P column at 150°, 40 cc of helium/min). Two peaks other than those of silane-derived products appeared having retention times of 4.2 and 7.4 min in relative amounts of 79 and 21%, respectively. The major component was identified as isodurene (1,2,3,5-tetramethylbenzene) by comparison with pure material purchased from Aldrich. The yield of isodurene was determined to be 67.6 mg (75%) by addition of 74.1 mg of tetralin to the product and analysis by glpc. Analysis of a known mixture of tetralin and isodurene verified that their molar responses to the thermal conductivity detector were the same.

A similar experiment in which the reaction time was extended to 1.5 hr showed isodurene with only trace amounts of the higher boiling component. The analytical yield was 89%.

The minor component was shown to be mesityl trifluoroacetate by independent synthesis and comparison of retention times.

Mesityl alcohol (36 mg, retention time 9.5 min) was dissolved in 1.0 ml of methylene chloride, and 0.1 ml of trifluoroacetic acid was added. After 20 min the reaction mixture was quenched with sodium carbonate and analyzed by glpc. A single peak with retention time 7.1 min was observed. The solution was filtered and evaporated to leave 43 mg of a clear syrup exhibiting trifluoroacetate ester carbonyl absorption in the ir at 1780 cm^{-1} and C–O absorption at 1142 cm^{-1}. The nmr spectrum was consistent with the structure showing four singlets at τ 7.70, 7.63 (nine protons), 4.56 (two protons), and 3.09 (two protons).

When the reduction of mesityl alcohol with triphenylsilane was carried out on a 10-mmol scale and the crude product purified by evaporative distillation 556 mg (41%) of isodurene was obtained which was further identified by its ir and nmr spectra. Both the crude and purified materials were void of absorbance in the 1700-cm^{-1} region which, if present, would be indicative of 2,4,6-trimethylbenzaldehyde formed by disproportionation.

Reduction of *cis*- and *trans*-4-*t*-Butyl-1-phenylcyclohexanols (15 and 16). *cis*-4-*t*-Butyl-1-phenylcyclohexanol (**15**), *trans*-4-*t*-butyl-1-phenylcyclohexanol (**16**), *cis*-4-*t*-butyl-1-phenylcyclohexane (**17**), *trans*-4-*t*-butyl-1-phenylcyclohexane (**18**), and 4-*t*-butyl-1-phenylcyclohexane (**19**) were prepared by the methods described by Garbisch and Patterson.[32] A solution of **15** or **19** (0.93 mmol) in 4.0 ml of methylene chloride plus 1.2 mmol of the appropriate silane was treated with 228 mg (2 mol) of trifluoroacetic acid and allowed to stand at 25° for 0.5 hr. Solid potassium carbonate was added and the reaction mixture analyzed by gas chromatography using a 10-ft 15% Carbowax 20M on Chromosorb P column at 190°. Peaks were identified by comparing retention times with those of the standards and areas determined by planimeter integration. Response ratios were taken as unity since Garbisch had previously shown no significant deviations from unity for a wide variety of similar compounds.[33]

In an experiment designed to test the possibility that the products were derived from initial elimination to the olefin followed by protonation of the olefin to the carbonium ion, **19** was subjected to the same reaction conditions and found to be less than 10% converted to **17** and **18**.

Attempted Reduction of Benzyl Alcohol. To a solution of 87.3 mg of benzyl alcohol (0.80 mmol) and 148 mg (0.57 mmol) of triphenylsilane in 0.5 ml of deuteriochloroform in an nmr tube was added ten drops of trifluoroacetic acid. After 19 hr at 25°, there was no diminution of the Si–H resonance at τ 4.5 and no formation of toluene. Similar results were obtained with cinnamyl alcohol.

Attempted Reduction of Sesquixanthydryl Cation (14). Sesquixanthydrol[10] (302 mg, 1 mmol) was dissolved in 7.0 ml of methylene chloride and 0.50 ml of triethylsilane, and 0.20 ml of trifluoroacetic acid was added. An orange solution resulted which did not lighten over the course of 24 hr. Potassium carbonate was added and the solution filtered and evaporated to leave 333 mg of orange solid, mp 205–215° dec. This material resisted purification. Sesquixanthene is reported as a white solid, mp 280–300° dec.[10]

In acetic acid containing triethylsilane again the orange color of cation **14** was not discharged.

Acknowledgment. We wish to thank Mr. Keith Hodgson and Miss Chia-Lin Wang for preparing some of the starting materials. The early stages of this work were supported by National Science Foundation Grant GU-1978 to the University of Virginia. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

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[32] (a) E. W. Garbisch, Jr., *J. Org. Chem.*, **26**, 4165 (1961); (b) E. W. Garbisch, Jr., and D. B. Patterson, *J. Am. Chem. Soc.*, **85**, 3228 (1963).

[33] E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson, and C. M. Sprecher, *ibid.*, **87**, 2932 (1965).

Stable Carbonium Ions. LXI.[1] Methylfluorobenzenonium Ions

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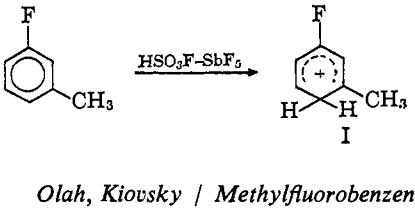
Contribution from the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received October 30, 1967

Abstract: Protonation of fluorotoluenes and fluoromesitylenes in fluorosulfonic acid–antimony pentafluoride solution gives stable methylfluorobenzenonium ions (methylfluorohexadienyl cations). ^{1}H and ^{19}F nmr spectra of these ions were obtained and structures assigned. It was found that a fluorine atom takes preference over a methyl group in directing the position of protonation.

As an extension of our previous work on fluorobenzenonium ions[3] we have studied methyl-substituted fluorocyclohexadienyl cations (methylfluorobenzenonium ions). Nuclear magnetic resonance investigations were expected to yield information about the structure as well as further information about nmr coupling constants in these new fluorocarbonium ions.

Results and Discussion

Mono-, di-, tri-, and tetrafluorotoluenes as well as mono-, di-, and trifluoromesitylenes were protonated in the extremely strong acid system FSO$_3$H–SbF$_5$. All the ions could be observed in neat fluorosulfonic



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[1] Part LX: G. A. Olah and M. Calin, *J. Am. Chem. Soc.*, **90**, 405 (1968).

[2] Postdoctoral research investigator, 1967.

[3] G. A. Olah and T. E. Kiovsky, *J. Am. Chem. Soc.*, **89**, 5692 (1967).

Table I. ^{1}H Magnetic Resonance Data of Methylfluorobenzenonium Ions[a,b]

	Methylfluorobenzene		Temp,	Methylfluorobenzonium Ion				
	CH_3	CH	°C	CH_3	CH_2	*m*-CH	*o*-CH	*p*-CH
o-Fluorotoluene	−2.08 (d) J_{HF} = 2	−6.86 (m)	−60	−2.84 (s)	−5.44 (d) J_{HF} = 5	−8.46 (m)	−9.76 (br)	
m-Fluorotoluene	−2.12 (s)	−6.77 (m)	−70	−3.52 (s)	−5.36 (d) J_{HF} = 5	−8.30 (q)	−9.84 (m)	
p-Fluorotoluene	−2.12 (s)	−6.82 (d) −6.94 (s)	−75	−2.84 (br)	−5.40 (br)	−8.24 (br)	−8.96 (br)	−9.94 (br)
2,4-Difluorotoluene	−2.18 (m)	−6.92 (m)	−40	−3.03 (s)	−5.40 (m, br)	−7.97 (t)	−9.03 (br)	
2,5-Difluorotoluene	−2.20 (d) J_{HF} = 2	−6.79 (m)	−40	−3.53 (br)	−5.54 (br)	−8.3 (br)	−8.3 (br)	
2,3,5,6-Tetrafluorotoluene	−2.27 (t) J_{HF} = 2	−6.83 (m)	−50	−3.50 (br)	−5.60 (br)			
Monofluoromesitylene	2.13 (s) 2.10 (sh)	−6.58 (d) J_{HF} = 7	−50	−2.88 (s) 3.00 (s) 3.03 (sh)	−4.99 (br)	−7.88 (d) J_{HF} = 5		
Difluoromesitylene	2.05 (s, br)	−6.53 (t) J_{HF} = 8	−40	−3.20 (s) −3.33 (s)	5.38 (br)			
Trifluoromesitylene	2.10 (q)		−40	−2.42 (d) −2.70 (s) J_{HH} = 7	−4.88 (q) J_{HH} = 7			

[a] Abbreviations used are: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, sh = shoulder. [b] δ values in parts per million (external TMS, capillary); *J* values in hertz.

Table II. ^{19}F Magnetic Resonance Data of Methylfluorobenzenonium Ions[a,b]

Compound	Methylfluorobenzene		Temp, °C	Methylfluorobenzenonium Ion		
				o-F	*m*-F	*p*-F
o-Fluorotoluene	+110.0 (m)		−60			+15.7 (br)
m-Fluorotoluene	+107.8 (m)		−70			+19.3 (br)
p-Fluorotoluene	+111.7 (qu)		−75	+14.2 (br)		
2,4-Difluorotoluene	+107.0 (m)	+107.9 (m)	−40	+12.2 (d) J_{FF} = 82		+2.87 (d) J_{FF} = 82
2,5-Difluorotoluene	+117.0 (m)	+113.6 (m)	−40	+15.1 (br)	+103.8 (br)	
2,3,5,6-Tetrafluorotoluene	+139.1	140.6	−50	+54.6 (br)	+122.2 (br)	
Monofluoromesitylene	+119.5 (m)		−50		+111.2	
Difluoromesitylene	+115.0 (d) J_{HF} = 8		−40		+103.7	
Trifluoromesitylene	+114.3 (m)		−40	+35.8 (qu) J_{FF} = 70, J_{HF} = 6		+1.8 (t) J_{FF} = 70

[a] Abbreviations used are: d = doublet, t = triplet, qu = quartet, m = multiplet, br = broad. [b] ϕ in parts per million (external CCl_3F), *J* values in hertz.

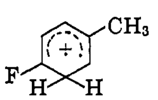
acid–antimony pentafluoride. Some of the more stable ions could also be observed when the solutions were diluted with SO_2. Dilution with SO_2, however, resulted in the case of the less stable ions in the formation of sulfinic acids (*vide infra*). The nmr spectra of the methylfluorobenzenonium ions in neat fluorosulfuric acid–antimony pentafluoride in some cases gave poor resolution due to the viscosity of the solvent at the low temperatures necessary to slow down exchange rates.

The proton spectra of the methylfluorobenzenonium ions are characterized by resonance in three distinct regions. The methyl protons appear between −2.5 and −3.5 ppm, relative to external TMS, the aliphatic methylene protons between −5 and −6 ppm, while the ring protons appear between −8 and −10 ppm. The fluorine resonance spectra show peaks at around 0 ppm and +100 ppm (relative to external CCl_3F) corresponding to fluorine atoms *ortho*, *para*, and *meta* to the methylene group.

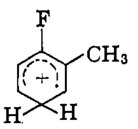
The acid, whether used neat or diluted with SO_2, was always in large excess as indicated by two characteristic nmr absorption peaks which have been assigned to the acid system.[4] The larger of the acid peaks appears at −11 to −12 ppm and the smaller one at −10.0 to −10.5 ppm. For the sake of simplicity these acid peaks were deleted from figures of all the spectra described in this paper.

Tables I and II summarize the ^{1}H and ^{19}F nmr data of the starting methylfluorobenzenes and the methylfluorobenzenonium ions obtained from them by protonation. Representative spectra are shown in Figures 1–3.

The ions resulting from protonation of *o*-, *m*-, and *p*-fluorotoluenes were found to be protonated *ortho–para* to the fluorine atom, as shown in the case of ions I, II, and III. The spectrum of ion II is shown in Figure 1. The position of the methyl peak in II and III is at −2.84 ppm indicating that it is *meta* to the position of protonation while that in I is at −3.52 ppm indicating that the methyl group is on a carbon atom *ortho* to the position of protonation.[3] The methylene protons in all three ions appear at about −5.4 ppm. The ring protons in I appear as two peaks at −8.30



II



III

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[4] G. A. Olah, D. H. O'Brien, and M. Calin, *J. Am. Chem. Soc.*, **89**, 3582 (1967).

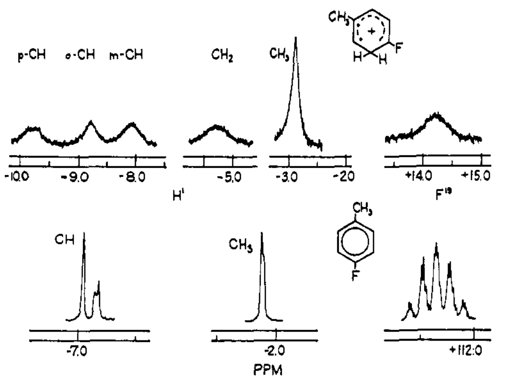
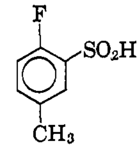


Figure 1. Proton and fluorine nmr spectra of *p*-fluorotoluene and the ion formed by its protonation in FSO_3H–SbF_5.

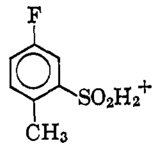
and −9.84 ppm in the ratio 2:1 indicating two *meta* and one *ortho* proton. In ion III the peak at lower field (−9.76 ppm) is twice as large as the one at higher field (−8.4 ppm) indicating two *ortho* and one *meta* proton. In the spectrum of ion II there are three peaks of equal size at low field (−8.24, −8.96, −9.94 ppm) indicating one *ortho*, one *meta*, and one *para* proton. The fluorine resonance spectra confirm these assigned structures. In each of the three ions the fluorine peaks are near 0 ppm relative to external CCl_3F (thus about 100 ppm downfield from the position in the starting materials) indicating that the fluorine atoms are *ortho* or *para* to the methylene group.

Fluorotoluenes and fluoromesitylenes were recovered unchanged from the acid mixture by quenching with cold methanol. Gas chromatography showed no significant peaks other than those of the starting fluorotoluenes and mesitylenes, the structure of which was verified by nmr and ir spectroscopy.

When the protonation of *p*-fluorotoluene was attempted using SbF_5–FSO_3H diluted with SO_2 the spectra obtained were those of the two possible protonated sulfinic acids IV and V. The two methyl peaks appeared at −2.6 and −2.7 ppm, the ring protons as a complex multiplet centered at −7.8 ppm, and the two $-SO_2H_2^+$ peaks for the two isomers at −9.57 and −9.63 ppm. The higher field methyl peak is assigned to IV and the lower field one assigned to V since the $-SO_2H_2^+$ substituent is strongly electron withdrawing. The peak area ratio is 1:3, which consequently is the ratio of isomers IV and V.



IV



V

The ^{19}F spectrum shows the fluorine resonance of IV and V at +119.2 and +122.1 ppm, respectively. The methyl esters of the two sulfinic acids derived from *p*-fluorotoluene were obtained by quenching the solution of IV and V with cold methanol.[5] The nmr spectrum of the mixture of the methyl esters of IV and V at room temperature in CCl_4 has two broadened singlets at −2.33 and −2.45 ppm corresponding to the ring methyls, two sharp singlets at −3.38 and −3.47 ppm corresponding to the ester methyls, and a multiplet centered at −7.10 ppm for the ring protons.

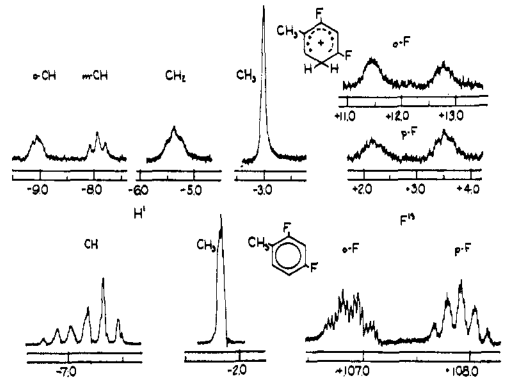


Figure 2. Proton and fluorine nmr spectra of 2,4-difluorotoluene and the ion formed by its protonation in FSO_3H–SbF_5.

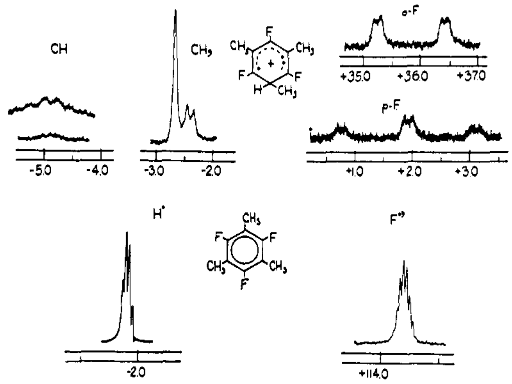
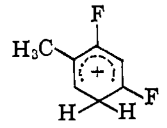
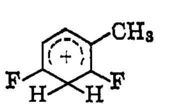


Figure 3. Proton and fluorine nmr spectra of trifluoromesitylene and the ion formed by its protonation in FSO_3H–SbF_5.

The ion resulting from the protonation of 2,4-difluorotoluene is VI and not VII, based on the interpretation of the nmr spectra as shown in Figure 2. The position of the methyl group at −3.03 ppm indicates that it is *meta* to the methylene group. The peak position of the ring protons at −7.97 and −9.03 ppm indicates that one is *meta* and one *ortho* to the methylene group. Finally the positions of the two fluorine atoms at +12.2 and +2.87 ppm (relative to external CCl_3F) indicate that they are respectively *ortho* and *para* to the position of protonation. The coupling constant between the *m*-fluorine atoms is 82 Hz while that in substituted fluorobenzenes is only 0–7 Hz.[6a]



VI



VII

It is expected that the *m*-fluorine coupling constant in the methylfluorobenzenonium ions should be considerably larger than the *m*-fluorine coupling in the starting methylfluorobenzenes in accordance with the value of J_{HF} = 24.7 Hz for the 1,3 coupling in *cis*-2-chloroheptafluorobutene-2 compared with J_{H-m-F} = 0.7 Hz in methylfluorobenzenes.[6b]

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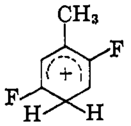
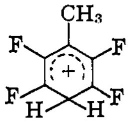
(5) A. J. H. Houssa, *et al.*, *J. Chem. Soc.*, 1707 (1929).

(6) J. W. Ensley, J. Feeny, and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. II, Pergamon Press, Oxford, 1966: (a) p 903; (b) p 912.

Protonation of 2,5-difluorotoluene results in ion VIII. The position of the methyl group in the proton spectrum is -3.53 ppm indicating that it is *para* to the methylene group. The fluorine spectrum shows a peak at $+103.8$ ppm and one at $+15.1$ ppm indicating fluorine atoms *meta* and *para* to the methylene group. Similar considerations allowed the assignment of structure IX to the methylfluorobenzenonium ion resulting from protonation of 2,3,5,6-tetrafluorotoluene.

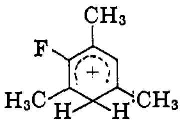


VIII

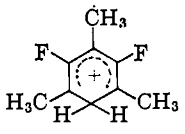


IX

Mono- and difluoromesitylene were found to protonate *ortho–para* to the methyl groups rather than to the fluorine atoms. The fluorine resonances in ions X and XI occur at ϕ $+111.2$ and $+103.7$ ppm, respectively, which indicates that the fluorine atoms are on carbons *meta* to the position of protonation.

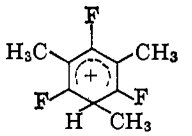


X



XI

Protonation of trifluoromesitylene gives ion XII. There are two methyl peaks, a doublet at -2.42 and a singlet at -2.70 ppm, which can be assigned to the aliphatic and the two *m*-methyl groups, respectively. The aliphatic methine protons appears as a quadruplet in the region where the methylene protons usually occur in benzenoium ions[3] (see Figure 3). The fluorine spectrum shows peaks at ϕ $+35.8$ and $+1.8$ ppm which are assigned to the *o*- and *p*-fluorines, respectively. The higher field peak is split into a doublet of doublets due to coupling to the *para* fluorine atom ($J_{\text{F-F}}$ = 70 Hz) and further coupling to the aliphatic proton (J_{HF} = 6 Hz). The *p*-fluorine peak is split into a triplet by the two *o*-fluorine atoms with a coupling constant of 70 Hz.



XII

Experimental Section

Materials. All the fluorotoluenes were commercially available materials and were used without further purification. Samples of mono-, di-, and trifluoromesitylenes were generously made available by Dr. G. Finger, and we are grateful for his help. Antimony pentafluoride and fluorosulfonic acid were purified as previously described.[3] The purified acids were stored in Teflon bottles.

Preparation of the Ions. Samples of the protonated methylfluorobenzenes for nmr studies were prepared by adding 2 ml of the HSO_3F–SbF_5 solution which had been cooled to $-78°$ to 0.1–0.2 g of the methylfluorobenzene which had also been cooled to $-78°$. Upon warning, while shaking, a clear solution was obtained. With the fluoromesitylenes spectra could be obtained using a sample which had been prepared by dissolving the fluoromesitylene in liquid SO_2 and then carefully adding to the cold solution excess antimony pentafluoride–fluorosulfonic acid mixture which had also been dissolved in liquid SO_2.

Quenching of the methylfluorobenzenonium ions resulting from protonation of the corresponding methylfluorobenzenes was accomplished by quenching the SbF_5–FSO_3H solution with cold ($-80°$) methanol. The methanol solutions were worked up in the usual ways and analyzed by gas chromatography using a Perkin-Elmer 226 gas chromatograph equipped with a 200-ft Carbowax K1540 capillary column, ir and nmr spectroscopy. Methyl sulfinates resulting from sulfination of *p*-fluorotoluene in FSO_3H–SbF_5–SO_2 solution were isolated by pouring the solution into cold methanol, then washing with water, whereupon the esters separate as an oil. 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.