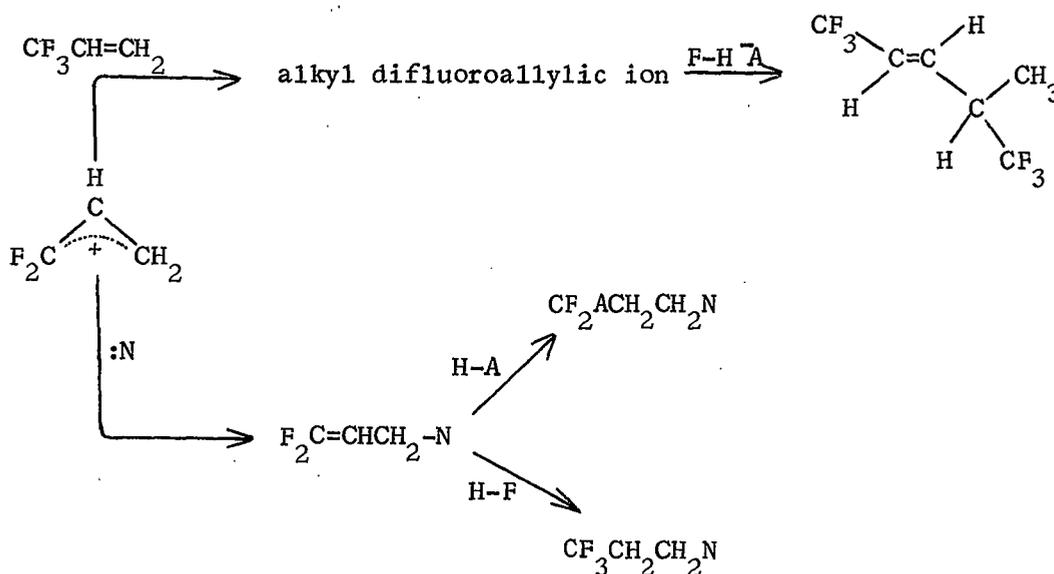
In the cases of ClSO_3H , HCl/AlCl_3 and HBr/AlBr_3 dimerization was not observed, but the products were consistent with the formation of an allyl cation which then reacted with the bulk solvent anion instead of the starting alkene. While N.M.R. data on the intermediate ion was not reported, in the case of ClSO_3H , the reaction was followed by N.M.R. and



34a

absorption bands for the product could be seen to appear as those for 34a disappeared. With HBr/AlBr_3 however only $\text{CF}_3\text{CH}_2\text{CH}_2\text{Br}$ was observed, with no trace of $\text{CF}_2\text{BrCH}_2\text{CH}_2\text{Br}$.

The authors have formulated a general reaction scheme, shown below, for the reactions investigated:



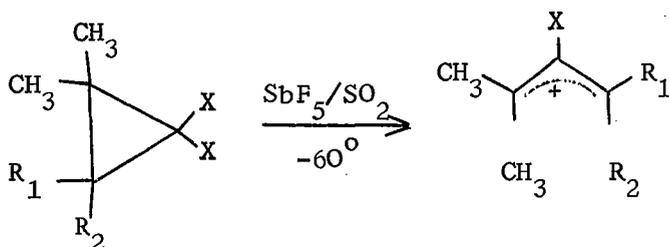
Where nucleophile :N may or may not correspond to the bulk solvent anion A^- .

2. Reactions of Chloropropenes with Lewis Acids.

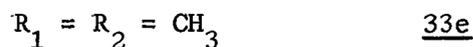
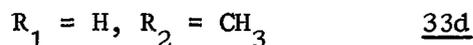
Hexachloropropene has been observed to form 1:1 complexes with the Lewis Acids AlCl_3 , GaCl_3 and SbCl_5 .¹²³ These complexes have been identified by their I.R. and electronic spectra as salts of the pentachloroallyl cation, 33b(ii).

2. Reactions of Lewis Acids with Dihalocyclopropanes.

A series of 2-haloallyl cations has been produced by ionization of gem-dihalocyclopropanes.¹⁹

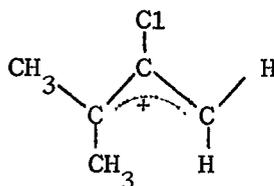


where X = Cl or Br



The ionization of gem-difluoro-1,1-dimethylpropane was also investigated, and although a complete analysis was not possible the resulting ion appeared to be the 2-fluoro-1,1-dimethyl allyl cation.

The ions were identified by their N.M.R. spectra, and in some cases free energies of activation and rotation were calculated. For example, the 2-chloro-1,1-dimethyl allyl cation 33c(ii) was found to exist as a nearly planar species, showing non-equivalent methyl groups separated by



33c(ii)

about 49 Hz at -70° . At around -39° these signals coalesced to a single broad line and at -7° rotation was rapid, the methyl resonances appearing as a triplet due to coupling with the vinylic protons.

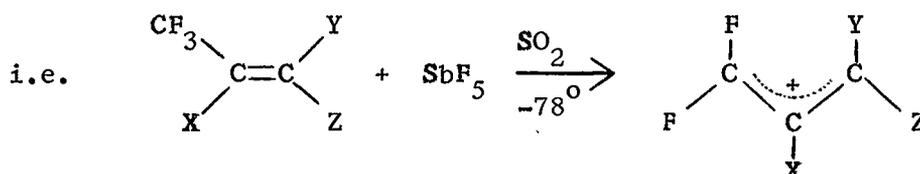
CHAPTER 3

Highly Fluorinated Propenyl Cations

3.1. Reactions of Substituted Fluoropropenes with Lewis Acids.

Some examples of halogenated allyl cations which have been generated were given in Chapter 2 (Section 2.6.). However no stable highly fluorinated allyl cations have been observed in the literature to date.

In the original work presented in this thesis, a number of attempts have been made to prepare such cations by reaction of substituted fluoropropenes with antimony pentafluoride, in which removal of fluoride ion from the saturated CF₃- group would be expected to yield an allyl cation:



where either X = substituent group, Y = Z = F
 Y = " " , X = Z = F
or Z = " " , X = Y = F

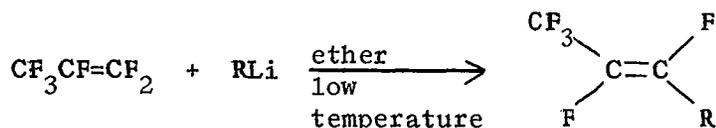
The substituents used were those with electron donating ability (e.g. CH₃O-; Ph-, CH₃O·C₆H₄-) which would be capable of stabilizing a positively charged intermediate. Whenever possible, starting materials were prepared by literature methods.

Analysis was effected in particular by use of F¹⁹ N.M.R. data. As explained in Chapter 2, from a consideration of deshielding effects and changes in coupling constants, it is possible to detect the presence of discreet ionic intermediates.

A. Preparation of Starting Materials.

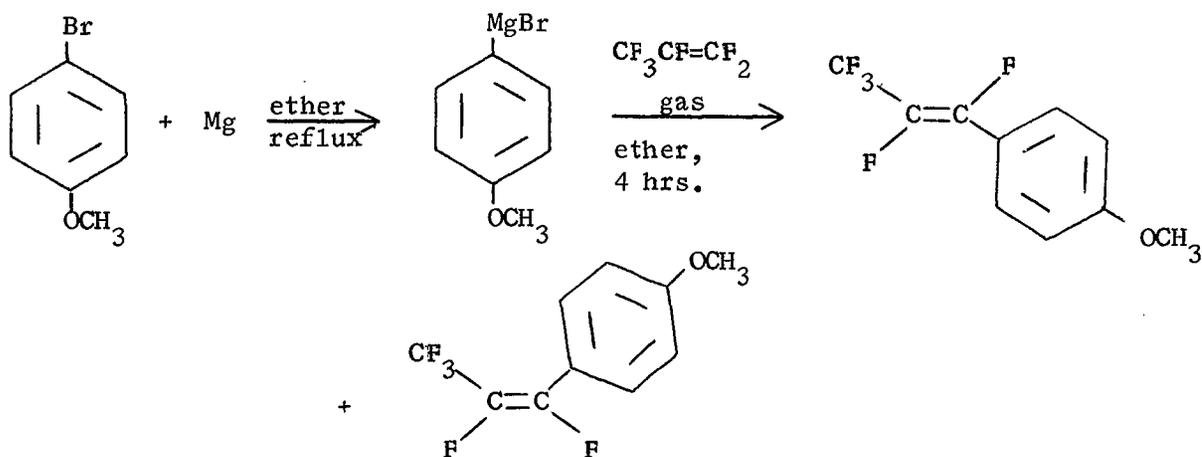
1. 1-Substituted Fluoropropenes.

In general, these were synthesised by literature methods, by reaction of the appropriate organo-lithium reagent,¹²⁵

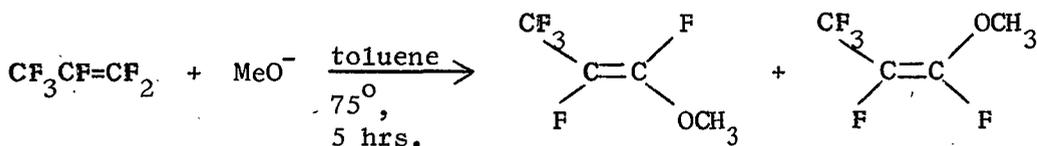


where in this case R = Ph- or CH₃-.

However this was not found to be a suitable method for the preparation of 1-p-anisylpentafluoropropene. When a mixture of p-bromoanisole and n-butyl-lithium were stirred at -10° for two hours and subsequently cooled to -78° and reacted with olefin, recovery of starting materials indicated that p-methoxyphenyl-lithium had not been formed. As the Grignard reagent of p-bromoanisole could be prepared quite easily, it was decided to use this reagent in the preparation of 1-p-anisylpentafluoropropene. The reaction was carried out under atmospheric pressure conditions.

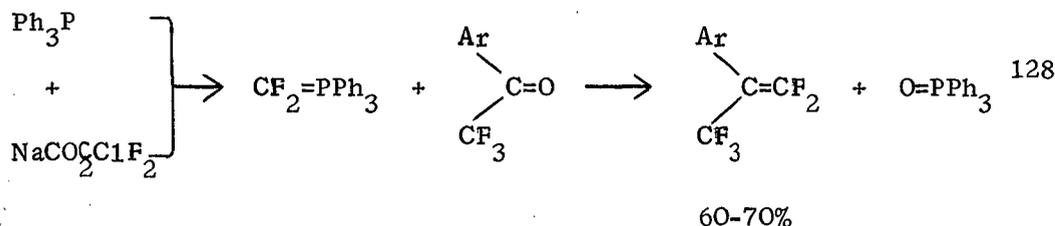
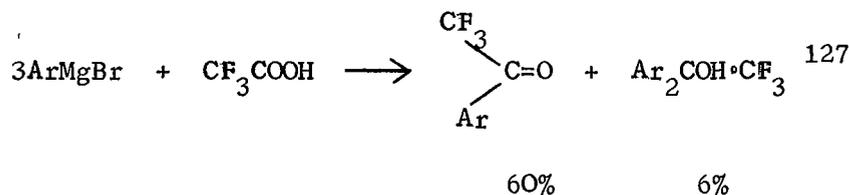


1-Methoxypentafluoropropene was prepared by reaction of hexafluoropropene with sodium methoxide in dry toluene:¹²⁶



2. 2-Substituted Fluoropropenes.

Synthesis of 2-substituted fluoropropenes is generally more difficult. However recent experiments by Burton involving Ylid reagents have facilitated these reactions. Thus the following route was used for the preparation of 2-phenyl- and 2-p-anisylpentafluoropropene:



where Ar = C₆H₅- or CH₃O·C₆H₄-.

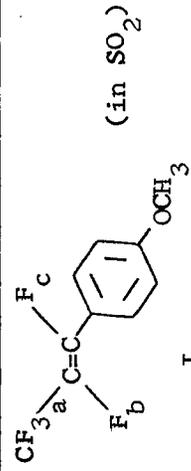
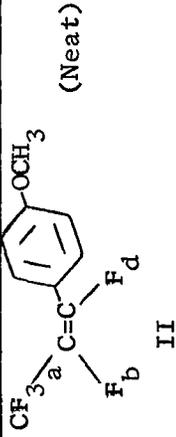
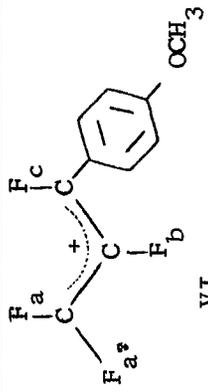
B. Reactions of 1-Substituted Fluoro-olefins with Antimony Pentafluoride in Sulphur Dioxide.

1. Reaction of 1-p-Anisylpentafluoropropene (Trans) with Antimony Pentafluoride in Sulphur Dioxide.

On addition of 1-p-anisylpentafluoropropene (trans) I to a solution of SbF₅ in SO₂, the N.M.R. spectrum of the olefin was dramatically altered. The N.M.R. data for the olefin and its solution in SbF₅/SO₂ are presented in Tables 13A and 13B, and the F¹⁹ spectrum of the solution in SO₂ is shown in

TABLE 13A

Chemical^a Shifts of Olefins I and II and of Ion VI

Olefin	Proton Shifts		Fluorine Shifts			
	CH ₃ O-	C ₆ H ₄ -	CF ₃ - ^a	F _b	F _c	F _d
 I	(in SO ₂) -3.21	-6.72	+68.22	+174.03	+147.09	
 II	(Neat) -3.68	-7.08	+65.86	+156.06		+107.03
Ion (in SO ₂)	Proton Shifts		Fluorine Shifts			
	CH ₃ O-	C ₆ H ₄ -	F _a	F _a [*]	F _b	F _c
 VI	-3.78 [-0.57] ^b	-7.34 [-0.62]	+64.88 [-3.34]	+68.64 [+0.42]	+180.61 [+6.31]	+53.14 [-94.76]

^a Chemical shifts in p.p.m. from TMS or CCl₄; ^b Figures in brackets represent shift from trans olefin in SO₂.

TABLE 13B
Coupling Constants (Hz) for I, II and VI

Olefin	J_{ab}	J_{ac}	J_{ad}	J_{bc}	J_{bd}	
<p style="text-align: center;">II</p>	13		8.5		10.5	
<p style="text-align: center;">I</p>	10.5	22		130		
Ion	$J_{aa'}$	J_{ab}	$J_{a'b}$	J_{ac}	$J_{a'c}$	J_{bc}
<p style="text-align: center;">VI</p>	105.5	97.5	70.5	59	3	22

Figs. 1, 2 and 3.

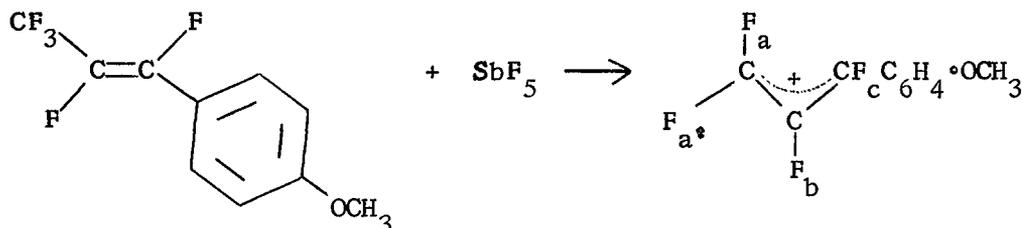
(a) Analysis of N.M.R. Data.

The F^{19} spectrum of this solution consists of three signals integrating in the ratio 1:2:1.

Fig. 1 shows the complex set of signals which integrated for two fluorines. On inspection it was possible to analyse the two separate signals. The signal at +64.88 p.p.m. showed doublet splittings of 105.5 Hz, 97.5 Hz, and 59 Hz, and that at 68.64 p.p.m. showed doublet splittings of 105.5 Hz, 70.5 Hz and 3 Hz. Clearly these signals belong to a CF_2 group in which the F-F geminal coupling is 105.5 Hz.

To low field of these signals could be seen a single fluorine peak at +53.14 p.p.m., which showed doublet splittings of 59 Hz, 22 Hz and 3 Hz (Fig. 3). At very high field was another single fluorine resonance, at +180.6 p.p.m., showing doublet splittings of 97.5 Hz, 70.5 Hz and 22 Hz (Fig. 2).

The presence of a CF_2 group in this spectrum indicates that the expected ionization has occurred.



Of the remaining two signals, the peak at +53.14 Hz is particularly noticeable in exhibiting a very small coupling constant of 3 Hz. This can only be due to long range coupling between F_c and either F_a or F_{a^*} . Thus this signal at +53.14 Hz can be assigned as F_c and that at +180.6 p.p.m. as F_b .

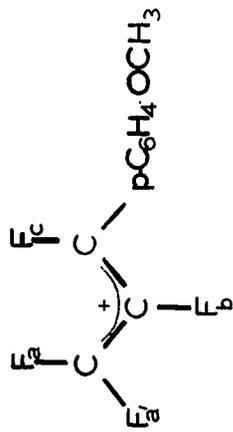


FIG.1. F^{19} NMR SPECTRUM OF

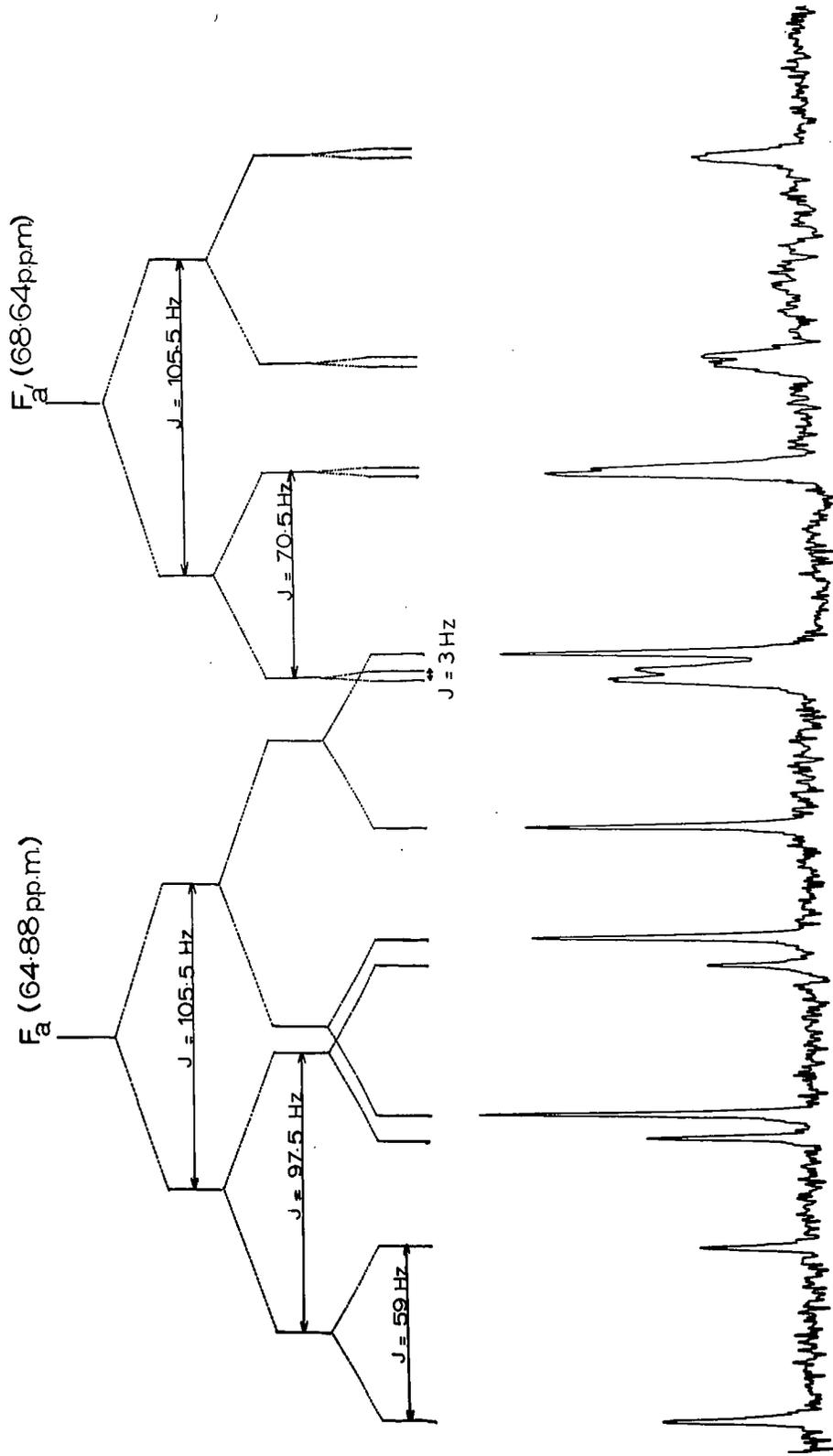
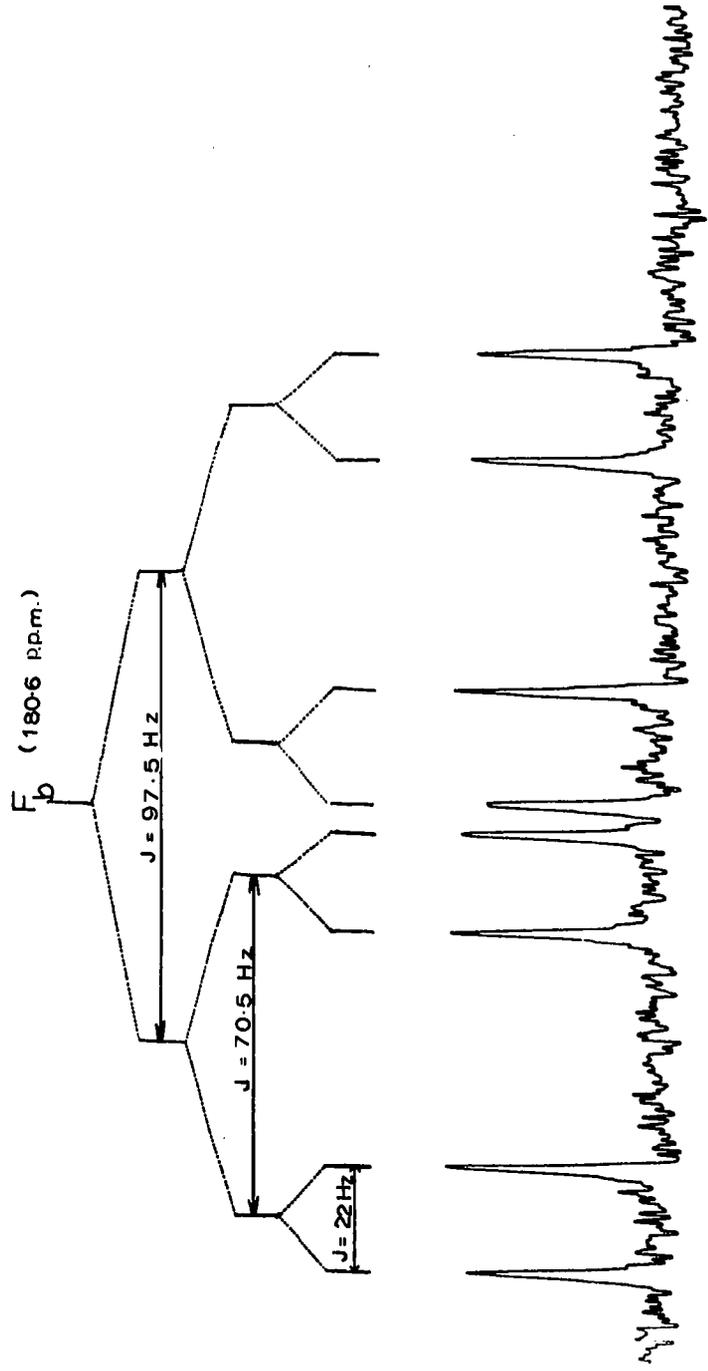
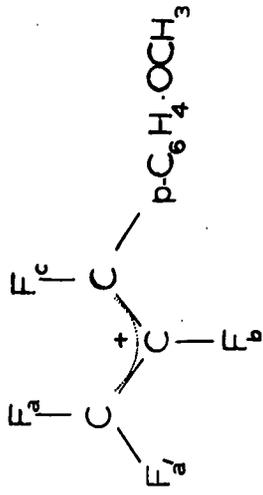
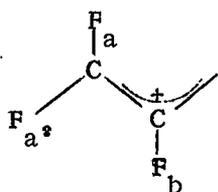


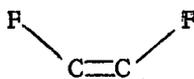
FIG. 2. F^{19} NMR. SPECTRUM OF



The couplings of 97.5 Hz and 70.5 Hz exhibited by F_b are also seen in the signals at 64.88 p.p.m. and 68.64 p.p.m. If an analogy is drawn between the system III and the cis and trans olefinic systems IV and V

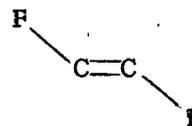


III



IV

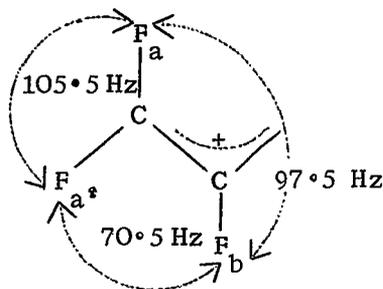
$$J_{F-F} = 0-58 \text{ Hz}$$



V

$$J_{F-F} = 105-148 \text{ Hz}$$

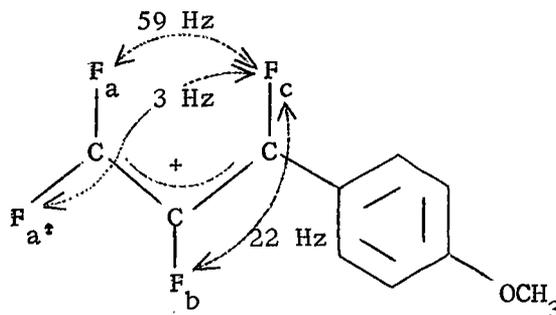
where J_{F-F} trans is always greater than J_{F-F} cis, the coupling constants may be assigned in the following way:



[It must be noted here that the cis and trans olefinic systems are by no means a perfect model for the allyl cation, but comparison of relative sizes of coupling constants is quite reasonable].

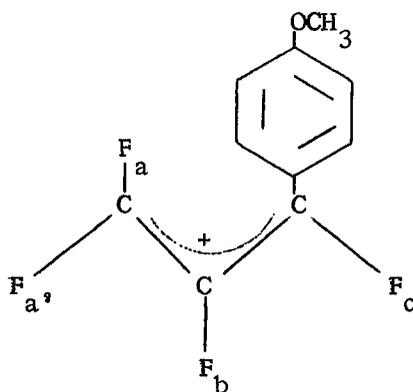
Thus the signal at 64.88 p.p.m. can be attributed to F_a and that at 68.64 p.p.m. to F_{a^*} .

The couplings of 59 Hz and 3 Hz exhibited by F_c and F_a and F_{a^*} respectively suggest a structure of the type VI,



VI

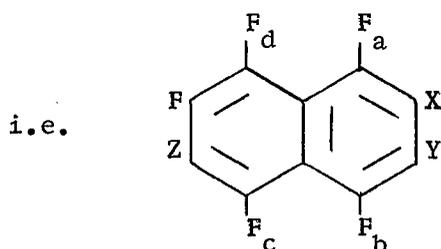
in which $J_{F_a-F_c}$ would be expected to be reasonably large and $J_{F_{a^*}-F_c}$ fairly small, rather than VII in which neither $J_{F_a-F_c}$ or $J_{F_{a^*}-F_c}$ would be



VII

expected to be as large as 59 Hz. Confirmation of structure VI will be presented in a later section (Section 3.1.B.1.(d)).

The large coupling between F_a and F_c is also reminiscent of peri fluorine-fluorine coupling constants in fluoronaphthalenes,¹²⁹



where $J_{F_a-F_d} = 60-70$ Hz
and $J_{F_c-F_d}$

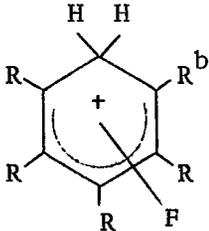
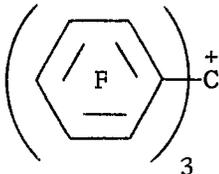
The remaining coupling of 22 Hz between F_b and F_c seems small for a trans F-F coupling. However some distortion of the system by the p-anisyl group might be expected.

(b) Chemical Shift Data.

Cation formation is generally accompanied by deshielding of the atoms involved. Examples of such effects reported in the literature are shown in Tables 14 and 15. This deshielding can be extremely great as in the case of cation 14b(i) (Table 15) in which a large proportion of the positive

TABLE 14

F¹⁹ N.M.R. Data^a for a Series of Aromatic Carbocations

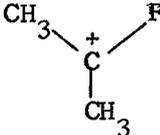
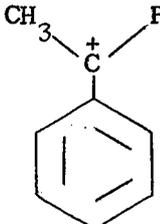
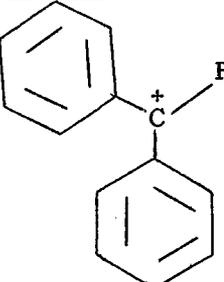
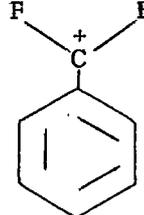
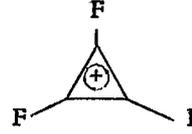
Ion	Chemical Shift p-F	Chemical Shift o-F	Chemical Shift m-F
	<p>-5 to +20 [~ -100]</p>	<p>+8 to +55 [-70 to -100]</p>	<p>+100 to +140 [~ -10]</p>
	<p>+112.1 [-40]</p>	<p>+126.3 [-14]</p>	<p>+154.3 [-7]</p>

^a Chemical shifts in p.p.m. from CFC₃; ^b R = H or CH₃ (or F);

^c Figures in brackets represent approximate downfield shifts.

TABLE 15

F¹⁹ N.M.R. Data^a on a Series of Carbocations

Ion	Ion No.	F ¹⁹ Chemical Shift	Deshielding from Covalent Precursor p.p.m.
	<u>14b(i)</u>	-181.9	-266.8
	<u>15a(i)</u>	-51.48	-140.2
	<u>16b(i)</u>	-11.26	-100.9
	<u>16a</u>	-11.99	-75.6
	<u>21a(i)</u>	+63.1	-57.8 ^b

^a Chemical shifts in p.p.m. from CFC1₃; ^b Downfield shift from average of signals of perfluorocyclopropene.

charge is delocalized onto the fluorine atom. The presence of substituent groups which are capable of charge delocalization reduces the amount of charge which is located on the fluorine atoms, thus reducing the deshielding experienced by these atoms.

Similarly when the charge is delocalized, as in the case of the trifluorocyclopropenium ion 21a(i), the individual fluorine atoms experience smaller shifts.

In the allyl cation the charge is delocalized but is considered to be located in particular on the terminal carbon atoms (Chapter 1, Section 1.3.B.). In ion VI one of the terminal carbons is substituted by a p-anisyl group, and the delocalization of charge on this group is evident from the downfield shift which it experiences (Table 13A). Thus one might expect to observe deshielding of the fluorine atoms F_a , $F_{a'}$, and F_c somewhere in the range between 60 p.p.m. and 140 p.p.m.

In fact it can be seen from Table 13A that F_c experiences a downfield shift of -95 p.p.m. (In order to compare stereochemically similar systems, downfield shifts were measured from the trans olefin).

However comparison of the chemical shifts of F_a and $F_{a'}$ with that of the original $-CF_3$ group leads to some confusion. The position of F_a is only 3 p.p.m. downfield and that of $F_{a'}$ actually 0.42 p.p.m. upfield from the CF_3 - group in the trans olefin I.

In fact it is dubious whether a comparison may be made between a CF_3 group, in which the carbon is sp^3 hybridized, and the CF_2 group of ion VI in which the carbon is sp^2 hybridized. (Further discussion of re-hybridization in this system will follow in Section 3.1.B.1.(c)). A more valid comparison may be made between a vinyl $=CF_2$ group from which it is

deshielded by about -40 p.p.m. This is still not as large as might be expected for ionization, but as the positive charge is delocalized over the system, it would seem more likely to expect the terminal fluorines to appear in the same region than to be shifted downfield by the same amounts (cf. the trifluorocyclopropenium ion).

However a comparison of the chemical shift of F_b in ion VI with that of F_b in the olefin I (a valid comparison as the atoms are in stereochemically similar situations) shows that F_b has actually been shifted upfield by 6.3 p.p.m.

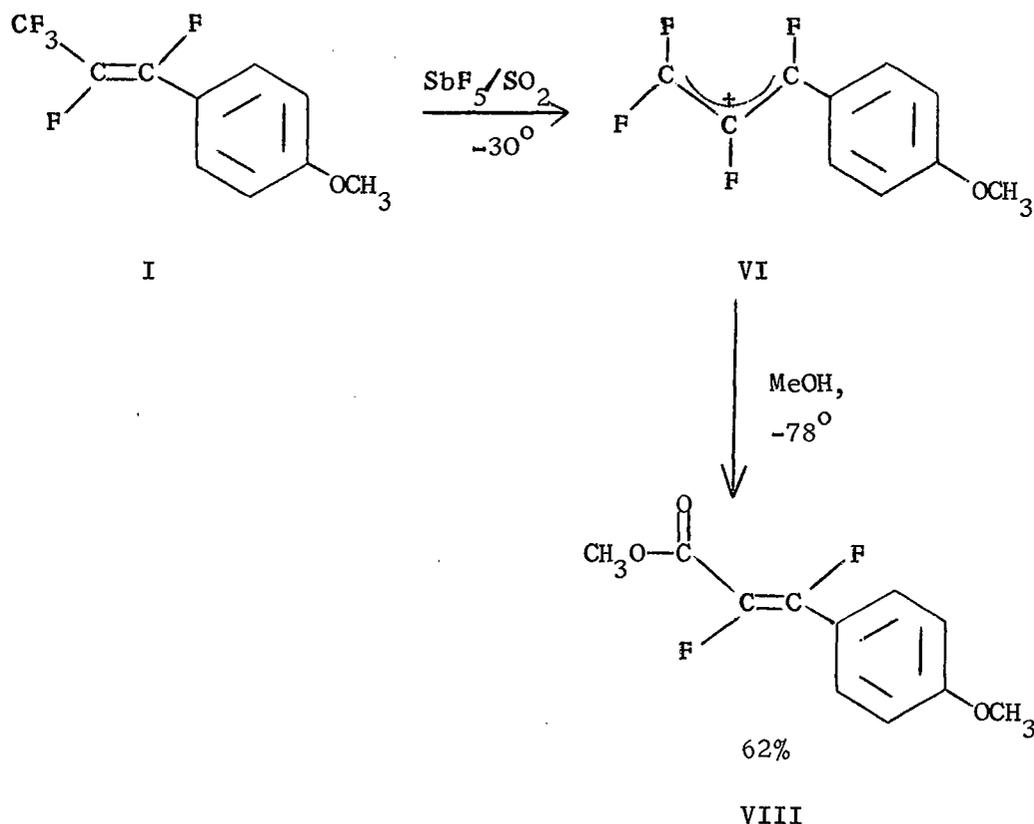
Whilst the charge on the allyl cation is generally considered to be located at the terminal carbons, experimental evidence has been presented to suggest that some charge is delocalized onto the central carbon (Chapter 1, Section 1.3.B.). If, in the case of ion VI some positive charge is located on the central carbon atom, one might expect to see deshielding of F_b . The observation that F_b is actually shielded excludes this possibility and is in fact an indication that the fluorine atom in this position actually has an inductive destabilizing effect on the ion as a whole (Chapter 2, Section 2.1.).

(c) Rehybridization.

There is a considerable amount of experimental evidence that on cation formation coupling constants are increased as a result of rehybridization (Chapter 2, Section 2.3.). Evidence of rehybridization in this system has already been presented in the previous section (Section 3.1.B.1.(b)). More evidence is obtained from the coupling constants exhibited by ion VI (Table 13B). In comparison to olefin I large increases are observed. The one exception to this is $J_{F_b-F_c}$, which as mentioned in Section 3.1.B.1.(a) is smaller than expected.

(d) Quenching with Dry Methanol.

On quenching the ionic solution with dry methanol a white crystalline solid was isolated, which was analysed as 1-p-anisyl-1,2-difluoro-3-methoxypropene-1-one (trans) VIII:

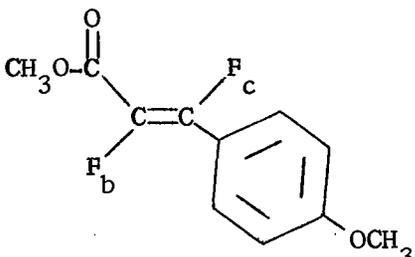


The trans fluorine system can be seen quite clearly in the N.M.R. spectrum of this olefin (Table 16). The carbonyl group was visible in the infra-red spectrum, and analysis and mass spectral data gave an empirical formula of C₁₀H₁₀F₂O₃, corresponding to olefin VIII.

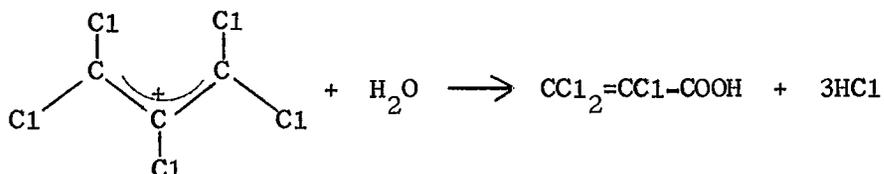
The isolation of this compound may be taken as positive proof of the structure of ion VI. Its formation is analogous to the formation of trichloroacrylic acid in the hydrolysis of the salts of the pentachloroallyl cation (Chapter 2, Section 2.6.A.1.(b).2.).

TABLE 16

N.M.R. Data^a of 1-p-Anisyl-1,2-difluoro-3-methoxypropene-1-one

Olefin	Proton Shifts		Fluorine Shifts		J _{F-F} Hz
	CH ₃ O- groups	Benzene Ring	F _b	F _c	
	-3.830	-7.33	+164.2	+135.4	130
	-3.833				

^a Chemical shifts in p.p.m. from T.M.S. or CFC1₃.

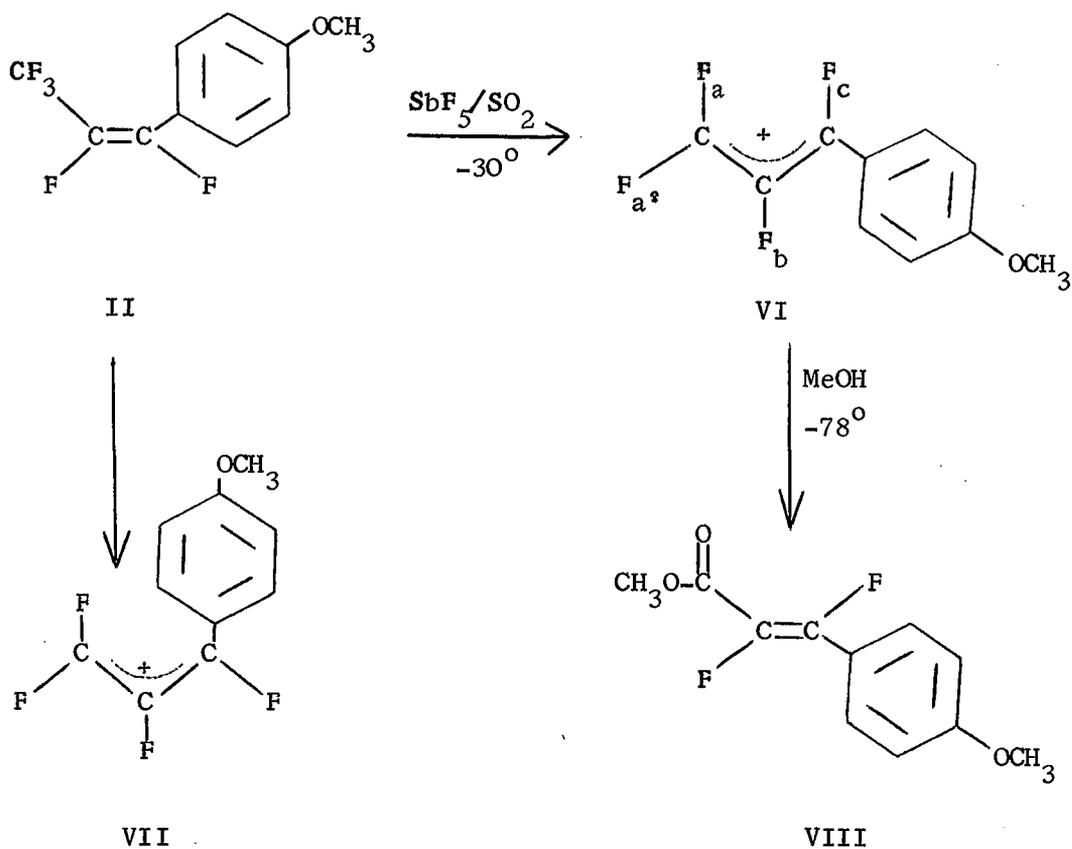


(e) Reaction of 1-p-Anisylpentafluoropropene (Cis) with Antimony Pentafluoride in Sulphur Dioxide.

The addition of the cis olefin II to SbF₅ in SO₂ at -30° produced a solution the N.M.R. of which was identical with that produced by dissolution of the trans olefin in this acid. Quenching of this solution resulted in the formation of VIII, the trans olefin.

Thus the cis olefin II is producing a *trans* ion VI, which is perhaps an indication of the greater stability of a trans fluorine system over a cis system such as II (or VII).

This in itself suggests that some stabilizing interaction is occurring between the non-bonding electrons on the fluorine atoms F_a and F_c. (Such



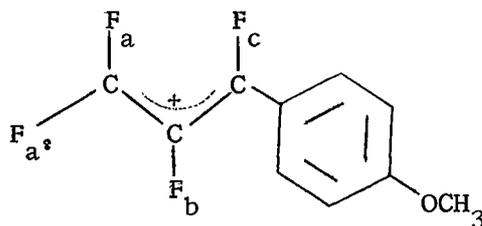
concepts have been used to explain the large peri F-F coupling constants in various cyclic compounds).^{129,130}

(f) Conclusions.

This is the first stable highly fluorinated allyl cation to be observed to date. The production of such a well defined allyl system has made possible the detailed analysis which has been presented here. It has shed some light on the question (mentioned previously) of the charge structure of the allyl cation (Chapter 1, Section 1.3.B.). P.M.R. data has already been used to estimate the charge distribution. However proton chemical shifts are small and thus present the possibility of even small errors leading to an erroneous impression.

The sizes of chemical shifts experienced by fluorine atoms are much larger than those experienced by protons in similar situations (Chapter 2, Section 2.1.A.3.(b)),⁶² thus providing a more sensitive measure of the charge distribution (Chapter 1, Section 1.3.B.2.(b)). In this respect F^{19} N.M.R. measurements resemble C^{13} N.M.R. measurements.

Thus the large deshieldings experienced by F_a , F_{a^*} and F_c in ion VI,



VI

are clear indication that the carbons to which they are attached possess a substantial amount of positive charge.

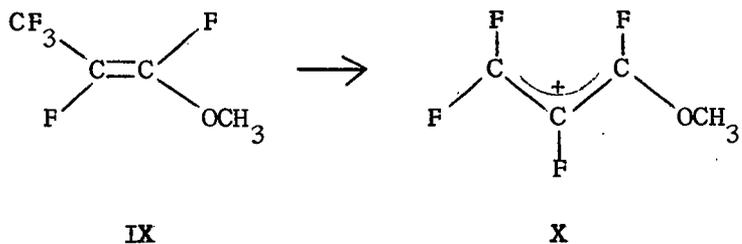
However the upfield shift of F_b in this ion is unique, as atoms not directly attached to a positive centre are still deshielded by inductive effects, and it does appear to contradict any arguments that charge might be located at this position.

This analysis has also facilitated future interpretation of fluorinated propenyl cations. In any unsymmetrical propenyl cation containing a CF_2 group, a large geminal coupling constant (in the region of 100 Hz) should be seen, unless the system is in some way distorted. Thus it has been possible to say that in the reactions investigated between other fluoro-propenes and antimony pentafluoride, which will be presented in the following section, formation of stable allyl cations has not occurred.

2. Reaction of 1-Methoxypentafluoropropene (Cis and Trans) with Antimony Pentafluoride in Sulphur Dioxide.

Since the p-anisyl group was sufficiently electron donating to produce

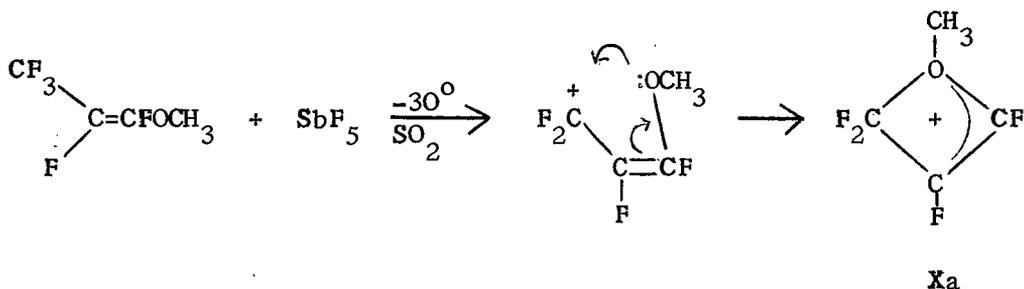
a stable highly fluorinated allyl cation, it was anticipated that reaction of 1-methoxypentafluoropropene with SbF_5/SO_2 would produce the cation X.



With a large excess of antimony pentafluoride (greater than 5:1 molar ratio), both cis and trans 1-methoxypentafluoropropene gave N.M.R. spectra as shown in Fig. 4 and Table 17.

The large downfield shift of the methoxy group suggests that ionization has occurred, and the fluorine integration corresponds to loss of one fluorine atom. However, there is no evidence in the F^{19} N.M.R. spectrum of an allyl cation such as X, and the complex nature of the F^{19} N.M.R. spectrum makes analysis impossible.

The large deshielding observed for the methoxy group suggests that a substantial amount of charge is located on the oxygen atom. This fact, coupled with the apparent loss of one fluorine, suggests that ionization is occurring with involvement of the oxygen atom, perhaps of the type:



Such a system would also account for the large deshielding observed for F_b (-121 p.p.m. or -118 p.p.m.), and would be expected to exhibit a

FIG. 4. F^{19} N.M.R. SPECTRUM OF
1-METHOXY-PENTAFLUOROPROPENE (TRANS) IN SbF_5/SO_2

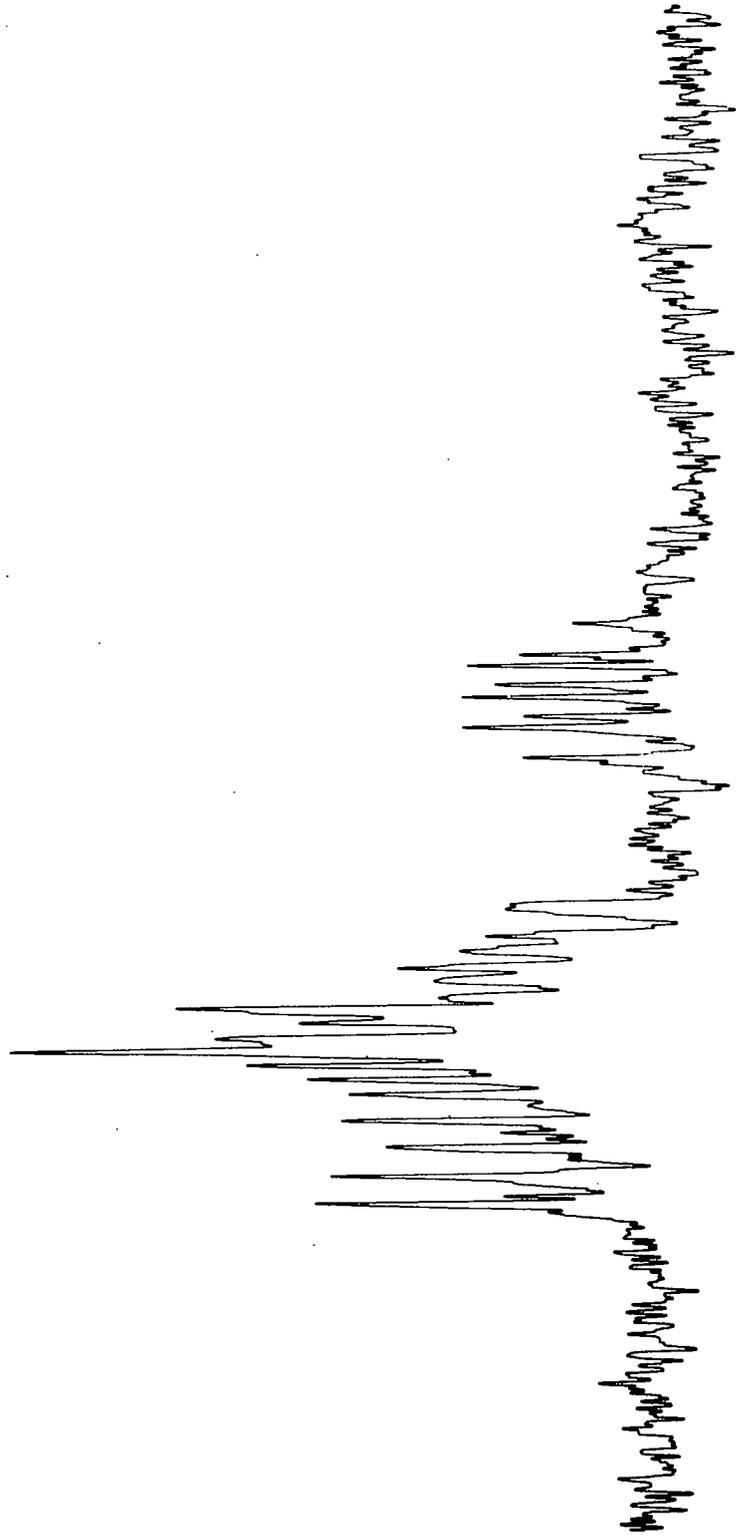


TABLE 17

N.M.R. Data^a of 1-Methoxypentafluoropropene (Trans) (i) in SO₂ and (ii) in
SbF₅/SO₂ at -30°.

$ \begin{array}{c} \text{CF}_3 \\ \text{a} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{F}_b \end{array} $	$ \begin{array}{c} \text{F}_c \\ \diagup \\ \text{C}=\text{C} \\ \diagdown \\ \text{OCH}_3 \end{array} $	Chemical Shift of CH ₃ O-	Fluorine Shifts		
			-CF ₃	F _b	F _c
(i) in SO ₂		-3.84	+66.6	+194.3	+110.3
(ii) in SbF ₅ /SO ₂		-5.93	+74.2(2) ^b	+73.7(1) ^b	+76.4(1) ^b
		[-2.09] ^c	[+7.6] ^c	$ \begin{array}{ c } \hline -120.6 \\ \hline \text{or} \\ \hline -36.6 \\ \hline \end{array} $ ^c	$ \begin{array}{ c } \hline -117.9 \\ \hline \text{or} \\ \hline -33.9 \\ \hline \end{array} $ ^c

^a Chemical shifts in p.p.m. from external CFC1₃ or T.M.S.;

^b Integral ratio;

^c Shift from original signals (assignments based on integral ratios).

complex spectrum. Unfortunately very poor yields of mixtures of products were obtained on quenching this solution with dry methanol and this fact, coupled with the incomplete N.M.R. analysis, prevents any definite conclusions being drawn.

3. Reactions of Other 1-Substituted Fluoropropenes with Antimony Pentafluoride in Sulphur Dioxide and in Fluorosulphonic Acid.

Attempts were made to generate other stable allyl cations using 1-methyl- and 1-phenyl-pentafluoropropenes. 1-Methylpentafluoropropene was found to be unreactive towards SbF_5 in SO_2 at temperatures up to -20° . In $\text{SbF}_5/\text{FSO}_3\text{H}$ at higher temperatures, extremely complex N.M.R. spectra were obtained, in which there was no evidence for an allyl cation.

In the case of 1-phenylpentafluoropropene (trans) ionization did occur with SbF_5 in SO_2 , but the mechanism of this was obscure. The phenyl signal experienced a large downfield shift and separate signals could be seen for ortho-, meta- and para-hydrogens (deshielded by -0.99 p.p.m., -0.39 p.p.m. and -2.43 p.p.m. respectively). However no reasonable analysis could be made of the fluorine spectrum and it was concluded that whatever reaction was occurring, it was not simply producing an allyl cation.

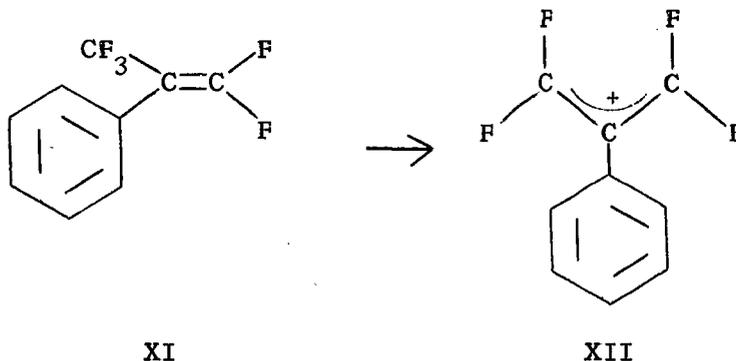
C. Reactions of 2-Substituted Fluoropropenes with Antimony Pentafluoride.

The charge structure of the allyl cation has been mentioned and evidence has been presented of the destabilizing inductive effect of a fluorine on the central carbon. This suggested that more stable ions might be formed by reactions of fluoropropenes substituted at the 2-position by electron donating groups (e.g. Ph- , $\text{CH}_3\text{O-C}_6\text{H}_4\text{-}$). However as mentioned in Section 3.1.A.2. the synthesis of such olefins is more difficult, thus limiting the range of substituents which could be used.

The ions produced from such olefins would be symmetrical if the allyl cation is planar. Unfortunately the reactions attempted were unsuccessful.

1. Reaction of 2-Phenylpentafluoropropene with Antimony Pentafluoride in Sulphur Dioxide.

It was hoped that reaction of this olefin with SbF_5/SO_2 would generate the symmetrical cation XII.



If this cation were planar only one fluorine resonance should be observed in the N.M.R. spectrum. However the F^{19} N.M.R. spectrum was somewhat more complex as can be seen from Table 18. Each of the three signals exhibited complex splitting patterns, and, although the deshielding of the phenyl group suggested that ionization had occurred and the fluorine integration corresponded to loss of one fluorine atom, there was no evidence of the allyl cation XII.

2. Reaction of 2-p-Anisylpentafluoropropene with Antimony Pentafluoride.

(a) In Sulphur Dioxide.

The p-anisyl group has been found to be sufficiently stabilizing to produce the allyl cation VI, and thus it was hoped that in the 2-position it would produce a stable cation such as XIV.

The solution of olefin XIII in SbF_5/SO_2 at low temperatures exhibited an extremely complicated P.M.R. spectrum, which suggested that ionization

TABLE 18

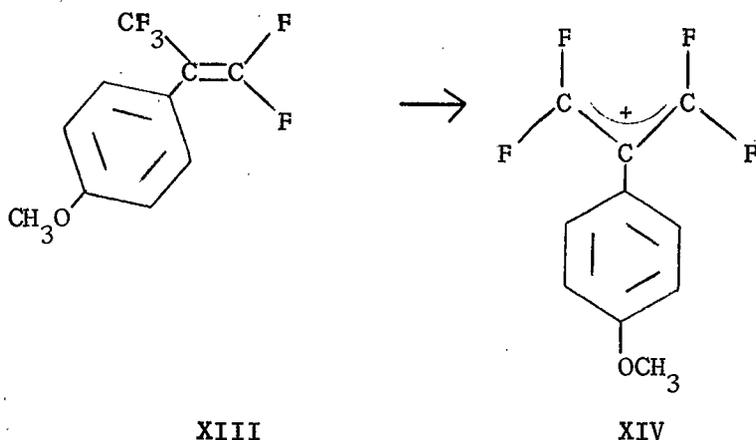
N.M.R. Data^a of 2-Phenylpentafluoropropene (a) in SO₂ and

(b) in SbF₅/SO₂

	Chemical Shift of Phenyl Group	Fluorine Shifts		
		CF ₃	F _c	F _d
(a) in SO ₂	-7.0	+58.7	+75.5	+80.4
(b) in SbF ₅ /SO ₂	-7.97	Peak 1 +54.5(1) ^b	Peak 2 +56.5(1)	Peak 3 +58.4(2)

^a Chemical shifts in p.p.m. from CFC₁₃ or T.M.S.;

^b Figures in brackets refer to integral ratios of peaks.

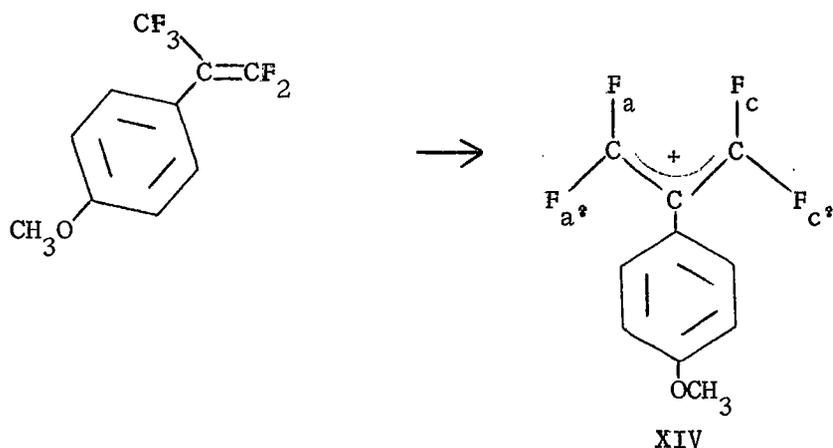


had occurred to produce a number of ionic species. The F^{19} spectrum was also very complicated, and no evidence was found for the existence of ion XIV although the presence of some starting material was indicated. Repeating the experiment using a twelve-fold excess of antimony pentafluoride produced a similar spectrum of weakened intensity.

(b) In Fluorosulphonic Acid.

The P.M.R. spectrum of the solution of this olefin in SbF_5/FSO_3H at $+10^\circ$ showed the p-anisyl group not substantially shifted from its original position. In the F^{19} spectrum two major peaks were visible, both singlets at $+66.35$ p.p.m. and $+66.5$ p.p.m., integrating in the approximate ratio of 3:2. Other minor signals due to impurities were visible in both proton and fluorine spectra. The spectrum remained the same on warming to $+30^\circ$.

As it is conceivable that the integration might be affected by these impurities, the fluorine spectrum might be consistent with the ion XIV,



if the two sets of fluorine atoms were in some way non-equivalent and did not couple together.

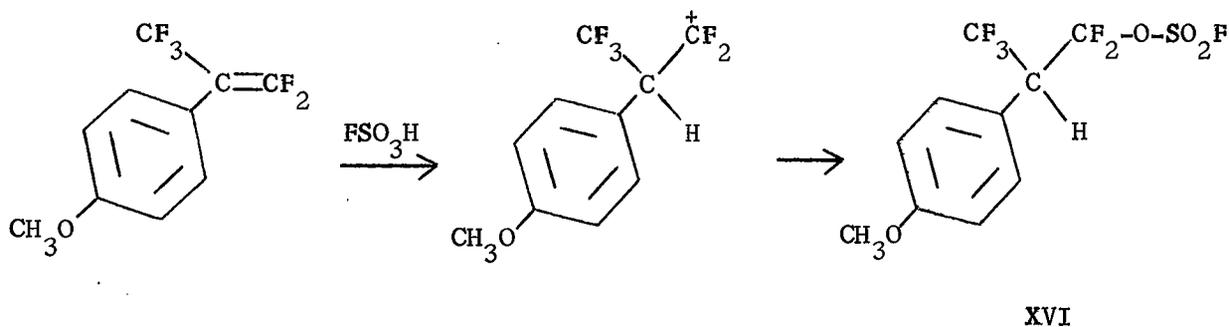
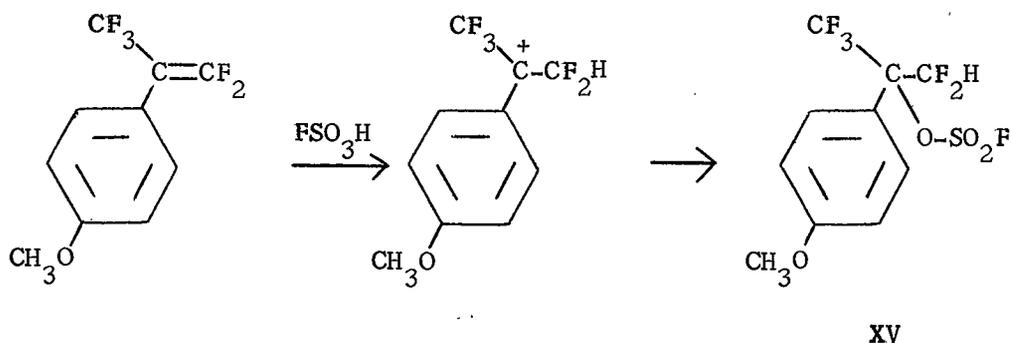
This of course seems very unlikely, and in fact on quenching the solution with dry methanol, the recovery of a product with an almost identical N.M.R. to that described above makes it clear that an ionization of this type has not occurred.

A viscous liquid was obtained from this quenching reaction. From its P.M.R. spectrum it could be seen that only one methoxy group, from the p-anisyl group, was present at -4.0 p.p.m. The phenyl ring could also be seen at -7.46τ , and to low field of this, at -7.93τ was another signal integrating for one proton.

In the fluorine spectrum the two signals could again be seen at $+66.29$ p.p.m. and $+66.43$ p.p.m. (the difference in chemical shifts being due to solvent effects). However to very low field was a single fluorine signal at -59.0 p.p.m. (downfield from CFCl_3). This would appear to be due to an $-\text{SO}_3\text{F}$ group and in the previous spectrum was probably masked by the strong solvent signal in HSO_3F .

Thus it would appear from the N.M.R. spectrum that addition of fluorosulphonic acid to the olefin has occurred, an observation which is not unusual in the chemistry of fluorinated olefins.⁷⁴ Two possible products XV or XVI may be formed from such an addition.

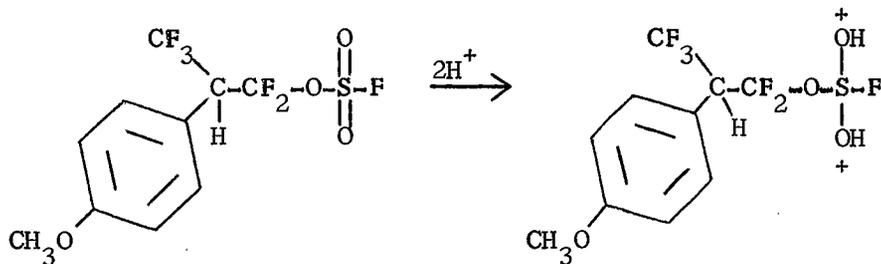
Unfortunately, as the fluorine signals showed broadening and thus couplings could not be measured, it was not possible to distinguish conclusively between these possibilities. However neither of the signals at $+66.4$ p.p.m. or $+66.3$ p.p.m. would appear to correspond to a $-\text{CF}_2\text{H}$ group (such groups appearing in the region $110 - 130$ p.p.m.) and no large geminal $-\text{CF}_2-\text{H}$ coupling was observed. The position of either of the peaks



would be more consistent with a CF_2 group attached to an electronegative group (such as $-\text{SO}_3\text{F}$).

Thus from the F^{19} chemical shifts it would appear that the adduct XVI has been formed.

Analysis figures agree with the formation of an adduct such as XVI, but mass spectral analysis gives a parent peak two mass units above that expected for XVI. The only likely explanation for this observation is that in the mass spectrometer, the molecule picks up two atoms of hydrogen, possibly by protonation of the $-\text{SO}_3\text{F}$ group.



Such behaviour, although unlikely, is not inconceivable.

D. Conclusions.

Both the successful and unsuccessful reactions which have been described in this Chapter have given rise to a number of interesting points. It is noticeable that there was no evidence for radical cations (which have been mentioned in the literature¹¹⁰⁻¹¹³) in these reactions. Although some intense colours were observed, especially for those fluoropropenes containing aromatic substituents, and signals were often weak and almost masked by background noise, it was possible in all cases to obtain reasonable spectra.

The 1,1,2,3-tetrafluoro-3-p-anisyl allyl cation has been discussed in detail, but as yet no attempt has been made to account for the surprising lack of success in generating allyl cations from the other systems attempted.

The failure to prepare the 1,1,2,3-tetrafluoro-3-methyl allyl cation, whilst surprising in comparison with the cyclobutene work which is described in Chapter 4, could be attributed to the necessity for a substituent which can stabilize the ion via π interaction. However this does not explain the amazing ability of the p-anisyl group to stabilize the allyl system when, taken singly, the phenyl and methoxy groups are not capable of so doing.

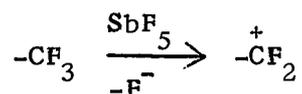
Similarly the lack of success in generating a 2-substituted tetrafluoroallyl cation is extremely interesting. As a fluorine atom at the 2-position is expected (and has been shown in Section 3.1.B.1.(b)) to exert a destabilizing effect on the allyl cation, it was anticipated that replacement of a fluorine in this position by an electron donating group

would encourage ionization and produce a more stable cation.

However this was not observed and, in the 2-position, even the p-anisyl group was not capable of stabilizing the formation of a 2-substituted tetrafluoroallyl cation.

The effect of a substituent group on the generation of an allyl cation can probably be split into two major factors:

1. Its ability to encourage the removal of a fluoride ion from the CF_3 - group of the fluoropropene,



2. Its stabilizing effect on the resulting cation,



If the most important factor in the generation of an allyl cation was the second of these, i.e. the stabilization of the product ion, one would expect a 2-substituent to favour the overall ionization, for the reasons previously discussed. However a 2-substituent might not be expected to have a great effect on the first step, i.e. the initial loss of fluoride ion.

Thus the lack of success in generating allyl cations with totally fluorinated terminal carbons might be due to the fact that the most important factor in their formation is the initial ionization, which itself requires the aid of a substituent group.

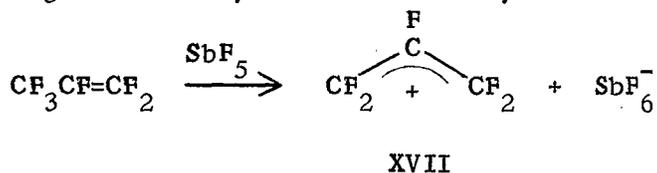
Such an explanation might also account for the complete unreactivity of 1-methylpentafluoropropene in comparison with 1-methoxypentafluoropropene which, although it did not generate a simple allyl cation, did undergo reaction with SbF_5/SO_2 at -30° . This could perhaps be a reflection of the inability of the methyl group to assist in the initial ionization, unlike the methoxy group which can encourage the ionization by conjugative

interaction.

Indeed, perhaps the outstanding ability of the p-anisyl group to stabilize the system is due to its particular ability to aid the initial ionization step by delocalizing charge over a greater number of sites.

3.2. Reaction of Hexafluoropropene with Antimony Pentafluoride.

As a result of the interesting observations described in the first part of this chapter, it was decided to investigate the reaction between hexafluoropropene itself with antimony pentafluoride, in the hopes of observing the totally fluorinated allyl cation XVII.



Initially N.M.R. studies were attempted to follow the reaction. It was found that at low temperatures (below -20°) in sulphur dioxide, no reaction occurred between hexafluoropropene and antimony pentafluoride (as later reported in the literature⁷⁴):

However when hexafluoropropene was sealed in an N.M.R. tube with an excess of antimony pentafluoride and the N.M.R. run from $+30^\circ$ to $+90^\circ$, it was quite apparent that a change was occurring, although the presence of broad SbF_5 signals prevented an analysis. It was also noticed that formation of a white solid occurred on raising the temperature.

A series of experiments was then carried out between hexafluoropropene and SbF_5 in sealed Carius tubes, at temperatures between 30° and 100° , and for a variety of reaction times. The volatile products were collected and were found to consist of quantities of hexafluoropropene with two other major components present.

At lower temperatures (i.e. around 30°), almost quantitative recovery of volatiles was achieved, but conversion of hexafluoropropene was low, while

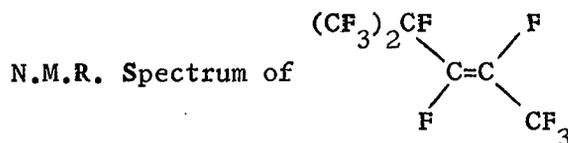
TABLE 18A

N.M.R. Spectrum of $(CF_3)_2CFH$

Group	Chemical Shift ^a	Coupling Constants Hz
$(CF_3)_2-C$	+76.5	$J_{(CF_3)_2-C-F} = 12$ $J_{(CF_3)_2-C-H} = 5$
Isopropyl F	+215	$J_{F-C-(CF_3)_2} = 12$ $J_{F-C-H} = 44$
H	-4.57	$J_{H-F} = 44$ $J_{H-C-(CF_3)_2} = 5$

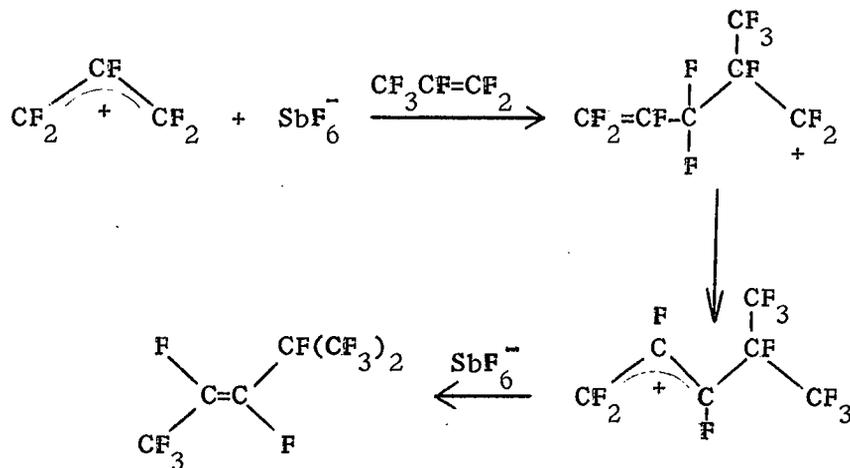
^a Chemical shifts in p.p.m. from T.M.S. or $CFC1_3$.

TABLE 18B



Group	Integration	Chemical Shift p.p.m. from $CFC1_3$
$CF_3-C=$	3	+72.4
$(CF_3)_2C-$	6	+77.1
Vinyl fluorines	1	+175.8
	1	+176.3
Isopropyl fluorine	1	+190

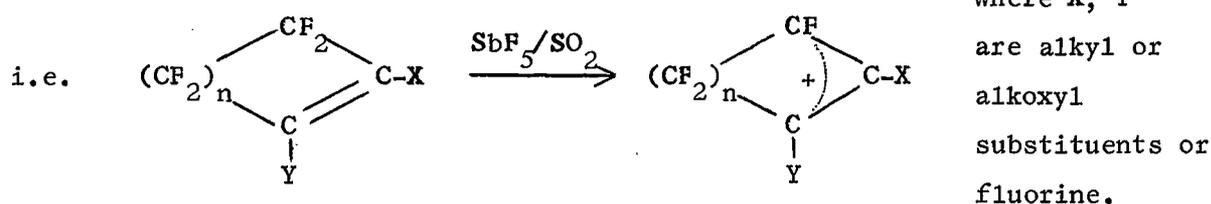
Thus whilst the dimer may be a simple product of nucleophilic attack on the olefin, the results described in the first part of this chapter, and the absence of other oligomers does allow the possibility that the dimer might be formed from an intermediate allyl cation, perhaps by a reaction mechanism of the type suggested by Mhyre and Andrews for the dimerization of 3,3,3-trifluoropropene; ^{121,122} i.e.



CHAPTER 4

Fluorinated Cyclic Allyl Cations

An extension of the investigation of some highly fluorinated allyl cations was a study of the reaction of some cyclic olefinic systems with antimony pentafluoride. It was hoped in these cases that removal of a fluorine from a $>CF_2$ group would occur to form an allyl cation via conjugation with the double bond:



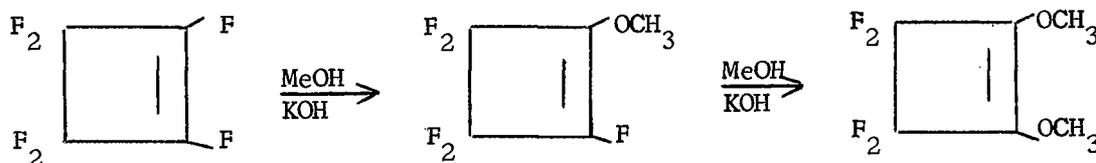
The preparation of a carbocation from the first member of this series ($n = 0$)⁹⁸ was described in Chapter 2 (Section 2.5.A.1.).

4.1. Cyclobutenyl Cations.

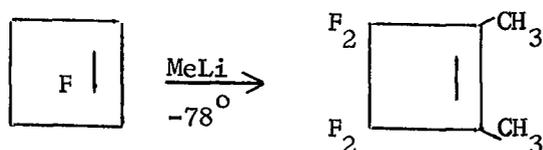
Perfluorocyclobutene itself was found to be unreactive towards antimony pentafluoride, both at low (i.e. -30°) and high (up to 60°) temperatures. However some interesting results were obtained on investigation of the reaction of a series of substituted cyclobutenes with this acid system.

A. Preparation of Starting Materials.

The cyclobutenes used were prepared by literature methods. Mono- and di-methoxycyclobutenes were prepared by the action of methoxide ion on perfluorocyclobutene:¹³¹



whilst 1,2-dimethyltetrafluorocyclobutene was prepared by reaction of methyl lithium with perfluorocyclobutene:¹²⁵



This was also reported as a method of preparing 1-methylpentafluorocyclobutene, but the reasonable yields reported in the literature could not be reproduced.

In the first part of this chapter an analysis will be presented of the N.M.R. spectra of solutions of these cyclobutenes in SbF_5/SO_2 and, in some cases, in $\text{SbF}_5/\text{FSO}_3\text{H}$. Collective discussion of the ions produced, and comparison with the results obtained in Chapter 3 will be presented in a later section (Section 4.1.F.).

B. Reaction Between 1,2-Dimethyltetrafluorocyclobutene and Antimony Pentafluoride

1. In Sulphur Dioxide.

The chemical shift data of 1,2-dimethyltetrafluorocyclobutene and its solution in SbF_5/SO_2 are presented in Table 19 and Figs. 5 and 6.

Evidence for ionization is immediately apparent from the proton spectrum. This originally consisted of one methyl signal, coupled by 1.25 Hz to the equivalent CF_2 groups. This signal is now split into a doublet and triplet which are deshielded by -1.50 p.p.m. and -0.50 p.p.m. respectively, and which integrate in the ratio 1:1. No quartet splitting between the methyl groups is observed.

Two signals are also visible in the fluorine spectrum. At very low field (-18.2 p.p.m.) is a signal which integrates for one fluorine, and

FIG. 5. P.M.R. SPECTRUM OF

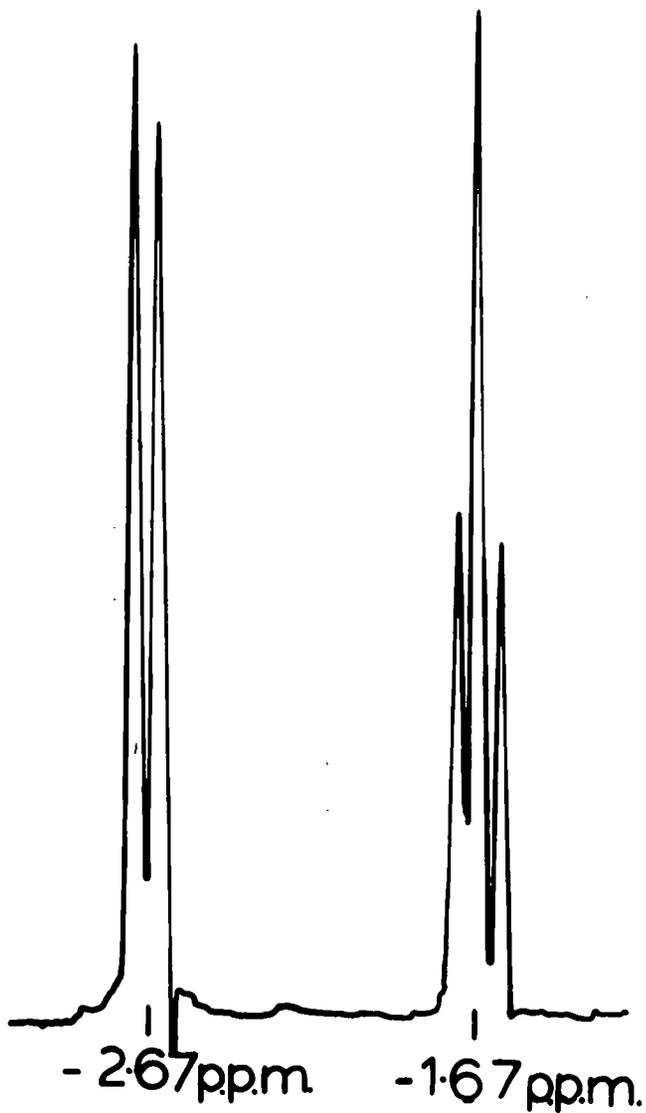
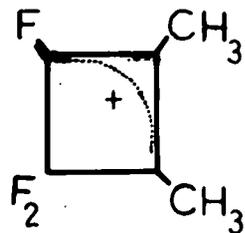


FIG. 6. F^{19} N.M.R. SPECTRUM OF

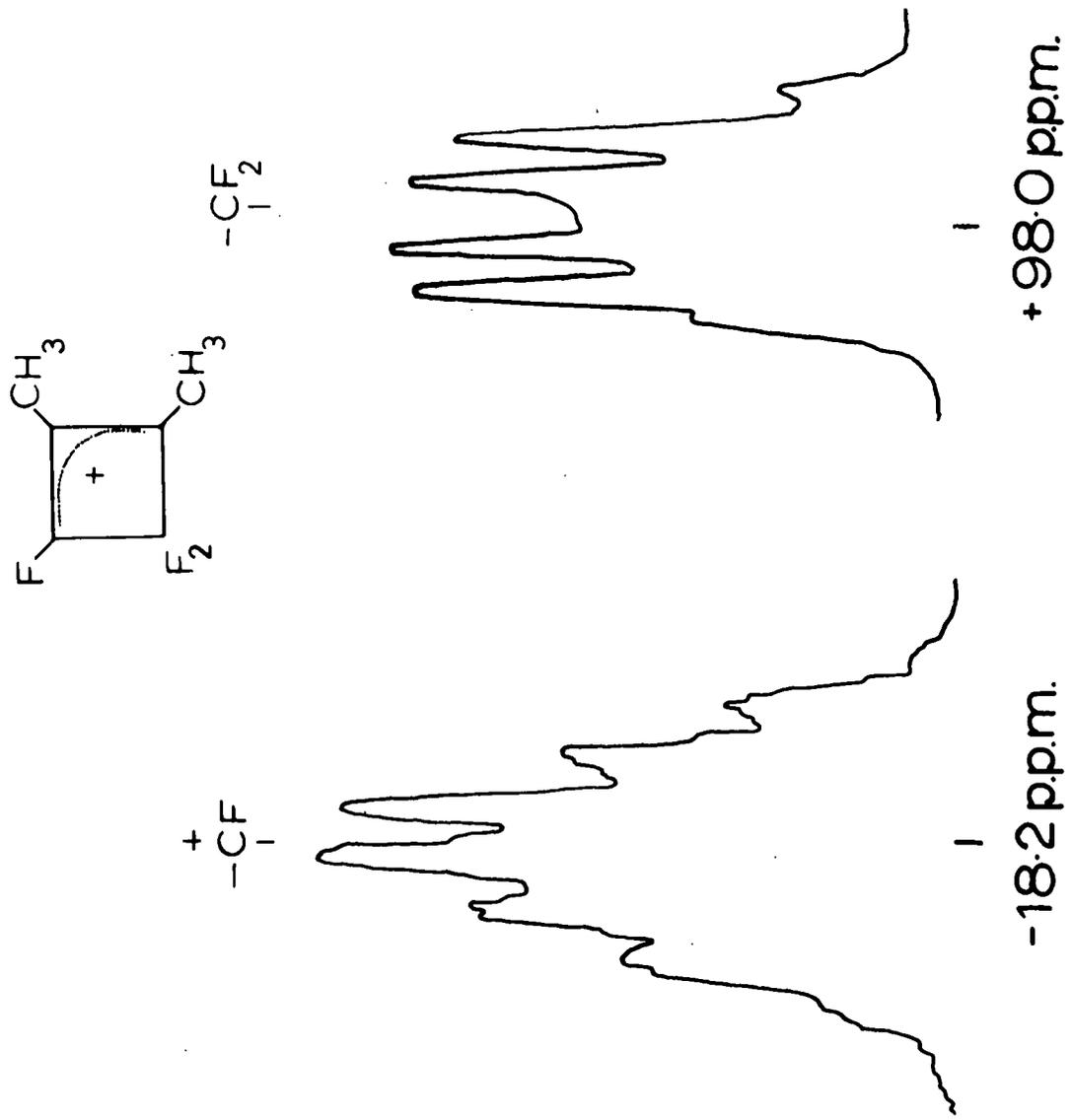
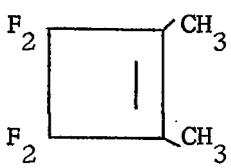
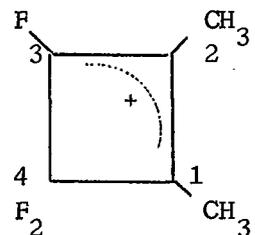


TABLE 19

Chemical Shifts^a for XXI and the Ion XXII at -30°

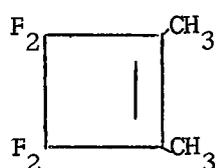
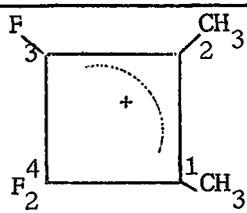
Cyclobutene (in SO ₂)	CH ₃				CF ₂
	-1.17				+115.6
Ion (in SO ₂)	CH ₃ (1)	CH ₃ (2)	-CF	CF ₂	
	-2.67 [-1.50] ^b	-1.67 [-0.50]	-18.2 [-133.8]	+98.0 [-17.6]	

^a p.p.m. from external TMS or CFC1₃.

^b figures in brackets represent downfield shift of signal.

TABLE 20

Coupling Constants for XXI and Ion XXII (Hz)

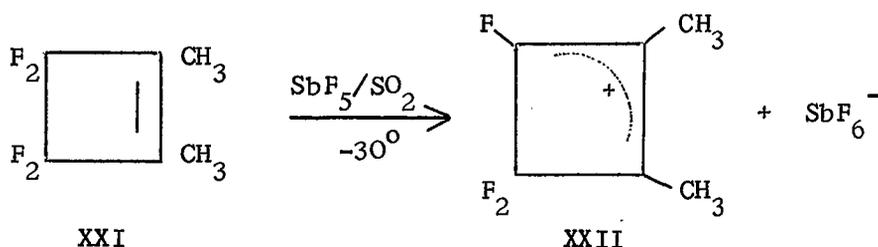
Cyclobutene	J _{H-F}	Ion	J ₁₃	J ₂₄	J _{F-F}
	1.25		4.5	3.9	10



which consists of a triplet of quartets. From its position (deshielded by -134 p.p.m. from the original signal) it is clear that it is caused by a fluorine atom directly attached to a positive centre, i.e. by a $\overset{+}{\text{C}}\text{-F}$ group.

The other fluorine resonance, which integrates for two fluorines, occurs at +98.0 p.p.m. and consists of a doublet of quartets.

This chemical shift data is consistent with the ionization of the cyclobutene to the 1,2-dimethyl-3,4,4-trifluorocyclobutenyl cation XXII.



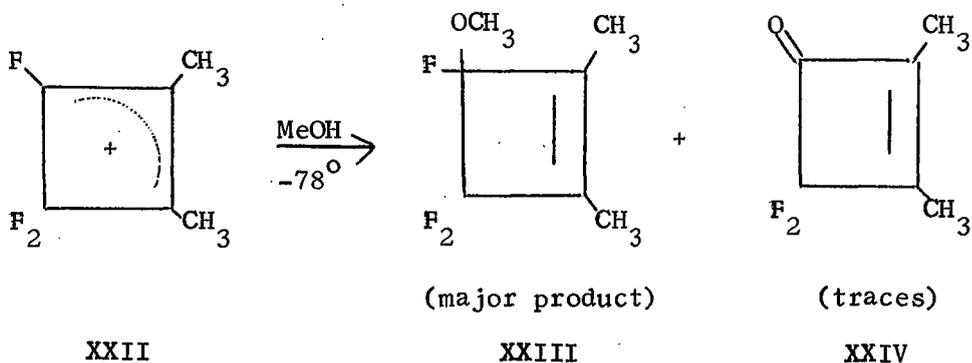
Such an ionization is also indicated by the coupling constant data, presented in Table 20.

Each type of methyl group couples with only one fluorine group, and as cross ring couplings in cyclobutenes are generally larger than couplings between adjacent sites,¹³² the assignments were made as shown in the Table.

The observation that cation formation brings about rehybridization, which is accompanied by an increase in coupling constants has been mentioned in Chapter 3. This effect is also seen in the spectrum of ion XXII in which quite substantial increases in proton-fluorine couplings are observed. Comparison with other systems will be made in a later section of this chapter (Section 4.1.F.4.).

(a) Quenching of the Ion with Dry Methanol.

Quenching the ion with dry methanol yielded two major products, 1,2-dimethyl-4-methoxytrifluorocyclobutene XXIII and 1,2-dimethyl-3,3-difluorocyclobutenone XXIV.



The structures of these cyclobutenes were deduced from their N.M.R. spectra, shown below in Table 21.

TABLE 21
N.M.R. Data^a for XXIII and XXIV

Cyclobutene	Proton Shifts		Fluorine Shifts		Coupling Constants (Hz)		
	CH ₃ -	-OCH ₃	CF	CF ₂	J _{H-F}	J _{F-F}	J _{H-H}
	-1.56 -1.71	-3.26	+111.26	+115.3	v. small	v. small	
	-1.99 -2.30			+110.8	3.7 1.1		1

^a Chemical shifts in p.p.m. from external T.M.S. or CFC₁₃

The cyclobutene XXIII showed two fluorine signals integrating in the ratio 1:2. Neither of these signals was in the vinyl-fluorine region and thus it was deduced that both were due to fluorines attached to saturated carbons. This information, coupled with the observation of two methyl signals and one methoxy-signal in the proton spectrum suggested a

structure such as XXIII.

The cyclobutenone XXIV showed one fluorine signal which exhibited couplings with two methyl groups. The larger coupling was attributed to cross-ring coupling.¹³² The observation of a carbonyl group in the infrared spectrum suggested the structure XXIV which was confirmed by its mass spectrum.

The formation of these cyclobutenes, coupled with the N.M.R. evidence, is proof of the intermediate existence of ion XXII.

C. Reaction Between 1,2-Dimethoxytetrafluorocyclobutene and Antimony
Pentafluoride.

It has been found that halogenated cyclobutene ethers are particularly susceptible to hydrolysis via loss of halide ion.¹³³ This indicated that such compounds should be especially capable of forming allyl cations with Lewis acids.

1. In Sulphur Dioxide.

An unusual effect was observed in the N.M.R. spectrum of 1,2-dimethoxytetrafluorocyclobutene in SbF_5/SO_2 solution. Two separate sets of signals, set A and set B, were seen.

The F^{19} spectrum of set A consisted of a triplet (integrating for one fluorine) at $+41.11$ p.p.m. and a doublet (integrating for two fluorines) at $+102.3$ p.p.m. That of set B also consisted of a triplet (integrating to one fluorine) at $+31.63$ p.p.m. and a doublet (integrating for two fluorines) at $+86.54$ p.p.m. Set B was of approximately half the intensity of set A.

The P.M.R. spectrum of the solution consisted of three singlets at -4.86τ , -4.64τ and -4.06τ , the latter signal consisting of two

FIG. 7 F^{19} NMR SPECTRUM OF 1,2-DIMETHOXYTETRAFLUORO-
CYCLOBUTENE IN SbF_5/SO_2

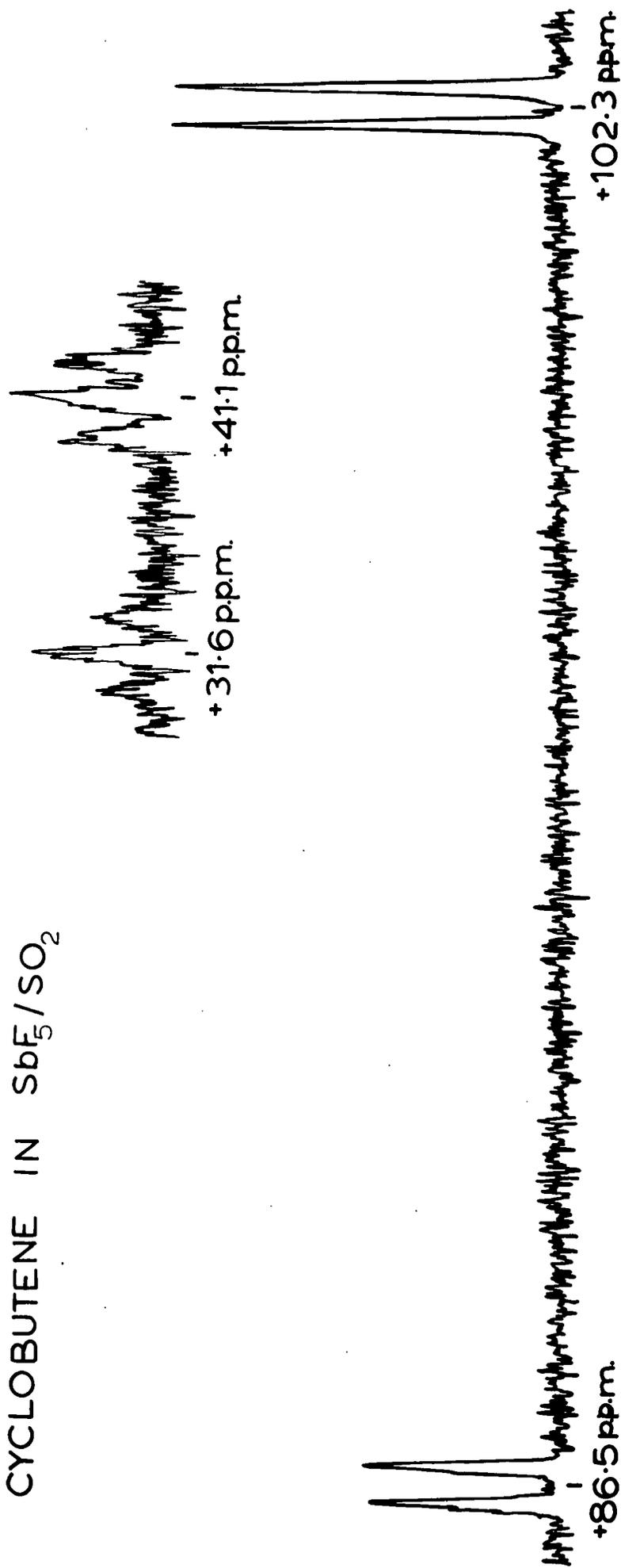
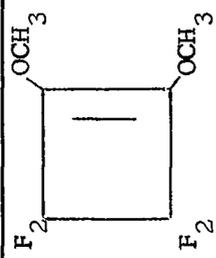
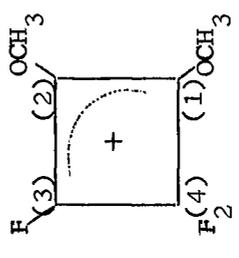


TABLE 22

N.M.R. Data^a for Cyclobutene XXV and Ion XXVI at -30°

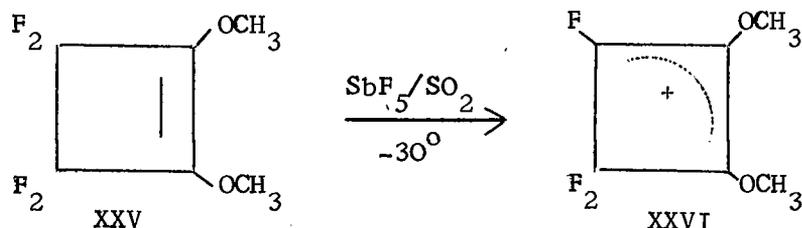
Cyclobutene (in SO ₂)	Chemical Shift -OCH ₃	Chemical Shift	CF ₂	Coupling Constants (Hz)
	-3.84	+111.4		0
Ion (in SO ₂)	OCH ₃ (1)	⁺ -CF	CF ₂	J _{F-F}
	-4.84 [-1.00] ^c	+41.11 [-70.29]	+102.3 [-9.1]	10.5
	-4.64 [-0.80]	+31.63 [-79.77]	+86.54 [-24.86]	10.5

^a Chemical shifts in p.p.m. from external T.M.S. or CFC1₃; ^b Set A are high field signals; ^c Figures in brackets represent downfield shifts from original signals.

overlapping proton resonances.

The N.M.R. data for this ion are presented below in Table 22 and in Fig. 7.

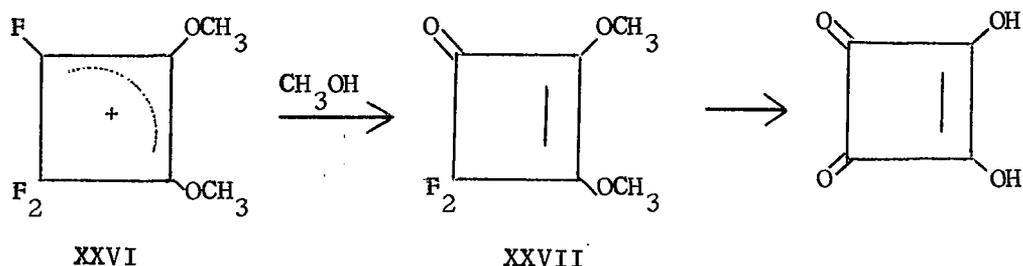
Clearly both sets of signals are consistent with ion XXVI.



(a) Quenching of the Ion with Dry Methanol.

Quenching of the ionic solution yielded a two component mixture. Any attempts to separate this mixture resulted in its vigorous hydrolysis, the product of which was a white solid which appears to be squaric acid, the end product of a number of hydrolyses of cyclobutene ethers.¹³³

The N.M.R. spectrum of the mixture showed only one fluorine singlet at 110.2 p.p.m. and three proton signals at -3.95τ , -3.79τ and -3.35τ . The F^{19} spectrum suggested the presence of a saturated $-CF_2$ group. The appearance of a carbonyl group in the infra-red spectrum of the mixture, coupled with the mass spectral data which showed a parent peak at 164, indicated the presence of the ketone XXVII.



Elimination of the signals due to this ketone from the N.M.R. spectrum of the mixture showed that the other component did not contain fluorine, suggesting that it might be an intermediate product in the ketone's hydrolysis.

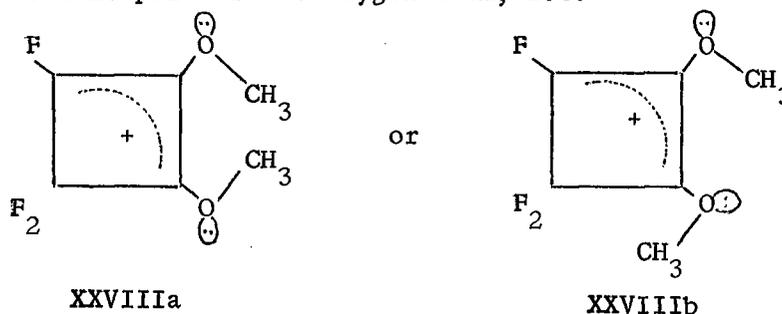
2. In Fluorosulphonic Acid.

Comparison of the spectrum of 1,2-dimethyltetrafluorocyclobutene in SbF_5/SO_2 with that of 1,2-dimethoxytetrafluorocyclobutene in the same medium indicates that the unusual effect observed in the latter case is in some way connected with the oxygen atoms. Three possible causes for this effect are immediately apparent.

- (a) SO_2 solvent molecules may be co-ordinated in some way with the ion. However on running the spectrum in $\text{SbF}_5/\text{FSO}_3\text{H}$ at -30° , an identical spectrum was obtained, thus eliminating this possibility.

[Use of FSO_3H brought about the expected uniform solvent shifts. For ease of comparison, the shifts in this section have been quoted in terms of the solvent system SO_2].

- (b) Identical ions may be formed with stereochemical differences, based on the lone pair of the oxygen atom, i.e.



However it is difficult to envisage how structures such as XXVIIIa and XXVIIIb could have such a profound effect on the chemical shifts of the fluorine atoms. Differences of 10 and 15 p.p.m. are observed between the fluorine atoms in sets A and B.

- (c) The ion may exist in varying states of co-ordination with the acid system via interaction with the methoxide groups.

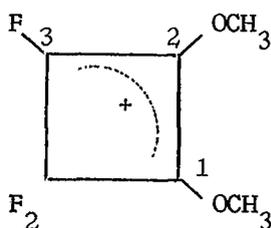
A variable temperature study in fluorosulphonic acid helped to explain this phenomenon. As previously mentioned, the spectrum at -30° in this medium was identical to that in SbF_5 in SO_2 at this temperature, but on raising the temperature, charges were observed.

In the initial proton spectrum, a signal was observed at -4.06τ , which apparently consisted of two overlapping proton peaks, one from set A and one from set B. At -7° this signal appeared to split.

A new signal was observed at -4.32τ , and as the temperature was raised, this signal increased in intensity while those at -4.64τ and -4.06τ decreased in intensity and the signal at -4.84τ broadened.

Eventually, at $+90^{\circ}$, the peaks at -4.32τ and -4.84τ were the only significant signals in the proton spectrum.

Although it is not possible to draw any definite conclusions from this experiment, the effect can reasonably be explained in terms of oxygen co-ordination. (Set B signals belonging to an ion in which oxygen co-ordination is quite strong). Whilst the charge on the oxygen atoms would be expected to be used to stabilize the ion, it is possible that the methoxy group in position (2) is not significantly involved in charge



XXVI

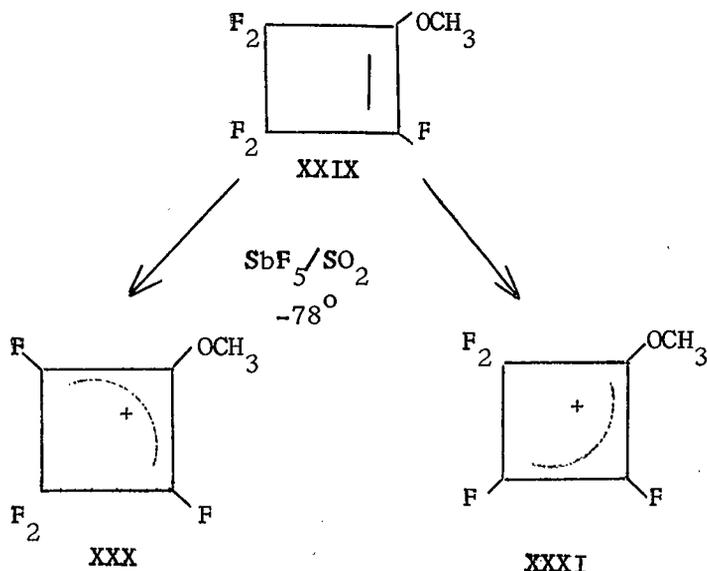
stabilization and thus possesses charge which is free to co-ordinate with the Lewis acid.

It must also be noted that in set B, the CF_2 group experiences an unusually large deshielding, indicating that it also is involved in the co-ordination in some way.

D. Reaction Between 1-Methoxyperfluorocyclobutene and Antimony
Pentafluoride.

1. In Sulphur Dioxide.

Ionization of this olefin could follow two conceivable routes:



and it was hoped that the N.M.R. spectrum of the ionic solution would help to determine which ion was formed. Unfortunately this spectrum was completely uninterpretable.

(a) Quenching of the Solution with Dry Methanol.

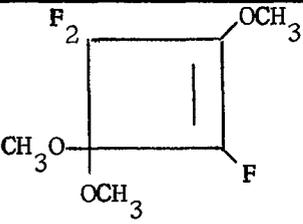
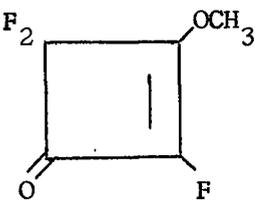
The two major products obtained from this quench were identified as 1,3,3-trimethoxytrifluorocyclobutene XXXII and 1-methoxy-2,4,4-trifluorocyclobutenone XXXIII.

The cyclobutenes were identified from their N.M.R. spectra, the data of which is presented in Table 23. The structures were assigned with the help of Table 24.

The cyclobutene XXXII showed two fluorine shifts at +117.0 p.p.m. and +135.2 p.p.m., integrating in the ratio 2:1. The signal at +135.2 p.p.m. was in the region for vinyl fluorines in such systems and the size of the

TABLE 23

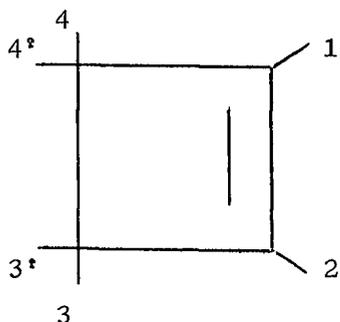
N.M.R. Data^a on XXXII and XXXIII

Cyclobutene	Proton Shifts		Fluorine Shifts J_{F-F}		
	$-\text{OCH}_3$	$(-\text{OCH}_3)_2$	CF vinyl	CF_2	Coupling Constants (Hz)
	-3.42	-2.86	+135.2	+117.0	23.5
	-4.24		+141.7	+118.2	22

^a Chemical shifts in p.p.m. from CFCl_3 or T.M.S.

TABLE 24

Typical Coupling Constants in Substituted Cyclobutenes (Hz)



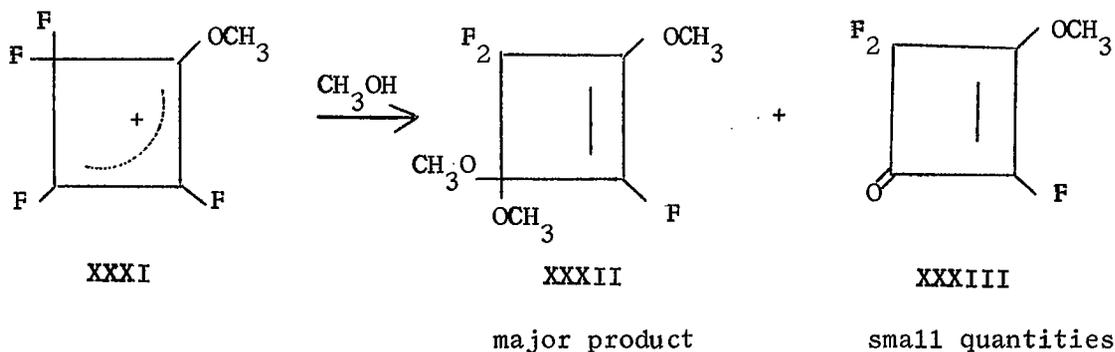
	J_{4-4^*}	J_{1-2}	J_{1-3}	J_{1-4}	J_{3-4}	J_{3^*-4}
J_{F-F}	+180 — +200	-8	+16 — +19	+4 — +8	-12 — -17	+24 — +30

fluorine-fluorine coupling constant suggested cross ring coupling. (It can be seen from Table 24 that such couplings are generally larger than couplings between fluorines on adjacent ring sites).

The proton spectrum showed the presence of three methoxy groups, and mass spectral data confirmed the presence of the cyclobutene XXXII.

The F^{19} spectrum of the cyclobutenone XXXIII showed the presence of a vinylic fluorine at +141.7 p.p.m. (integrating for one fluorine) and a saturated CF_2 group at 118.2 p.p.m. (integrating for two fluorines). Again the value of J_{F-F} suggested cross ring coupling. The P.M.R. spectrum showed the presence of only one methoxy group, and the infra-red spectrum showed the presence of a carbonyl group. Mass spectral analysis confirmed the presence of the cyclobutenone XXXIII.

Both of these products could have been formed from ion XXXI.



However they could also have been formed by acid catalysed nucleophilic attack on the original olefin. This seems less likely as in general hydrolysis of cyclobutene ethers requires high temperatures and long reaction times.¹³² However in the absence of N.M.R. data this possibility cannot be eliminated and thus the existence of ion XXXI cannot be proven.

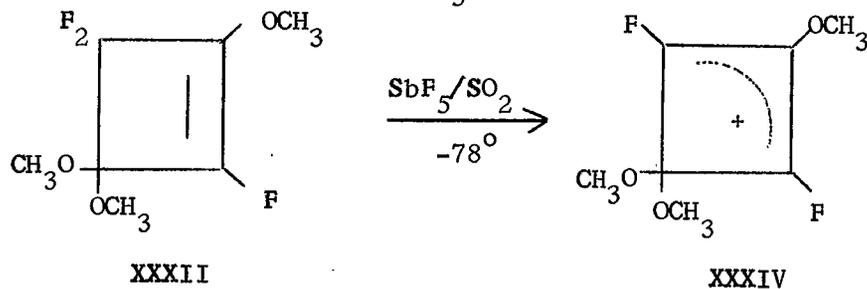
2. In Fluorosulphonic Acid.

It was hoped that reaction in this solvent might clarify the situation, but unfortunately this was not the case. An almost identical spectrum to that in SO₂ was observed, and the spectrum remained uninterpretable at higher temperatures.

B. Reaction Between 1,3,3-trimethoxytrifluorocyclobutene and Antimony Pentafluoride.

1. In Sulphur Dioxide.

From a consideration of previous results, it seemed likely that this cyclobutene might react with SbF₅ to form ion XXXIV.



The N.M.R. data for the product obtained on reaction of XXXII with SbF_5 is presented in Table 25. As can be seen, little information was acquired from the fluorine spectrum, the signals being broad and confused with the SbF_5 resonances. Certainly there is no evidence of the presence of a $-\overset{\dagger}{\text{C}}-\text{F}$ group.

TABLE 25

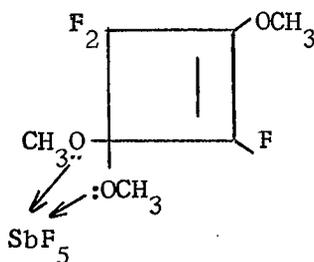
N.M.R. Spectrum^a of XXXII (a) in SO_2 , and (b) in SbF_5/SO_2

Solution	Proton Shift		Fluorine Shift	
	Vinylic $\text{CH}_3\text{O}-$	$(\text{CH}_3\text{O})_2$	Vinylic C-F	CF_2
(a) in SO_2	-3.41	-2.87	+135.2	+113.6
(b) in SbF_5/SO_2	-3.85 [-0.44] ^b	-4.58 [-1.71]	Broad, weak signals in region 105-120 p.p.m.	

^a Chemical shifts in p.p.m. from external T.M.S. or CFCl_3 ; ^b Figures in brackets represent downfield shifts from original signals.

More information is available from the proton spectrum. In an ion such as XXXIV the dimethoxy-group would not be expected to contribute significantly to the ionization of the ion. However this group experiences a large deshielding effect of -1.71 p.p.m. in comparison to the small deshielding of -0.44 p.p.m. experienced by the vinylic methoxide group. Inductive effects alone would not be expected to cause such a large downfield shift.

The results are more consistent with the formation of a donor-acceptor complex, of the type



The vinylic methoxy group and fluorines would experience only a small inductive deshielding in such a case.

Comparison of the large downfield shift of the dimethoxy group in this case with the shifts of the methoxy groups in the case of 1,2-dimethoxy-tetrafluorocyclobutene (Sec. 4.1.C.) indicates that oxygen co-ordination is much stronger in this case. This also gives some support to the possibility of co-ordination by the CF_2 group in 1,2-dimethoxy-tetrafluorocyclobutene.

(a) Quenching of the Solution with Dry Methanol.

Recovery of only starting material on quenching the solution with dry methanol also indicated that a donor acceptor complex was formed, rather than ionization.

2. In Fluorosulphonic Acid.

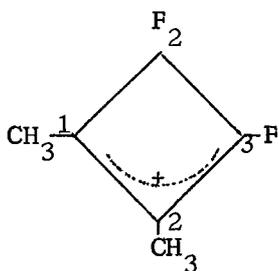
It was hoped that on heating the solution in magic acid, breakdown of the donor acceptor might occur (as observed for 1,2-dimethoxy-tetrafluorocyclobutene). However this was not the case, and an identical spectrum to that observed in SO_2 was obtained. The solution was heated to 60° with no noticeable changes.

F. Discussion.

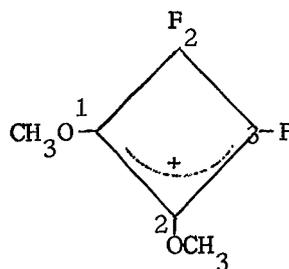
1. Chemical Shift Data.

The amount of deshielding experienced by a fluorine atom in varying charge situations has already been discussed (Chapter 3, Sec. 3.1.B.1.(b)), and some literature examples have been given in Tables 14 and 15.

Some interesting information has also been obtained by comparison of the downfield shifts experienced by the fluorine atoms in ions XXII and XXVI.



XXII



XXVI

In considering the downfield shifts of substituents, it has been shown (Chapter 3, Section 3.1.B.1.(b)) that care must be taken to compare stereochemically equivalent situations. In the formation of the ions shown above, rehybridization of the carbon at position 3 has occurred, from sp^3 to sp^2 . Thus measurement of the fluorine deshielding of the $-CF^+$ group from the original CF_2 group might again not necessarily be a true reflection of the charge situation.

However a comparison between the ions XXII and XXVI themselves of the deshieldings of the single fluorines is valid, and gives a good indication of the extent to which the fluorines are responsible for stabilizing the charge centre.

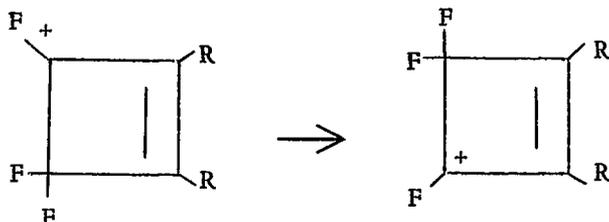
In fact the single fluorine in ion XXII is deshielded by 134 p.p.m. from the original signal, and that in ion XXVI by 70 p.p.m. This is of course the expected trend, as one might anticipate the methoxy group to be more capable of charge delocalization than the methyl group.

It is difficult to establish from the proton data the extent to which the hydrocarbon groups are involved in charge stabilization. The methyl group at position 1 in the ion XXII experiences quite a large downfield shift of -1.50 p.p.m. Its chemical shift is comparable to those quoted in the literature for methyl-cyclobutenyl cations (Chapter 1, Section 1.3.B.2.(b).2.(ii)).

The methoxy group at position 1 in ion XXVI experiences a smaller shift of -1.0 p.p.m., but it must be remembered that in this case the protons

are yet another atom removed from the cationic centre, and thus this shift is quite large.

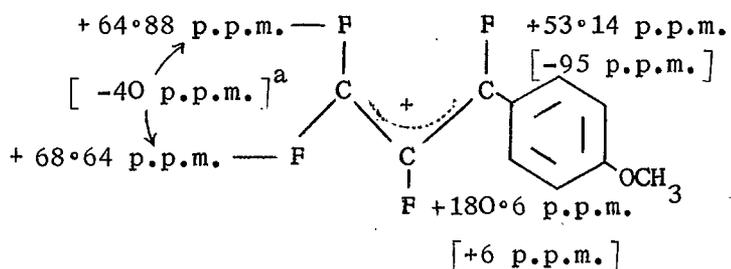
It is noticeable that in these cyclobutenyl cations sharp signals were observed for the fluorine atoms, and there was no evidence for fluorine 1,2-shifts, which would have led to equilibration of the signals, even in the variable temperature work, i.e.



did not occur. This contrasts with hydrocarbon cations in which 1,2-hydride shifts are quite common.

2. Comparison with 1,1,2,3-Tetrafluoro-3-p-anisylallyl Cation (VI).

The N.M.R. spectrum of this cation was discussed in detail in Chapter 3, and its chemical shift data are shown in brief below.



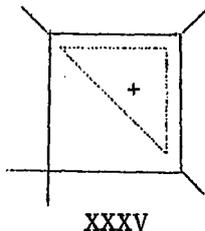
^a Figures in brackets represent deshielding as explained in Chapter 3.

VI

Comparison with the spectra obtained for the cyclobutenes shows the expected results. In ion VI the charge can be delocalized over a greater number of atoms than is possible in ions XXII and XXVI. Thus individual deshieldings are generally less than those observed for the cyclobutenyl cations, and the fluorine signals occur to slightly higher field.

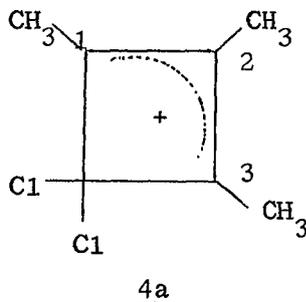
3. Charge Distribution.

Evidence has been reported in the literature for 1,3-interaction in cyclobutenyl cations (Chapter 1, Section 1.3.B.2.(b).1.).



It has been postulated that charge structures such as XXXV might exist in situations in which they are encouraged by steric factors.

The evidence put forward to support this theory has been in the chemical shifts of substituents at the 2-positions.^{15,33,39,40} In particular C^{13} N.M.R. measurements showed a large downfield shift for the carbon atom at position 2 in the ion 4a. The magnitude of this shift could not be accounted for by inductive effects from the 1 and 2 positions.

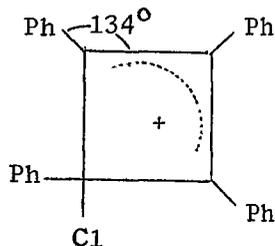


However in the ions investigated here there is no substantial evidence for positive charge being located at the 2-position. The downfield shifts of -0.5 p.p.m. for the methyl group and -0.22 p.p.m. for the methoxy group could be explained quite satisfactorily by inductive effects, from the 1 and 3 positions.

4. Rehybridization.

In the cyclobutenes, as in the propenyl systems, cation formation does involve a change in hybridization, as was mentioned in previous sections.

In general bond angles in allyl cations are considered to be 120° , but in the case of cyclobutenes, some distortion is to be expected, and in fact the external angles of 5a have been measured by crystallography and have



5a

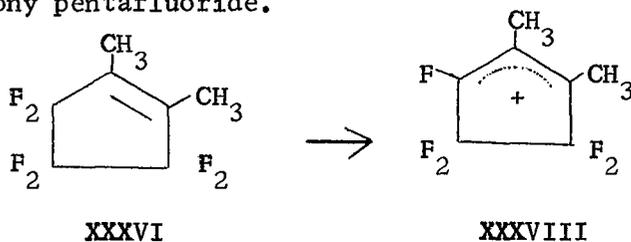
been found to be 134° (Chapter 1, Section 1.3.A.).

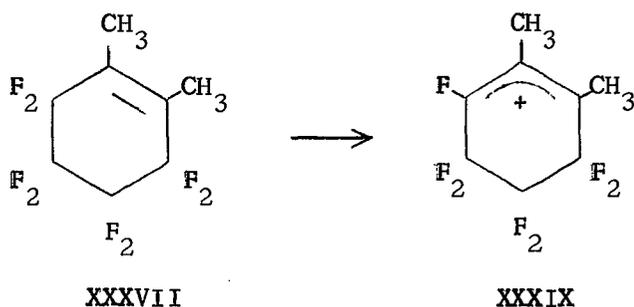
As anticipated this rehybridization brings with it an increase in coupling constants, and the increase in $J_{\text{H-F}}$ observed in the dimethyl system of 1.25 Hz to 3.9 Hz and 4.5 Hz has already been mentioned (Section 4.1.B.1.). This increase is not quite as dramatic as those observed in the 1,1,2,3-tetrafluoro-3-p-anisyl-allyl cation (VI) in Chapter 3, but is still a substantial increase for a methyl-fluorine coupling.

In discussing the fluorine-fluorine coupling constants, it is difficult to make comparisons, as both systems were initially symmetrical and thus increased couplings were unavoidable. However it is noticeable that in both cases couplings of about 10 Hz were observed.

4.2. Cyclopentenyl and -hexenyl Cations.

It was hoped to extend the investigation of fluorinated cyclic allyl cations into pentenyl and hexenyl cations, by reaction of 1,2-dimethyl-hexafluorocyclopentene **XXXVI** and 1,2-dimethyloctafluorocyclohexene **XXXVII** with antimony pentafluoride.

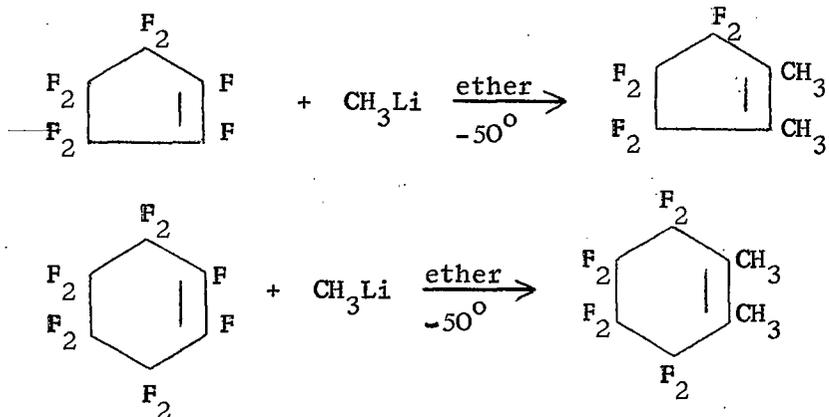




In each case the N.M.R. spectra of ions XXXVIII and XXXIX should show two distinct methyl signals and one low field fluorine signal (as in the case of 1,2-dimethyltetrafluorocyclobutene).

A. Preparation of Starting Materials.

The dimethyl-olefins were both prepared by the reaction of perfluoro-cyclopentene and perfluorocyclohexene with methyl lithium. Addition of the olefin to the methyl lithium at -50° produced solely di-substituted product.



B. Reaction of 1,2-Dimethylhexafluorocyclopentene with Antimony Pentafluoride.

No reaction occurred between XXXVI and SbF_5 when sulphur dioxide was used as the solvent. However the addition of XXXVI to $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2$ at -78° did produce a change in the N.M.R. spectrum as can be seen from Table 26 which presents the N.M.R. data of the olefin (a) neat and (b) in $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2$ at -30° .

From the shapes of the signals, it would appear that peaks 1, 3 and 5 in the neat liquid (a) correspond to peaks 1, 3 and 5 in the acidic solution (b),

TABLE 26

N.M.R. Data^a of XXXVI (a) Neat and (b) in $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2$ at -30°

Solution	Proton Shifts			Fluorine Shifts	
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
Neat	-1.57		116.4		133.6
$\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2$	-1.98	-4.49	109.2	116.5	131.6

^a Chemical shifts in p.p.m. from T.M.S. or CFC1_3 .

and the shifts observed are merely due to solvation effects. Thus in case (b) two new signals appear, at -4.49τ in the proton region and $+116.5$ p.p.m. in the fluorine region.

These results are not consistent with those expected for formation of the ion XXXVIII. Variable temperature investigation using neat $\text{SbF}_5/\text{FSO}_3\text{H}$ showed the same proton spectrum but an even more complex fluorine spectrum, and an analysis was not possible.

Quenching the solution with dry methanol gave very poor yields of a mixture of products.

C. Reaction Between 1,2-Dimethyloctafluorocyclohexene and Antimony Pentaffluoride.

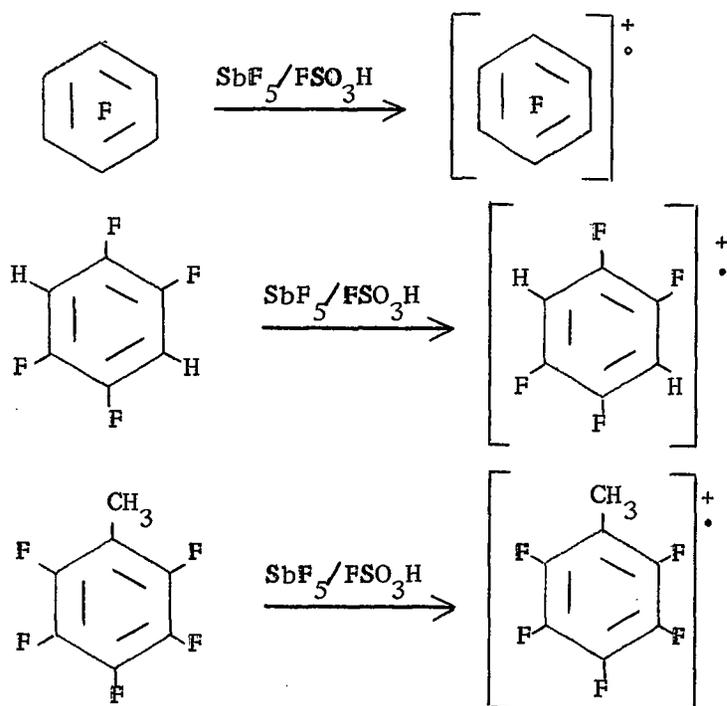
The cyclohexene XXXVII did not react with SbF_5/SO_2 or $\text{SbF}_5/\text{FSO}_3\text{H}/\text{SO}_2$ at low temperatures. The olefin was then mixed with the neat acid at 0° , but the resulting solution showed only broad solvent peaks in its N.M.R. spectrum, despite homogeneous mixing. This result suggested free radical formation

which was confirmed by preliminary E.S.R. studies in which an extremely strong signal was observed. However it was not possible from this signal to determine the number or type of species present, and a more detailed investigation of the E.S.R. spectrum was not possible.

D. Conclusions.

From a consideration of the success obtained with 1,2-dimethyl-tetrafluorocyclobutene, it seemed reasonable to expect similar results from the systems XXXVI and XXXVIII. However this was not the case, and these initial attempts to expand the series of cyclic fluorinated allyl cations were unsuccessful.

In the case of 1,2-dimethyloctafluorocyclohexene, the formation of free radicals is analogous to the formation of radical cations in the reaction of some highly fluorinated benzenes (and naphthalenes) with Lewis Acids,¹¹⁰⁻¹¹³ e.g.



Unfortunately lack of experimental evidence prevents a more detailed comparison.

These experiments do not of course preclude the possibility of producing fluorinated allyl cations from five or six membered rings, but the results do suggest that it may not be possible to produce ions with a high degree of fluorination.

CHAPTER 5

Experimental

5.1. Reagents.

Hexafluoropropene and perfluorocyclobutene were purchased from Peninsular Chem. Research Inc. Methyl lithium was obtained from R.N. Emanuel and antimony pentafluoride from Columbia Chemicals.

5.2. Instrumentation.

Infra-red spectra were recorded on a Grubb-Parsons [®]Spectromaster[®]. Volatile liquid or gaseous samples were vaporized into an evacuated cylindrical cell with potassium bromide end windows. Liquid samples were recorded in the form of a thin contact film between potassium bromide plates, and solid samples pressed into homogeneous thin discs with potassium bromide.

Proton (¹H) and fluorine (¹⁹F) nuclear magnetic resonance spectra were recorded on a Varian A56/60D, operating at 60 and 56.4 Mc/s respectively; the normal running temperature being 40^o.

Mass spectra were recorded on an A.E.I. M.S.9 spectrometer, and all molecular weights were determined by this means.

Carbon and hydrogen analyses were obtained using a Perkin-Elmer 240 Elemental Analyser. Analysis for halogens was carried out as described in the literature.¹³⁵

Analytical gas/liquid chromatography was carried out using Column A (di-n-decyl phthalate on celite) in a Perkin-Elmer 452 and Column O (silicone elastomer on celite) in a Pye 104. Preparative scale separations were carried out using either columns O or A in a Perkin-Elmer F21 or Varian [®]Aerograph[®] instrument.

Boiling points were determined by Siwoloboff's method and are not corrected for changes in atmospheric pressure.

5.3. Preparation of Starting Materials.

Starting materials were prepared in general by literature methods, although in some cases adaptations of these methods were used for ease of preparation. The syntheses of 1-p-anisylpentafluoropropene and 1,2-dimethylhexafluorocyclopentene, both new compounds, are described below. The adapted method for the synthesis of the methoxycyclobutenes is also described.

5.3. A. Preparation of 1-p-anisylpentafluoropropene.

Using ethylene dibromide as an initiator, para-bromoanisole (20.5 gm., 110 mm.) was added dropwise to magnesium turnings (3.0 gm., 115 mm.) in 80 ml. dry ether, in a three-necked flask equipped with a water condenser, under a nitrogen atmosphere. After the addition was completed the mixture was refluxed for 30 minutes.

The dropping funnel was removed from the flask and replaced by a stopper. The flask was cooled in liquid air, under a nitrogen atmosphere.

The inlet and outlet taps were closed and the flask disconnected from the nitrogen line. A rubber bladder was attached to the outlet tap. The inlet tap was connected to a vacuum line and the flask evacuated. The outlet tap was opened to evacuate the bladder.

Hexafluoropropene (15 gm., 100 mm.) was condensed into the flask, the tap closed, and the apparatus allowed to warm-up to room temperature. After a few hours of stirring the reaction mixture the bladder appeared to be completely deflated, but it was left overnight to ensure that reaction was complete.

Hydrolysis was carried out using dilute HCl (0°). The resulting solution was ether extracted, washed with aqueous bicarbonate and dried over $MgSO_4$. The ether layer was removed leaving a dark brown liquid which was

partially purified by vacuum transfer (yield 12.5 gm., 52%).

Purification of this liquid was achieved using preparative scale gas/liquid chromatography, Column O, 160°. The first product to be eluted was cis-1-p-anisylpentafluoropropene, b.pt. >200°, yield after purification 1 gm., 5%. (Found: C, 50.54; H, 2.67; F, 39.86; M, 238. $C_{10}H_7F_5O$ requires C, 50.42; H, 2.94; F, 39.92; M, 238) I.R. No. 2. The second product to be eluted was trans-1-p-anisylpentafluoropropene, b.pt. >200°, yield after purification 8 gm., 42%. (Found: C, 50.47; H, 2.61; F, 39.49; M, 238. $C_{10}H_7F_5O$ requires C, 50.42; H, 2.94; F, 39.92; M, 238) I.R. No. 1.

B. Preparation of 1,2-Dimethylhexafluorocyclopentene.

Methyl lithium (65 mm.) in 130 ml. ether was cooled to -50° in a three necked flask fitted with vacuum-jacket condenser and dropping funnel, under an atmosphere of dry nitrogen. [At this temperature a slight amount of crystallization occurred so lower temperatures were not used].

Perfluorocyclopentene (6.0 gm., 29 mm.) was added dropwise and immediate reaction was observed by the dissolution of the suspended methyl lithium, and discolouration of the solution.

The solution was allowed to warm up to room temperature, hydrolysed with ice cold dilute HCl, ether extracted and the ethereal layer dried over magnesium sulphate.

After removal of the ether layer, the resulting coloured liquid was vacuum transferred to give a colourless liquid (2.3 gm.) which consisted of one major component (~90%). On purification by preparative-scale gas-liquid chromatography (Column A) this liquid was found to be 1,2-dimethyl-hexafluorocyclopentene, b.pt. 140°, 40% yield. (Found: C, 40.89; F, 55.88; M, 204. $C_7H_6F_6$ requires C, 41.18; F, 55.88; M, 204) I.R. No. 4.

The low yield of product was attributed to the temperature used, which was higher than usual for organo-lithium reactions, which are usually carried out at -78° . However solubility problems prevented a temperature of lower than -50° being used.

C. Preparation of 1-Methoxypentafluorocyclobutene and 1,2-Dimethoxy-tetrafluorocyclobutene.

The literature preparation of these cyclobutenes involves bubbling perfluorocyclobutene through a 10% solution of potassium hydroxide in methanol.¹³¹ This method was adapted to an atmospheric pressure reaction which produced good yields and was a more convenient preparation.

1. 1-Methoxypentafluorocyclobutene.

Potassium hydroxide (3.2 gm., 57 mm.) was dissolved in methanol (32 gm., 100 mm.) in a flask, two-necked, fitted with a bladder and condenser. The flask was frozen in liquid air and evacuated. Perfluorocyclobutene (10 gm., 62 mm.) was condensed into the flask and the apparatus closed and allowed to warm up to room temperature.

The olefin reacted immediately with the methanolic KOH, and in fact expansion of the bladder was not observed. As soon as all the contents of the flask had melted, the apparatus was opened to the atmosphere and the solution poured into cold water. The lower layer was separated and dried over magnesium sulphate. Analysis showed it to consist only of the mono-substituted product 1-methoxypentafluorocyclobutene, obtained in 76% yield (8.2 gm.).

2. 1,2-Dimethoxytetrafluorocyclobutene.

1-Methoxypentafluorocyclobutene (10 gm., 57 mm.) was refluxed for about 30 minutes with a 10% solution of potassium hydroxide (3.2 gm., 57 mm.) in methanol (32 gm., 100 mm.). The solution was then poured into water and the

lower layer separated and dried over magnesium sulphate.

This layer was found to consist of the disubstituted cyclobutene; 1,2-dimethyltetrafluorocyclobutene, obtained in 60% yield (6.4 gm.).

5.4. Preparation of the Ions.

The general procedures outlined below were followed for the preparation of the ionic solutions.

A. In Antimony Pentafluoride/Sulphur Dioxide.

An N.M.R. tube was cooled in an acetone/CO₂ bath (-78°) and into this was condensed sulphur dioxide to the depth of 1-1.5 inches. Small amounts of antimony pentafluoride were stored in a Teflon bottle, and portions of this were added to the tube by means of a teat dropper, in quantities in the region of 0.3 to 0.4 gm. The quantities were measured by differential weighing of the Teflon bottle. Care was taken to ensure that the inside of the teat dropper was thoroughly wetted with antimony pentafluoride before weighings commenced. After addition the tube was carefully shaken to effect dissolution.

To this solution was added dropwise the olefin under investigation, in a quantity so that the ratio of SbF₅ : olefin was 5 : 1 m. (unless otherwise stated in the discussion). The tube was shaken carefully to produce a homogeneous solution. If necessary, to avoid overheating of the solution, thorough mixing was brought about by agitating the solution with a long length of capillary tubing.

B. In Antimony Pentafluoride/Fluorosulphonic Acid.

In this case, the N.M.R. tube was cooled in an ice bath and approximately 1 gm. of SbF₅/FSO₃H was introduced into the tube. The olefin was then added dropwise to this solution, again so that the ratio of SbF₅ : olefin was 5 : 1 m. Homogeneity was achieved by gentle agitation with a long length of capillary tubing. Care was taken to ensure that overheating did not occur.

5.5. Quenching Reactions.

A. General Procedure.

The general procedure for quenching the ionic solutions will first be outlined, and specific examples given later.

1. In Antimony Pentafluoride/Sulphur Dioxide.

Sulphur dioxide was condensed into a two-necked flask which had been cooled to -78° under a nitrogen atmosphere. Antimony pentafluoride was then introduced into this flask, and this time dissolution was achieved by agitation with a magnetic stirrer. The olefin was slowly added dropwise with stirring to this solution (again keeping the molar ratio of SbF_5 : olefin 5 : 1).

After addition was completed, the flask was warmed in another bath at -30° (or at the temperature at which the corresponding N.M.R. of the ionic solution had been run) to ensure that complete ionization had occurred. (This procedure was found to be particularly important in the case of 1-p-anisylpentafluoropropene, when quenching reactions carried out at lower temperatures resulted in recovery of a certain proportion of starting material).

In some cases at this stage a small portion of the ionic solution was transferred to an N.M.R. tube and the spectrum run to check the identity of the intermediate. This transfer was performed with the aid of a cold box. This apparatus consisted of a large polystyrene box containing an asbestos tray supported about three inches above the floor of the box. Liquid nitrogen was poured into the box to a depth of about 1 cm. This level was maintained throughout the experiment. After a few minutes an equilibrium was reached and the temperature on the surface of the asbestos tray was about -60° . The rapid evaporation of the liquid nitrogen ensured that a dry atmosphere was maintained.

The flask was then placed on this tray, and liquid transferred from it to an N.M.R. tube (in an acetone/CO₂ bath) by means of a glass dropper which had also been cooled on the asbestos tray.

The flask was then re-cooled to -78°. Dry methanol (pre-cooled to -78°) was then added dropwise and with caution to the solution. Reaction usually was immediate and quite vigorous. After excess methanol had been added, solutions which had exhibited intense colourations became colourless.

The solution was then allowed to warm up to room temperature and poured into dry ether to help prevent any hydrolysis which might occur. This solution was then poured into water, and ether extraction carried out in the usual way. However this ethereal solution contained large quantities of dissolved sulphur dioxide, and thus care was necessary in the ether extraction. This SO₂ was removed by cautious neutralization with sodium bicarbonate, vigorous effervescence invariably occurring.

The ether layer was then dried over magnesium sulphate and removed by fractionation, if the product was suspected to be volatile, or by means of the rotary evaporator.

2. In Antimony Pentafluoride/Fluorosulphonic Acid.

The general procedure in this case was the same, but the ionic solution was cooled to 0°. The methanol was again cooled to -78° to prevent too vigorous a reaction from occurring.

B. Quenching Reactions of Fluoropropenes.

1. Quenching of Solution of Trans-1-p-anisylpentafluoropropene in Antimony Pentafluoride/Sulphur Dioxide.

Quenching of a solution containing 5 gm. (20 mm.) of trans-1-p-anisylpentafluoropropene produced trans-1-p-anisyl-1,2-difluoro-3-methoxypropene-1-one (3.0 gm., 62% yield) m.pt. 72-72.5° on recrystallization from hexane.

(Found: C, 57.61; H, 4.45; F, 16.43; M, 228. $C_{11}H_{10}F_2O_3$ requires C, 57.9; H, 4.38; F, 16.67; M, 228) I.R. No. 3.

An identical procedure was carried out in the quenching of a solution of cis-1-p-anisylpentafluoropropene in antimony pentafluoride/sulphur dioxide with dry methanol, but very small quantities of starting materials were used and it thus proved impossible to estimate the yield of trans-1-p-anisyl-1,2-difluoro-3-methoxypropene-1-one produced from this reaction.

2. Quenching of Solution of 2-p-anisylpentafluoropropene in Antimony Pentafluoride/Fluorosulphonic Acid.

Quenching of a solution containing 2 gm. (8 mm.) of this olefin produced an extremely involatile liquid which was analysed from its N.M.R. spectrum as an addition product 2-hydro-2-p-anisylpentafluoro-1-propane sulphonic acid, b.pt. $>200^{\circ}$. The material was purified by preparative scale gas/liquid chromatography, using Column O at 200° . Unfortunately the liquid was so viscous that handling losses were great and it was not possible to calculate the yield of product. (Found: C, 35.23; H, 2.57; F, 34.06; M, 340. $C_{10}H_8F_6O_4S$ requires C, 35.5; H, 2.37; F, 33.7; M, 338. Anomalous mass spectrum discussed in Section 3.1.C.2.(b)). I.R. No. 7.

C. Quenching Reactions of Fluorocyclobutenes.

1. Quenching of Solution of 1,2-Dimethyltetrafluorocyclobutene in Antimony Pentafluoride/Sulphur Dioxide.

Quenching of a solution containing 2.5 gm. of this olefin produced 1.5 gm. of a mixture containing two major components. Separation was achieved by preparative scale gas-liquid chromatography using Column A at 150° . The minor component was found to be 1,2-dimethyl-4,4-difluorocyclobutene-3-one (0.3 gm.) analysed by its N.M.R. spectrum, mass spectrum (M, 132. $C_6H_6F_2O$ requires M, 132) and I.R. (No. 5).

The major product was found to be 1,2-dimethyl-3-methoxy-3,4,4-trifluorocyclobutene (1.05 gm.) analysed by its N.M.R. spectrum and I.R. (No. 6). Mass spectral analysis did not show a parent peak ($C_7H_9F_3O$ requires M, 166) but showed immediate loss of CH_3F to give M, 132 corresponding to the cyclobutenone above.

2. Quenching of a Solution of 1-Methoxypentafluorocyclobutene in Antimony Pentafluoride/Sulphur Dioxide.

Quenching of a solution containing 5.0 gm. of the olefin produced 3.7 gm. of product which consisted of two major components. These products were separated using preparative scale gas-liquid chromatography, Column A at 120° . The minor component was analysed as 1-methoxy-2,4,4-trifluorocyclobutene-3-one (0.3 gm., 7% yield) (Found: C, 39.2; H, 2.31; F, 36.8; M, 152. $C_5H_3F_3O_2$ requires C, 39.5; H, 1.97; F, 37.5; M, 152) I.R. No. 8.

The major component (2.7 gm., 63%) was analysed as 1,3,3-trimethoxy-2,4,4-trifluorocyclobutene, b.pt. 169° . (Found: C, 42.8; F, 28.4; M, 198. $C_7H_9F_3O_3$ requires C, 42.4; F, 28.78; M, 198) I.R. No. 9.

5.6. Reaction of Hexafluoropropene with Antimony Pentafluoride.

A variety of different conditions were investigated for the reaction between hexafluoropropene and antimony pentafluoride in sealed tubes. As mentioned in Section 3.2., lower temperatures and short reaction times resulted in good recovery of volatiles, but lower conversion of hexafluoropropene, whilst higher temperatures and longer reaction times resulted in higher conversion of hexafluoropropene, but lower total recovery of volatiles. Eventually conditions of 70° and ~20 minutes reaction time were adapted as giving the optimum conversion of hexafluoropropene and total recovery of volatile products.

An example of one of these reactions is given below:

Antimony pentafluoride (18 gm., 85 mm.) was introduced into a Carius tube of 50 ml. capacity, which had previously been filled with a nitrogen atmosphere. The tube was then cooled in liquid air, evacuated, and hexafluoropropene (2.5 gm., 17 mm.) was added under vacuum. The tube was sealed and agitated for 20 mins. at 70°. It was then cooled in liquid air and the volatile products removed under vacuum (2.2 gm. recovered).

G.l.c. analysis on a low temperature analytical column at 0° showed the presence of unreacted hexafluoropropene and two other products.

The hexafluoropropene was removed by shaking the volatiles in a sealed tube with excess bromine at room temperature. Under these conditions hexafluoropropene is brominated almost instantaneously, with production of heat, and no other brominated products were recovered.

The excess bromine was removed by reaction with powdered copper at 0°.

1,2-Dibromohexafluoropropane was then removed from the other volatile components by preparative scale gas-liquid chromatography, using Column O at 40°. The two volatile products were further separated by preparative scale g.l.c. using Column A at 25°, with a very low gas flow rate. They were identified from their N.M.R. and mass spectra as 2-hydroheptafluoropropane (Found: M, 169. C_3HF_7 requires M, 169) and a dimer of hexafluoropropene (Found: M, 300. C_6F_{12} requires M, 300).

APPENDIX 1

Mass Spectral Data

Mass Spectral Data of Polyfluoro-propene, -cyclobutene and -cyclopentene
Derivatives

[^m/e values; relative abundance (% of base peak in parentheses)]

All peaks >5% of base peak (arbitrarily 100%) are recorded; * indicates parent peak.

1-p-anisylpentafluoropropene (trans) (I).

239(12), 238*(100), 223(8), 219(10), 195(10), 175(7), 145(29), 125(6),
119(6).

1-p-anisylpentafluoropropene (cis) (II).

239(13), 238*(100), 223(11), 219(18), 195(18), 175(13), 158(6), 145(53),
138(7), 126(8), 125(14), 119(10), 107(7), 99(9), 81(7), 75(7), 69(8), 50(7).

1-p-anisyl-1,2-difluoro-3-methoxypropene-1-one (trans) (VIII).

229(13), 228*(100), 198(5), 197(38), 170(25), 169(8), 155(5), 154(12),
126(8), 125(6).

2-Hydro-2-p-anisylpentafluoro-1-propane Sulphonic Acid (XVI).

342(7), 341(12), 340*(82), 321(17), 273(6), 272(11), 271(100),
255(9), 221(9), 173(14), 158(6), 145(13), 123(7), 84(16), 81(8), 73(10),
69(7), 59(22), 56(6), 46(6), 45(17), 44(26), 43(33), 42(9), 41(20), 40(18),
39(8), 31(16).

1,2-Dimethyl-4-methoxytrifluorocyclobutene (XXIII).

133(8), 132(100), 104(28), 103(27), 89(27), 85(13), 84(8), 83(9),
77(20), 76(9), 75(6), 65(11), 64(16), 57(7), 56(19), 55(42), 51(13), 50(10),
40(36), 39(40).

1,2-Dimethyl-3,3-difluorocyclobutenone (XXIV).

133(16), 132*(100), 104(26), 103(23), 89(23), 85(13), 84(15), 83(16),
79(19), 77(18), 76(16), 65(20), 64(16), 57(11), 54(17), 53(30), 51(13),
50(17), 40(35), 39(37), 38(12).

1,3,3-Trimethoxytrifluorocyclobutene (XXXII).

198*(34), 183(47), 168(11), 167(100), 153(11), 152(11), 149(6), 147(7), 139(6), 133(8), 124(8), 123(8), 121(40), 119(13), 109(29), 105(13), 101(6), 94(16), 93(20), 87(26), 81(11), 75(6), 59(16), 58(9), 51(5), 50(13), 45(9), 44(32), 43(23), 32(7), 31(13).

1-Methoxy-2,4,4-trifluorocyclobutenone (XXXIII)

153(8), 152*(100), 124(7), 109(77), 105(9), 94(53), 93(15), 87(19), 81(29), 75(15), 74(7), 59(11), 50(6), 43(6).

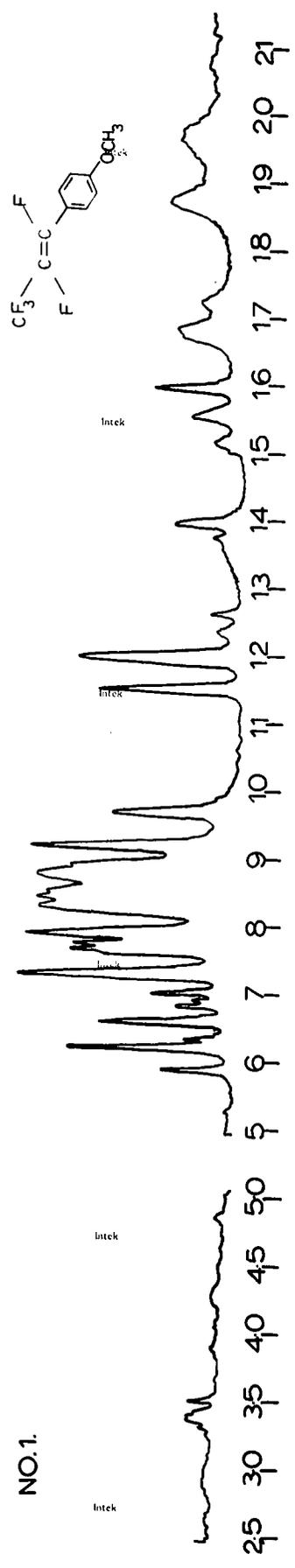
1,2-Dimethylhexafluorocyclopentene (XXXVI).

205(9), 204*(100), 189(21), 185(24), 169(6), 154(26), 153(16), 140(6), 139(8), 135(59), 133(10), 115(23), 104(9), 103(10), 101(7), 95(10), 89(10), 88(5), 85(12), 83(5), 77(13), 76(5), 75(9), 69(8), 65(10), 57(9), 53(5), 51(11), 50(5), 39(12), 32(26).

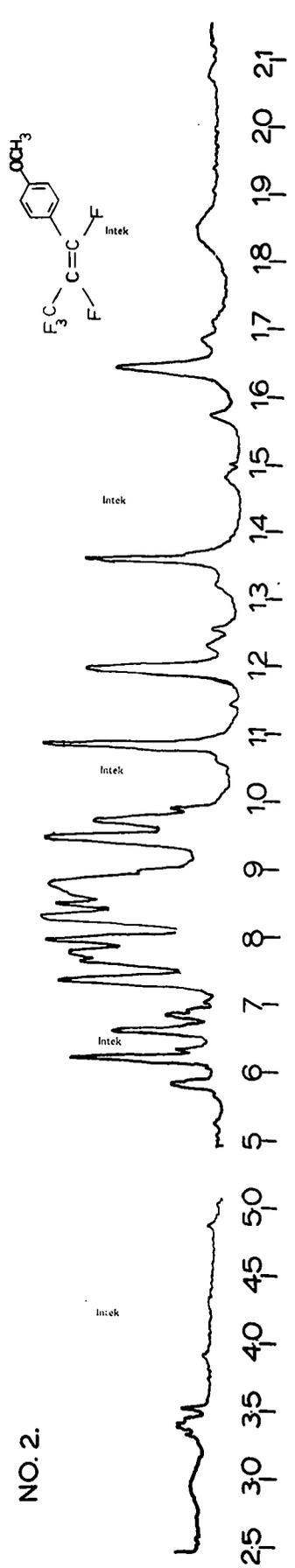
APPENDIX 2

Infra-red Spectra

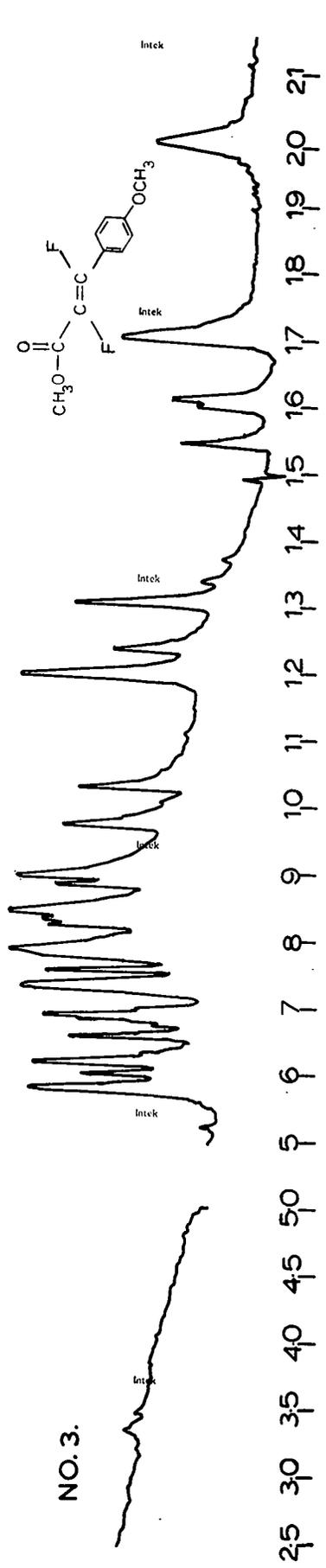
NO. 1.



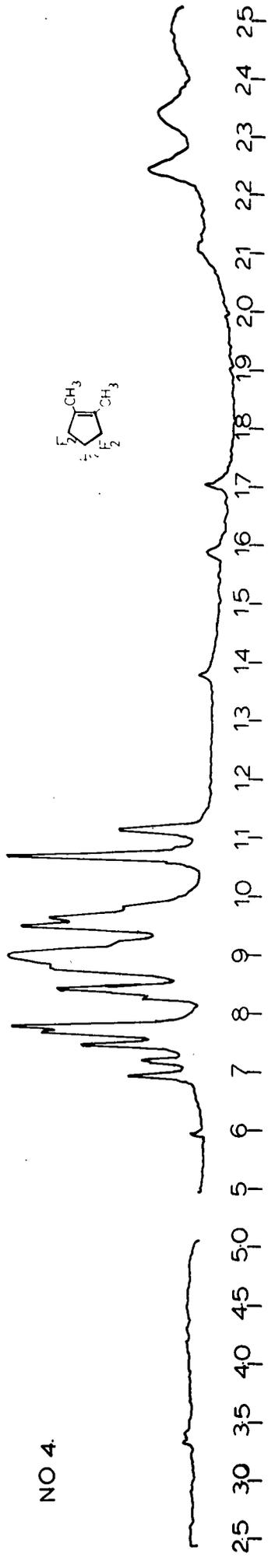
NO. 2.



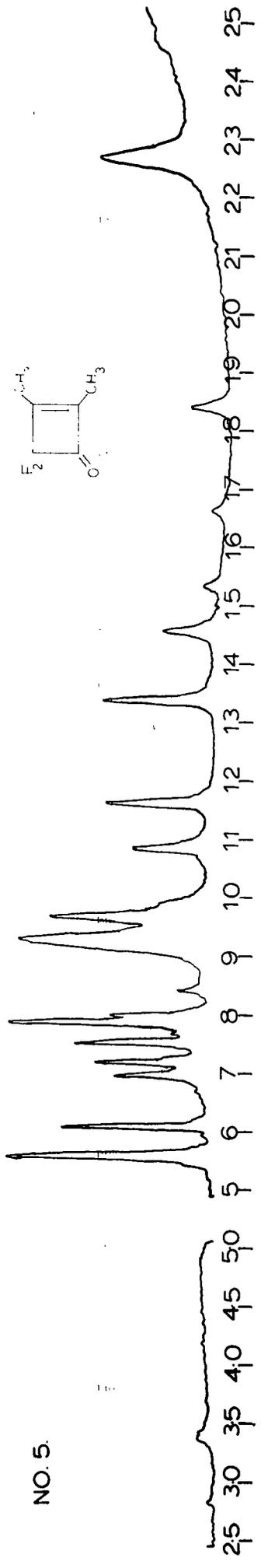
NO. 3.



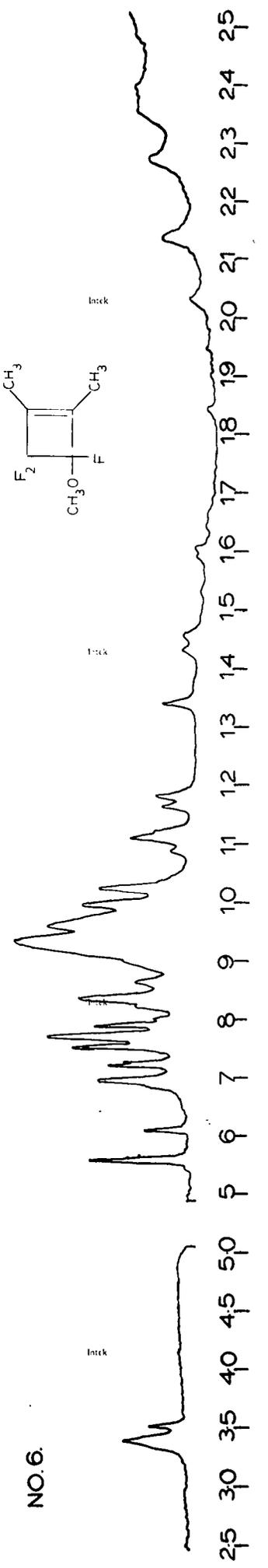
NO 4.

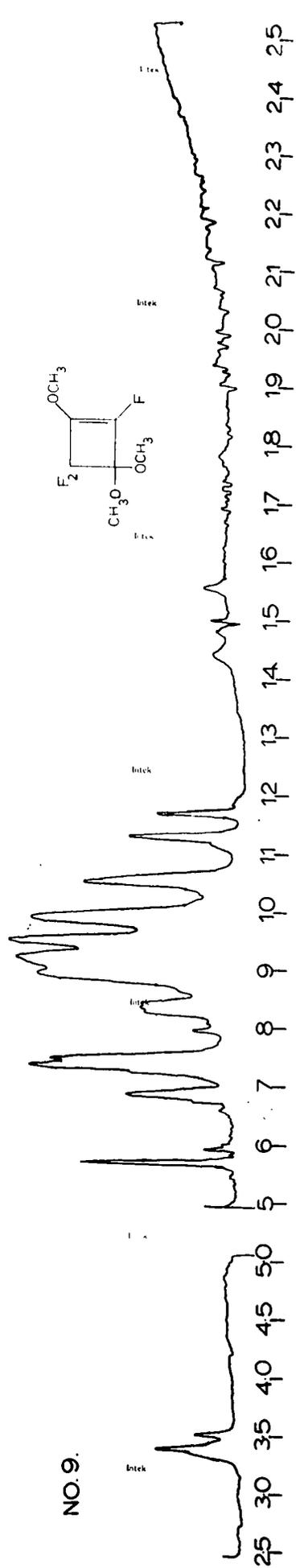
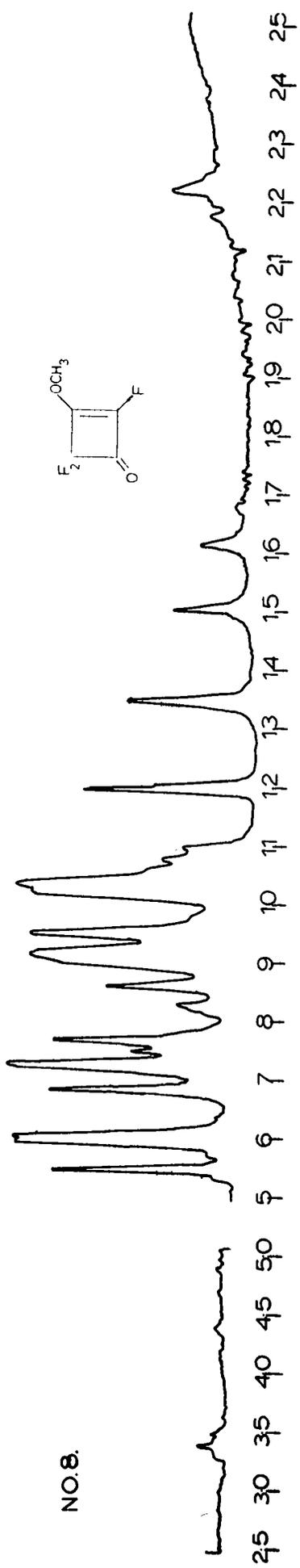
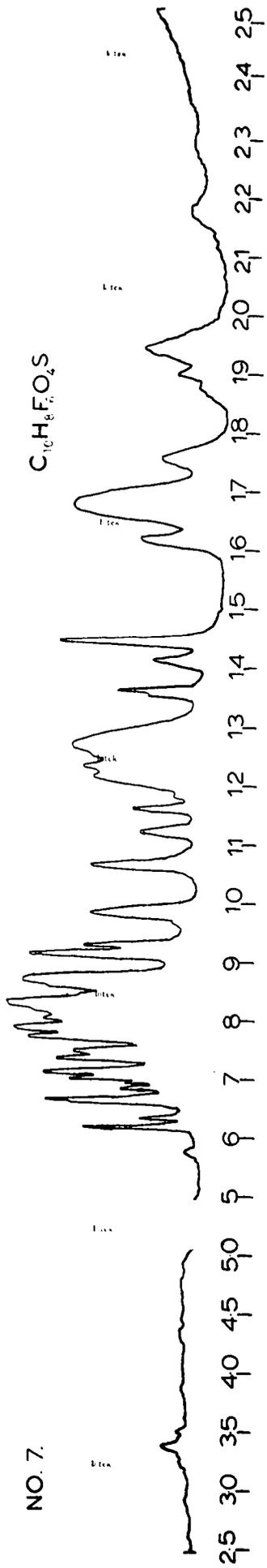


NO 5.



NO 6.





REFERENCES

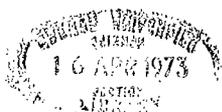
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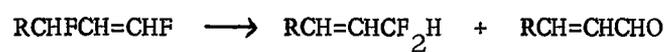
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Corrections

p.25. 2. Solvolysis Reactions - should read:-

While the solvolysis of the cis- and trans-olefins 11a and 11b yielded a mixture of 11c and 11d,



their isomer RCHFCH=CH_2 11e was completely unreactive.