Stable Carbonium Ions. LI.[1] Fluorobenzenonium Ions

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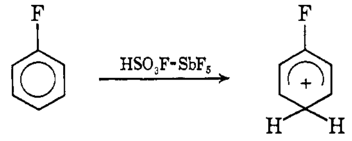
Abstract: Protonation of fluorobenzene as well as di-, tri-, and tetrafluorobenzenes in fluorosulfonic acid–antimony pentafluoride solution gives stable fluorobenzenonium ions (fluorocyclohexadienyl cations). H^1 and F^{19} nmr spectra of the ions were obtained and their structures interpreted based on these spectra.

In view of our continued interest in fluorocarbonium ions[3–6] as well as in alkylbenzenonium ions[7] it seemed of interest to study fluorinated cyclohexadienyl cations (fluorobenzenonium ions). Particularly nuclear magnetic resonance investigations were expected to yield useful information about the charge distribution in these ions as well as further information about nmr coupling constants in carbonium ions.

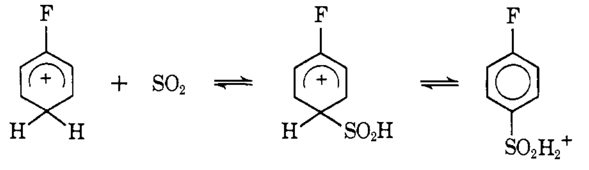
Results and Discussion

Mono-, di-, tri-, and tetrafluorobenzenonium ions were obtained by protonation of the corresponding fluorobenzenes in the extremely strong acid system, FSO_3H–SbF_5.



I

The fluorobenzenonium ions could be observed only in neat fluorosulfonic acid–antimony pentafluoride solution. When the solutions were diluted with SO_2 sulfonylation usually occurred.[8]



The fluorobenzenonium ions in some cases gave poorly resolved nmr spectra due to the viscosity of the acid at the low temperature necessary to slow down exchange rates.

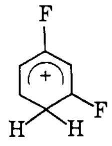
The proton spectra of the ions are characterized by resonance in two distinct regions. The aliphatic methylene protons appear between −5 and −6 ppm and the ring protons between −8 and −10 ppm. The fluorine spectra show peaks at around 100 and 10 ppm downfield from the starting material peaks, corresponding to fluorine atoms *ortho–para* and those *meta* to the methylene group.

The neat acid, used as solvent, was always in large excess as indicated by two nmr absorption peaks which have been assigned to the acid system.[9] The larger of the acid peaks appears at −11 to −12 ppm and the smaller one at −10.0 to −10.5 ppm. For simplicity these acid peaks were deleted from figures of all the spectra described in this paper.

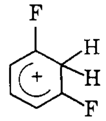
In Tables I and II are summarized the H^1 and F^{19} nmr data of the starting fluorobenzenes and the fluorobenzenonium ions obtained. Representative spectra are shown in Figures 1–3. Protonated *o*-difluorobenzene, 1,2,3,4-tetrafluorobenzene, 1,2,4,5-tetrafluorobenzene, pentafluorobenzene, and hexafluorobenzene were not observable.

The methylene protons of monofluorobenzenonium ion I appeared as a doublet at −5.50 ppm. The coupling due to the *p*-fluorine atom is 12 Hz as compared to about 2 Hz[10] in fluorobenzene itself. The absorption peaks at −8.40 and −10.00 ppm are assigned to the protons *meta* and *ortho* to the methylene group, respectively, since the *ortho* positions are expected to bear more of the positive charge than the *meta* positions. The fluorine resonance appeared at ϕ = +11.2 ppm, nearly 100 ppm downfield from the position in fluorobenzene. The peak is broadened due to viscosity of the acid and coupling of the fluorine atom with ring protons as well as the methylene protons.

The proton spectrum of 2,4-difluorobenzenonium ion (II) is similar to that of I, showing absorption peaks for methylene protons, as well as for ring protons. The assignment of structure II rather than III to the ion is based on the fluorine spectrum (see Figure 2). The two sets of peaks at +3.7 and +8.3 ppm indicate that the two fluorines are not equivalent and form an AB quartet with J_{F-F} = 80 Hz. The *meta* F–F coupling constant in substituted fluorobenzenes is 2–4 Hz.[10]



II



III

The 2,5-difluorobenzenonium ion (V) shows expected spectral features for the proton resonance spectrum

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[1] Part L: G. A. Olah and P. Kreienbuhl, *J. Am. Chem. Soc.*, **89**, 4756 (1967).

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[3] G. A. Olah, C. A. Cupas, and M. B. Comisarow, *J. Am. Chem. Soc.*, **88**, 362 (1966).

[4] G. A. Olah and C. U. Pittman, Jr., *ibid.*, **88**, 3310 (1966).

[5] G. A. Olah and M. B. Comisarow, *ibid.*, **89**, 1027 (1967).

[6] G. A. Olah, R. D. Chambers, and M. B. Comisarow, *ibid.*, **89**, 1268 (1967).

[7] G. A. Olah, *ibid.*, **87**, 1103 (1965), and previous references given in this paper.

[8] M. Brookhart, F. A. L. Anet, and S. Winstein, *ibid.*, **88**, 5657 (1966); G. A. Olah, C. U. Pittman, Jr., E. Namanworth, and M. B. Comisarow, *ibid.*, **88**, 5571 (1966).

[9] G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967).

[10] J. W. Ensley, J. Feeny, and L. H. Sutcliffe, "High-Resolution Nmr Spectroscopy," Vol. II, Pergamon Press, Inc., Oxford, 1966, p 903.

Table I. Pmr Data of Fluorobenzenes and Their Fluorobenzenonium Ions in $FSO_3H–SbF_5$ Solution[a,b]

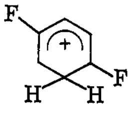
	Fluorobenzene	Ion CH_2	 H_{meta}	 H_{ortho}
Fluorobenzene	−7.2 (m)	−5.50 (d) $J_{H-F} = 8$	−8.40 (m)	−10.00 (m)
p-Difluorobenzene	−6.78 (t)	−5 (very br)	−9 (very br)	
m-Difluorobenzene	−6.8 (m)	−5.32 (t, br)	−7.64 (m)	−8.94 (s, br)
1,3,5-Trifluorobenzene	−6.7 (m)	−5.35 (d, br) $J_{H-F} = 8$	−7.8 (s, br)	
1,2,4-Trifluorobenzene	−7.0 (m)	−5.69 (s, br)	−8.20 (s, br)	−8.94 (s, br)
1,2,3,5-Tetrafluorobenzene	−6.8 (m)	−5.0 (s, br)	−7.2 (s, br)	

[a] Abbreviations used are: s = singlet; d, doublet; t, triplet; q, quintet; br, broad; m, multiplet. [b] *J* values in hertz.

Table II. F^{19} Nmr Data of Fluorobenzenes and Their Fluorobenzenonium Ions in $FSO_3H–SbF_5$ Solution[a,b]

	Fluorobenzene	Ion H_{para}	 H_{ortho}	 H_{meta}
Fluorobenzene	+106.3 (m)	+11.2 (s, br)		
p-Difluorobenzene	+113.2	+1.7 (very br)		+100.0 (very br)
m-Difluorobenzene	+104.8 (m)	+3.7 (d) $J_{F-F} = 80$	+8.3 (d) $J_{F-F} = 80$	
1,3,5-Trifluorobenzene	+101.0 (m)	−5.4 (nine lines) $J_{F-F} = 70, J_{H-F} = 8$	+21.2 (d) $J_{F-F} = 70$	
1,2,4-Trifluorobenzene	+108.8 (m), +125.2 (m), +133.8 (m)	−0.67 (four lines) $J^m{}_{F-F} = 80, J^o{}_{F-F} = 20$	+17.7 (d) $J^o{}_{F-F} = 80$	+118.2 (d) $J^o{}_{F-F} = 20$
1,2,3,5-Tetrafluorobenzene	+107.6 (m), +124.4 (m), +156.3 (m)	+14.2 (m, br)	+50.0 (d, br) $J_{F-F} = 70$	143.0 (t, br) $J_{F-F} = 20$

[a] s, singlet; d, doublet; t, triplet; q, quintet; br, broad; m, multiplet. [b] *J* values in hertz.



V

(methylene protons, *ortho* and *para* ring protons) and the fluorine resonance spectrum.

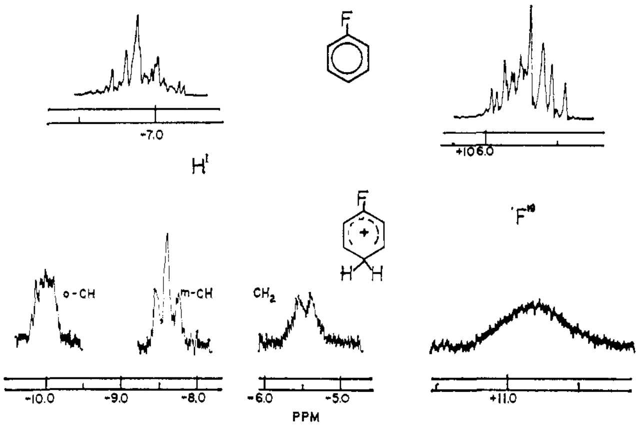
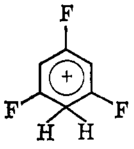


Figure 1. Proton and fluorine nmr spectra of monofluorobenzene and its benzenonium ion.

The 2,4,6-trifluorobenzenonium ion (IV) is very stable, allowing the spectrum to be taken at higher temperature (−40°) and thus obtaining better resolution (see Figure 3). The proton spectrum of ion IV shows peaks for the methylene protons and the ring protons. The methylene protons appear as a doublet due to coupling to the *p*-fluorine atom but broadened by coupling to the other nuclei. The *o*-fluorine atoms give rise to a doublet at +21.2 ppm due to coupling to the *p*-fluorine atom (J_{F-F} = 80 Hz). The *p*-fluorine signal which occurs at −5.4 ppm is a triplet of triplets due to coupling to the *o*-fluorine atoms (J_{F-F} = 80 Hz) and further coupling to the methylene protons (J_{H-F} = 8 Hz).



IV

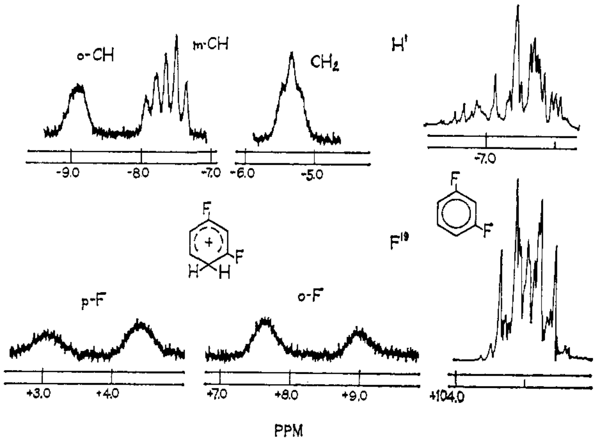


Figure 2. Proton and fluorine nmr spectra of *m*-difluorobenzene and its benzenonium ion.

In the spectra of the unsymmetrically substituted ions, 2,4,5-trifluorobenzenonium ion (VI) and 2,3,4,6-tetrafluorobenzenonium ion (VII), the *ortho* F–F coupling is observable and is 20 Hz. The *ortho* F–F coupling in fluorobenzenes is *ca.* 20 Hz.[4]

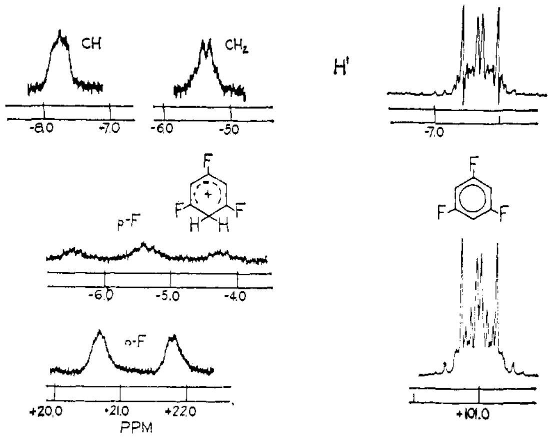
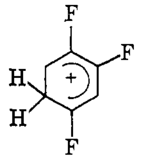
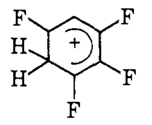


Figure 3. Proton and fluorine nmr spectra of 1,3,5-trifluorobenzene and its benzenonium ion.



VI



VII

We feel that the data obtained concerning nmr chemical shifts and coupling constants yield useful information about the charge distribution in benzenonium ions and about the nature of fluorine proton coupling. Copla, MacLean, and Mackor[11] have calculated the charge distribution in alkylbenzenonium ions based on the chemical shifts of methyl groups in various ring positions. Due to the large difference in chemical shifts of fluorine nuclei in the different ring positions in fluorobenzenonium ions, some similar calculation might lead to interesting conclusions about the ability of fluorine to polarize the π-electron system in reaction intermediates involving fluorinated rings. At the present time we are extending this investigation to include alkylfluorobenzenes, which, it is hoped, will yield useful information about the relative effects of fluorine and alkyl groups on such ions.

Experimental Section

Materials. Fluorobenzene, *m*-, *p*-, and *o*-difluorobenzene, 1,2,3,4- and 1,2,3,5-tetrafluorobenzene, pentafluorobenzene, and hexafluorobenzene were commercially available materials and were used without further purification. Samples of 1,2,4- and 1,3,5-trifluorobenzene and 1,2,4,5-tetrafluorobenzene were generously made available by Dr. G. Finger, and we are grateful for his help.

Antimony pentafluoride (Allied Chemical Co.) was refluxed overnight while passing a stream of dry nitrogen over it. The material was then twice distilled (bp 150°). Fluorosulfonic acid (Allied Chemical Co.) was distilled (bp 160–164°) before use. The purified acids were stored in Teflon bottles.

Preparation of the Ions. Samples of the protonated fluorobenzenes for nmr studies were prepared by adding 2 ml of the HSO_3F–SbF_5 solution (the ratio of HSO_3F to SF_5 varied between 1:1 and 6:1) which had been cooled to −78° to 0.1–0.2 g of the fluorobenzene which had also been cooled to −78°. Upon warming, while shaking, a clear solution was obtained.

A Varian Associates Model A-56–60A nmr spectrometer equipped with a variable-temperature probe was used for all spectra.

Acknowledgment. Support of this work by a grant of the National Science Foundation is gratefully acknowledged.

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Stable Carbonium Ions. LII.[1] Protonated Esters and Their Cleavage in Fluorosulfonic Acid–Antimony Pentafluoride Solution

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Abstract: A series of protonated esters was studied in HSO_3F-SbF_5-SO_2 solution. Carbonyl oxygen protonation was observed by nmr spectroscopy with negligible exchange rates. Spectral evidence was found for the existence of isomers of protonated formates. Kinetics of cleavage of a series of protonated methyl esters was studied. Both acyl oxygen and alkyl oxygen cleavage was observed for esters of primary aliphatic alcohols.

We have previously reported the observation of protonated aldehydes,[3] ketones,[4] and acids[5] by nmr spectroscopy. The protonation of esters and their cleavage under acidic conditions has been extensively investigated.[6] Birchall and Gillespie reported the nmr observation of protonated ethyl acetate in HSO_3F–SbF_5 solution at −75° and concluded that only carbonyl oxygen protonation takes place.[7]

We wish now to report the nmr observation of a series of protonated esters in the strongly acidic medium

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[2] (a) National Science Foundation Postdoctoral Research Investigator, 1966–1967. (b) National Institutes of Health Postdoctoral Research Investigator, 1966–1967.

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