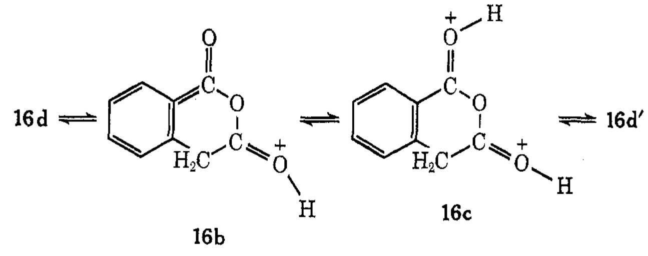
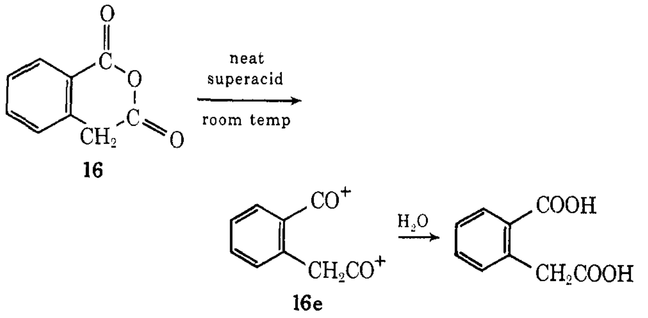


In neat magic acid at room temperature, **16** was cleaved and dehydrated to the corresponding diacyl cation **16e**. The methylene protons of **16e** show a singlet absorption at δ 5.50. Quenching of the solution with ice–water gave homophthalic acid exclusively.



In conclusion cyclic carboxylic acid anhydrides behave differently from their acyclic analogs in superacid solutions. Aromatic and unsaturated cyclic anhydrides (in which the carbonyl carbons are directly attached to the sp^2 olefinic carbons) are not cleaved, even in neat magic acid at room temperature. Maleic anhydride and related unsaturated anhydrides thus show remarkable stability in superacid media. One possible explanation is that they contain four adjacent sp^2 carbon atoms and thus favor for the formation of a five-membered ring. Even if this would be cleaved in superacid media, the recyclization process may be extremely rapid. This is evidenced by the ease of cyclodehydration of phthalic and maleic acid in neat magic acid at room temperature to the corresponding anhydrides. In contrast acyclic saturated dicarboxylic acids (such as glutaric acid) are dehydrated to diacyl cations.

Experimental Section

Materials.—Carboxylic acid anhydrides used, when not otherwise indicated, were commercial material of high purity (Aldrich Chemical Co.). They were used without further purification. Dimethylmaleic anhydride was made available by Dr. H Bosshard of CIBA-GEIGY Limited, Basel, Switzerland, and we are grateful for his assistance. 3,6-Dimethylphthalic anhydride (**4**) and 1,4-dimethyl-2,3-naphthalic anhydride (**7**) were gifts from Professor M. S. Newman. Antimony pentafluoride and fluorosulfuric acid were purified as previously described.[12] Magic acid solutions were stored in Teflon bottles.

Nmr Spectra.—A Varian Associates Model A-56/60A spectrometer with variable temperature probe was used for all spectra. Chemical shifts are reported in parts per million (δ) from external (capillary) TMS.

Protonation of Cyclic Carboxylic Acid Anhydrides.—Protonated cyclic acid anhydrides were prepared by slow addition, with efficient stirring (vortex mixer), of generally a 10% (w/w) solution of the anhydride in SO_2 to a SO_2 solution of fluorosulfuric acid–antimony pentafluoride (in proportions of the reagents indicated in Table I). Samples were transferred to a precooled nmr tube and studied by nmr.

Quenching of protonated anhydrides was carried out by adding, with efficient stirring, their solution to ice-water. The quenched products were isolated and analyzed by comparison with authentic samples of starting material or their corresponding carboxylic acids by glc, ir, and nmr. Details of all studies were similar to those reported previously in the case of acyclic anhydrides[2].

Acknowledgment.—Support of our work by the National Institutes of Health and the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged. Professor M. S. Newman is thanked for arousing our interest in the topic and stimulating discussion.

Registry No.—**1**, 108-31-6; **2**, 766-39-2; **3**, 2426-02-0; **4**, 85-44-9; **5**, 5463-50-3; **6**, 81-84-5; **7**, 40682-58-4; **8**, 89-32-7; **9**, 81-30-1; **10**, 699-98-9; **13**, 108-30-5; **14**, 108-55-4; **15**, 4480-83-5; **16**, 703-59-3.

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(12) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967).

Stable Carbocations. CLVIII.[1a] Degenerate 1,2-Hydrogen Shifts in Fluorobenzenium Ions and Their Comparison with Those in Methylbenzenium Ions[1b]

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Protonation of fluorinated benzenes was studied in fluoroantimonic acid SbF_5–HF (1:1 mol:mol)–SO_2ClF (1:1 v:v) solution at low temperature. Temperature dependent nmr (^1H and ^{19}F) spectra of protonated fluorobenzene, *o*- and *p*- difluorobenzene, and 1,2,3,4-tetrafluorobenzene were observed indicating stepwise 1,2-hydrogen shifts in all these benzenium ions. The activation energies for the two, different, stepwise processes in the 3,4-difluorobenzenium ion were found to be 5.7 ± 0.8 and 11.2 ± 0.9 kcal/mol.

In previous studies of protonation of fluorinated benzenes in FSO_3H–SbF_5 solution, *o*-difluorobenzene, 1,2,3,4-tetrafluorobenzene, pentafluorobenzene, and hexafluorobenzene were not observed to be protonated.[2] We have consequently applied the more suitable superacid medium, SbF_5–HF (1:1 mol:mol)–SO_2ClF (1:1 v:v), for the protonation of some weak aromatic bases.[3] The advantages of this superacid system are the increased solubility of substrate, lower freezing

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(1) (a) G. A. Olah, S. Kobayashi, and Y. K. Mo, *J. Org. Chem.*, submitted. (b) A preliminary communication has appeared: G. A. Olah and Y. K. Mo, *J. Amer. Chem. Soc.*, **94**, 9241 (1972).

(2) G. A. Olah and T. E. Kiovsky, *ibid.*, **89**, 5692 (1967).

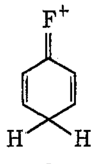
(3) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and Gh. D. Mateescu, *ibid.*, **94**, 2034 (1972).

point and lesser viscosity of the medium even at very low temperatures, and the acid's protonating ability toward weak bases. The resolution of spectra of protonated fluorinated benzenes also showed marked improvement over earlier studies in neat FSO_3H-SbF_5 at low temperature and allowed observation of fine structure of spin-spin couplings. This system allowed us to carry out a systematic investigation of protonated fluorinated benzenes and the study of 1,2-hydrogen shifts in the formed ions. Temperature-dependent nmr study of fluorobenzenium ions was used to investigate the nature of intra- and intermolecular hydrogen exchange reactions.

Results and Discussion

Protonation of fluorinated benzenes was carried out in SbF-HF (1:1 mol:mol)-SO_2ClF (1:1 v:v) solution, generally at low temperatures. The nmr (^1H and ^{19}F) parameters of parent fluorobenzenes and the related fluorobenzenium ions are summarized in Tables I and II, respectively.

Fluorobenzene (**1**) was protonated in SbF_5-HF (1:1 mol:mol)-SO_2ClF (1:1 v:v) solution at −78° to give 4-fluorobenzenium ion **2**. The nmr (^1H and ^{19}F) spectra are temperature dependent (Figure 1). The pmr spectrum of the static "frozen-out" ion **2** (at −84°) is well resolved and shows the methylene protons as a doublet at δ 5.43 (J_{HF} = 11 Hz); the coupling is due to the long-range H-F spin-spin interaction (through five bonds). The slight broadening of the CH_2 absorption indicates coupling of CH_2 to the ortho protons. The meta protons show a triplet at δ 8.33 ($J_{HH} = J_{HF}$ = 9 Hz) indicating about equal coupling to the ortho protons and the para fluorine atom. The ortho protons display a multiplet at δ 9.93. As the temperature of the solution is increased, the methylene and the ortho proton absorptions become broadened and merge into the base line at −21°. Meanwhile, the triplet of the meta protons changes to a doublet. The doublet is due to the proton-fluorine coupling. The ^{19}F nmr absorption of ion **2** shows a multiplet at φ 10.0 (96.3 ppm deshielded from fluorobenzene). The substantial deshielding effect is due to the resonance contribution of form **3**. These results indicate that rapid 1,2-hydrogen shifts occur between the CH_2 and the ortho protons. The interconversion of **2** and **2b** is considered to involve two-electron, three-center bonded benzonium ion (**2a**) type transition states.[3,4] There is no indication, however, in the low-temperature nmr spectra for observable benzonium ion intermediates.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When the temperature of the solution of ion **2** is further raised (owing to the relatively low boiling point of SO_2ClF, 7°, these studies were carried out in neat SbF_5-HF solution), a second set of degenerate hydrogen shifts is observed. The pmr spectrum of ion **2** at −10° is essentially the same in SbF_5-HF solution with or without SO_2ClF as cosolvent. The meta protons will show a broadened doublet at δ 8.33. There is a very broad peak at δ 7.7 which is about equal to the average shift of CH_2 and ortho-proton absorptions [(9.93 + 5.43)/2 = δ 7.68] (due as discussed to the intramolecular 1,2-hydrogen shift between the methylene and ring hydrogens ortho to them). On further

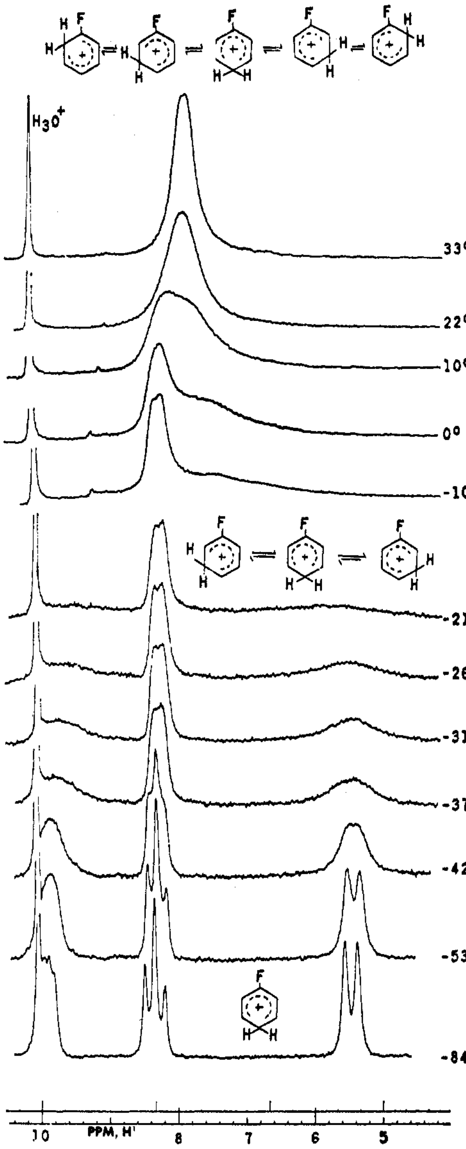
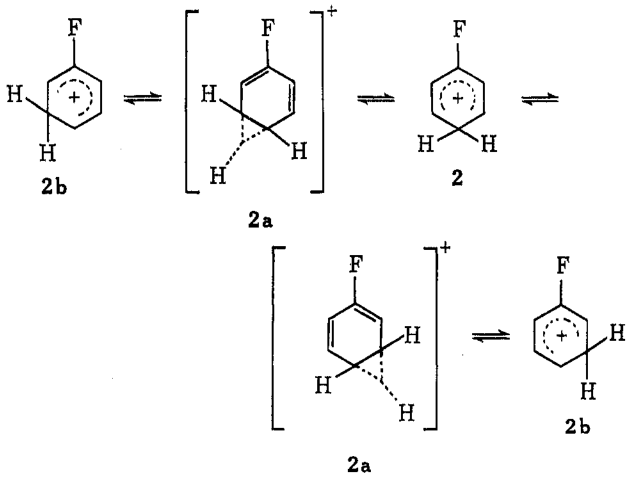


Figure 1.—Temperature-dependent pmr spectra of 4-fluorobenzenium ion **2**.



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(4) G. A. Olah, *Accounts Chem. Res.*, **4**, 240 (1971).

TABLE I

PMR DATA OF FLUOROBENZENES AND THEIR FLUOROBENZENIUM IONS IN SbF_5–HF (1:1 mol:mol)–SO_2ClF (1:1 v:v) SOLUTIONS[a,b]

Registry no.	Fluorobenzene		Ion				Registry no. (ion)
			CH_2	H_{meta}	H_{ortho}	H_{para}	
462-06-6	Fluorobenzene	7.2 (m)	5.43 (d), J_{HF} = 11 Hz	8.33 (t), $J_{HF} = J_{HH}$ = 9 Hz	9.93 (m)		18535-68-7
540-36-3	*p*-Difluorobenzene	6.78 (t)	5.73 (d), J_{HF} = 11 Hz	8.3 (br)	8.6 (br)	9.9 (br)	18535-69-8
367-11-3	*o*-Difluorobenzene	7.1 (m)	5.8 (s, br)	8.7 (br)	9.5 (br)		40719-16-2
372-18-9	*m*-Difluorobenzene	6.8 (m)	5.40 (t, d), J_{HF} = 9 Hz, J_{HH} = 2 Hz	7.90 (t), J_{HF} = 8 Hz 8.20 (t), J_{HF} = 8 Hz	9.3 (m)		18497-70-6
367-23-7	1,2,4-Trifluorobenzene	7.0 (m)	5.43 (t, br) J_{HF} = 9 Hz	7.9 (m)	8.54 (8 lines, d q) J_{HF} = 8, J_{HH} = 3 Hz		18497-72-8
372-38-3	1,3,5-Trifluorobenzene	6.7 (m)	5.30 (q), J_{HF} = 8 Hz	7.64 (8-line m)			18497-71-7
2367-82-0	1,2,3,5-Tetrafluorobenzene	6.8 (m)	5.62 (q), J_{HF} = 8 Hz	7.87 (d, t), J_{HF} = 4 and 8 Hz			18497-73-9
551-62-2	1,2,3,4-Tetrafluorobenzene	6.9 (m)	5.8 (t, br), J_{HF} = 10 Hz		8.8 (br)		40719-21-9
327-54-8	1,2,4,5-Tetrafluorobenzene	7.1 (q) J_{HF} = 8 Hz	5.8 (br)			8.7 (br)	40719-22-0
363-72-4	Pentafluorobenzene	6.9 (m)	5.8 (m)				40719-23-1

[a] Abbreviations used are: s = singlet; d = doublet; t = triplet; q = quartet; br = broad; m = multiplet. [b] Proton shifts are referred to external capillary TMS and *J* values are in hertz.

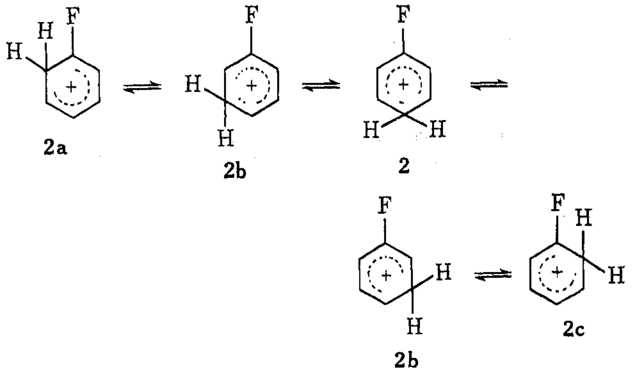
TABLE II

^{19}F NMR DATA OF FLUOROBENZENES AND THEIR FLUOROBENZENIUM IONS IN SbF_5–HF (1:1 mol:mol)–SO_2ClF (1:1 v:v) SOLUTION[a,b]

Fluorobenzene		Ion		
		H_{para}	H_{ortho}	H_{meta}
Fluorobenzene	+106.3 (m)	+10.0 (m)		
p-Difluorobenzene	+113.2 (m)	+0.5 (m)		+106.0 (m)
o-Difluorobenzene	+140.1 (m)	+32.4 (br)		+124.4 (br)
m-Difluorobenzene	+104.8	0.0 (dm), J_{FF} = 80 Hz	+7.3 (dm), J_{FF} = 80 Hz	
1,2,4-Trifluorobenzene	+108.8 (m), +152.2 (m), −133.8 (m)	+1.0 (dm), J^{m}_{FF} = 80 Hz	+18.80 (dm) J^{o}_{FF} = 80 Hz	−125.57 (dm), J^{o}_{FF} = 20 Hz
1,3,5-Trifluorobenzene	+101.0 (m)	−7.45 (t qu), J_{FF} = 70, J_{HF} = 8 Hz	+21.45 (dm), J_{FF} = 70 Hz	
1,2,3,5-Tetrafluorobenzene	+107.6 (m), +124.4 (m), +156.3 (m)	+12.4–16.6 (m)[c]	+12.4–16.6 (m)[c] +53.2 (dm), J_{FF} = 70 Hz	+152.02 (tm), J_{FF} = 20 Hz
1,2,3,4-Tetrafluorobenzene	+158.5 (dd), J_{FF} = 18.0 and 4.0 Hz +141.0 (m)	+28.0 (dd), J^{p}_{FF} − 90, J^{m}_{FF} = 24 Hz	+41.1 (dt), J^{o}_{FF} = 90, J^{m}_{FF} = 24 Hz	+143.3 (td), J^{p}_{FF} = 24, J_{HF} = 9 Hz, +137.5 (m)
1,2,4,5-Tetrafluorobenzene	+141.2 (t), J_{HF} = 8 Hz		+45.7 (br)	+121.4 (br)
Pentafluorobenzene	+164.4 (m), +156.4 (m), +140.8 (m)	+33.5 (tt), J^{o}_{FF} = 76 Hz, J^{m}_{FF} = 25 Hz	+47.6 (dm), J^{p}_{FF} = 76 Hz	+146.6 (dm), J^{p}_{FF} = 25 Hz

[a] Abbreviation used are: s = singlet; d = doublet; t = triplet; q = quartet; br = broad; m = multiplet; and qu = quintet. [b] Fluorine shifts are referred to external capillary $CFCl_3$ in parts per million and *J* values are in hertz. [c] See text.

raising the temperature of the solution to 10°, the broad peak at δ 7.7 collapses together with the meta-proton peak at δ 8.33 and finally (at 33°) appears as a broadened singlet at δ 7.9. This singlet absorption at δ 7.9 is also equal to the average of all the proton absorptions of ion **2** [$(5.43 + 8.33 + 9.93)/3 = \delta\ 7.9$]. These data show that at this temperature, a second set of degenerate intramolecular 1,2-hydrogen shifts occurs (**2c** $\rightleftharpoons$ **2b** $\rightleftharpoons$ **2a**).



A comparison of the temperature-dependent nmr behavior of the 4-fluorobenzenium ion **2** and the 4-methylbenzenium ion (toluenium ion)[3] shows that both ions undergo intramolecular 1,2-hydrogen shifts. However, whereas all the ring hydrogens of the *p*-toluenium ion are rapidly exchanging with one another upon raising the temperature of the solution of the static ion to −60°,[3] this is not the case in ion **2**. The 1,2-hydrogen shifts of ion **2** are taking place in a stepwise process, *i.e.*, **2** undergoes intramolecular 1,2-hydrogen shifts in two separate steps which can be separately observed by nmr spectroscopy. The difference in behavior is mainly due to the relative instability of ion **2c** caused by the inductive effect of fluorine on its ortho position. In addition, this is strongly indicated by results of electrophilic aromatic substitution of fluorobenzene, generally showing high para/ortho isomer ratio.[5] Consequently, ion **2** is much more stable than ion **2c** and the 4-methylbenzenium ion is only slightly more stable than the 2-methylbenzenium ion.

Difluorobenzene (**4**) was protonated in SbF_5–HF (1:1 mol:mol)–SO_2ClF (1:1 v:v) solution at −82° to give 2,5-difluorobenzenium ion **5**. The nmr (^1H and ^{19}F) spectra of ion **5** are also temperature dependent (Figure 2). The methylene protons of ion **5** show a doublet pmr absorption at δ 5.73 ($J_{HF} = 11$ Hz) owing to the ortho-fluorine coupling. It should be noted that the coupling constants of CH_2 to ortho F and para F are about equal (similar as in ion **2** and also ion **7**, see subsequent discussion). The ortho, meta, and para protons show slightly broadened absorption at δ 8.6, 8.3, and 9.9, respectively. The not completely resolved spectrum may be due to more complicated couplings (higher than first order) and viscosity of the medium. The ortho proton has a surprisingly shielded absorption (δ 8.6) when compared to that of ion **2** (δ 9.93), indicating the more important resonance contribution of **5a** over **5b**. Of course, the back donation of fluorine can also stabilize ion **5c**, as shown by the substantially deshielded (by 112.7 ppm from *p*-difluorobenzene) fluorine absorption at ϕ 0.5 for the ortho fluorine atom.

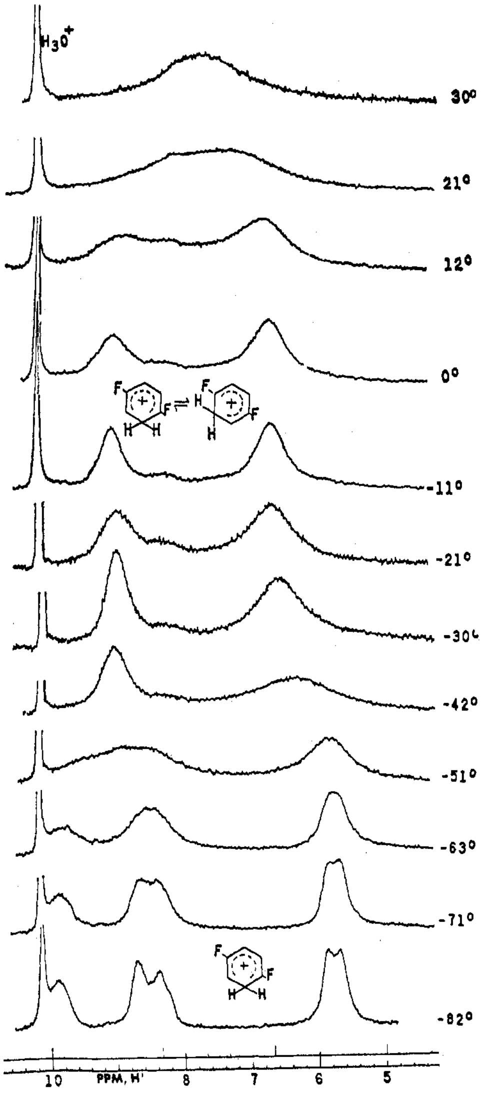
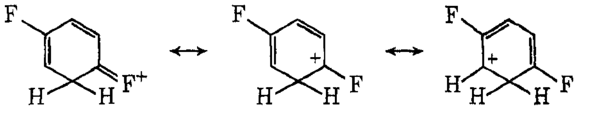
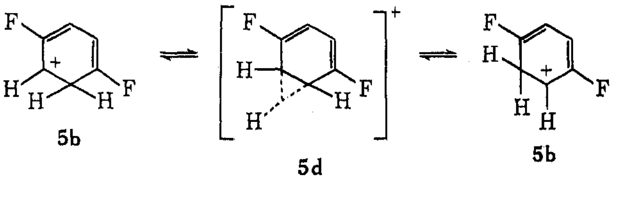


Figure 2.—Temperature-dependent pmr spectra of 2,5-difluorobenzenium ion **5**.



As the temperature of the solution containing ion **5** is raised, all the four proton absorptions broaden. At −11°, they appear as two slightly broadened peaks at δ 6.7 and 9.1. The ^{19}F nmr spectrum of ion **5** shows two multiplets at ϕ 0.5 (ortho F) and 106.0 (meta F). As the temperature of the solution is further raised, the two fluorine absorptions broaden and finally merge into the base line at −11°. The temperature-dependent behavior of ion **5** indicates that intramolecular 1,2-hydrogen shifting occurs, *via* two-electron three-center bonded benzonium ion **5d** as transition state. The exchange reaction is an intramolecular process because the observed pmr shifts at δ 6.7 and 9.1 are equal to the cal-



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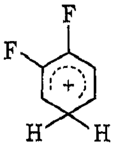
(5) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Amer. Chem. Soc.*, **83**, 4581 (1961).

culated average shifts [$(5.73 \times 2 + 8.6)/3 = \delta\ 6.69$ and $(8.3 + 9.9)/2 = \delta\ 9.1$, respectively].

For studies at higher temperatures, we also protonated *p*-difluorobenzene (**4**) in neat SbF_5–HF solution. The pmr spectra of ion **5** are identical at −11° with or without SO_2ClF diluent. Temperature-dependent pmr spectra thus could be studied above −11° (Figure 2). The two pmr absorptions (δ 6.7 and 9.1) became broad when the temperature was raised above 0°. At 30°, they became a single very broad peak at δ 7.8 (the calculated average shift is δ 7.9). These data indicate that ion **5** also deprotonates above 0° and undergoes both intra- and intermolecular hydrogen exchange (with the solvent system).

o-**Difluorobenzene** (**6**) was protonated in HF–SbF_5 (1:1 mol:mol)–SO_2ClF (1:1 v:v) solution to give 3,4-difluorobenzenium ion **7**. The pmr spectrum of ion **7** is temperature dependent, as it is shown in Figure 3 (left). At −103°, a broadened absorption is observed at δ 5.8, corresponding to the methylene protons (as usual in benzenium ions[6-9]). In the vinylic ring proton region, two broadened absorption lines at δ 8.7 and 9.5 are observed (the resonance line at δ 10.5 being due to the oxonium ion, H_3O^+ impurity in the solvent system). The integration of peak areas gives the number of protons corresponding to each signal; the more deshielded vinylic proton absorption has twice the intensity of that of the more shielded absorption. In the ^{19}F nmr spectrum, two very broad absorptions were found at ϕ 32.4 and 124.4 corresponding to the fluorine shifts of para and meta fluorine atoms in fluorobenzenium ions.[2] These data clearly suggest observation of the static ("frozen-out") 3,4-difluorobenzenium ion **7**.



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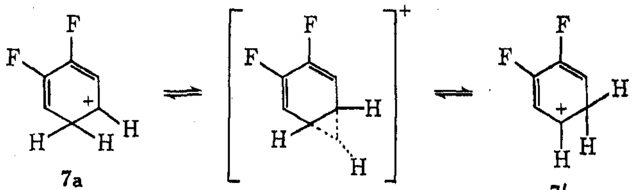
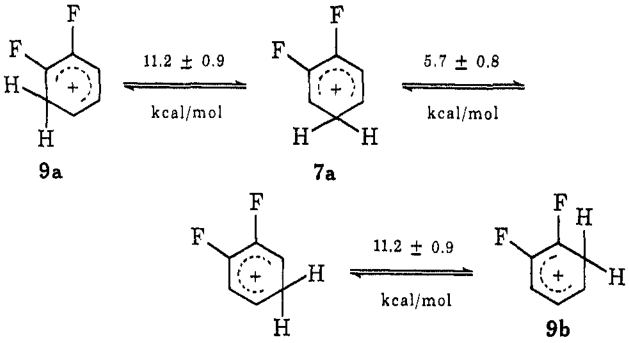
As the temperature of the solution was raised (*e.g.*, to −94°), the two vinylic proton absorption lines collapsed to a broadened peak at δ 9.2 and the methylene proton absorption line also broadened and became slightly deshielded. Further warming of the solution caused the methylene proton resonance to become more deshielded and also broad. Meanwhile, the deshielded vinylic proton absorption line became less broadened as the temperature was raised. At −52°, only two resolved absorption lines were observed at δ 7.1 and 9.1 with a peak area ratio of 3:2. In the ^{19}F nmr spectrum, the two absorptions became broadened as the temperature was raised and at −77° merged into the base line. These observation indicate a rapid degenerate equilibration of 3,4-difluorobenzenium ion **7** through equivalent (degenerate) forms **7a** and **7b**. The interconversion of **7a** and **7b** takes place by a 1,2-hydrogen shift *via* a transition state of benzonium ion nature (**8**).



7a **8** **7b**

As the temperature is further raised, the two absorption lines become again broad and finally collapse into a single absorption at δ 7.9 (from −52 to 0°). In the ^{19}F nmr spectrum, no new absorption lines were observed (except those of the solvent).[10] Thus, there is a second temperature-dependent dynamic process in the 3,4-difluorobenzenium ion, *i.e.*, **9a** ⇄ **7a** ⇄ **7b** ⇄ **9b**.



9a **7a** **7b** **9b**

When the exchange rate exceeds that of the nmr time scale (at 0°), then all the protons are becoming equivalent. This process also takes place through 1,2-hydrogen shifts. Since the two processes can be separately observed by pmr, the corresponding activation parameters can be obtained. The activation energies, E_a, of the two processes were calculated by a multiple-site exchange program[11] and were found to be 5.7 ± 0.8 kcal/mol with a preexponential factor, A, of $10^{8.9 \pm 0.7}$ and 11.2 ± 0.9 kcal/mol with a preexponential factor, A, of $10^{12.4 \pm 0.9}$, respectively.

In the benzenium ion[7] and alkylbenzenium ions,[3,9] both intra- and intermolecular exchanges are possible. In the case of 3,4-difluorobenzenium ion, intermolecular exchange is unlikely, even at 0°, when considering the experimental evidence of the pmr spectra. The calculated average proton shift of CH_2 and ortho H in ion **7a** or **7b** is $(5.8 \times 2 + 9.5)/3 = \delta\ 7.03$, in good agreement with the experimentally observed value (δ 7.1). A similar calculated average shift of one of the ortho and meta protons is δ 9.1, which is identical with the experimentally observed value. This is also the case when all protons become equivalent (at 0°). The calculated average shift is $(8.7 + 9.5 \times 2 + 5.8 \times 2)/5 = \delta\ 7.9$. Besides the excellent agreement of pmr parameters with those calculated for intramolecular exchange processes, further evidence for the purely intra-

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(6) G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 1103 (1965).

(7) G. A. Olah, R. H. Schlosberg, D. P. Kelly, and G. D. Mateescu, *ibid.*, **92**, 2548 (1970).

(8) G. A. Olah and Y. K. Mo, *ibid.*, **94**, 5341 (1972).

(9) D. M. Brouwer, E. L. Mackor, and C. MacLean, in "Carbonium Ions," Vol. 2, G. A. Olah, and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 864.

(10) No ^{19}F nmr resonance was detectable for the rapidly equilibrating ions **7a** and **7b**. This is because the ortho and meta F shifts are separated by 92 ppm and the rate constant for observing the coalescence of the two signals is calculated to be 11,526 sec^{-1}. Thus, at the temperature used in this work, the rate constant is expected to be much smaller than this value. Consequently, the two resonances became too broad to be observed even at 0°.

(11) The theoretical spectra were obtained by using a Fortran IV coded program based on the equation of Gutowsky and Holm: H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). The program was obtained originally from Dr. T. Gerig and was adapted to the Univac 1108 computer by Dr. W. E. Heyd.

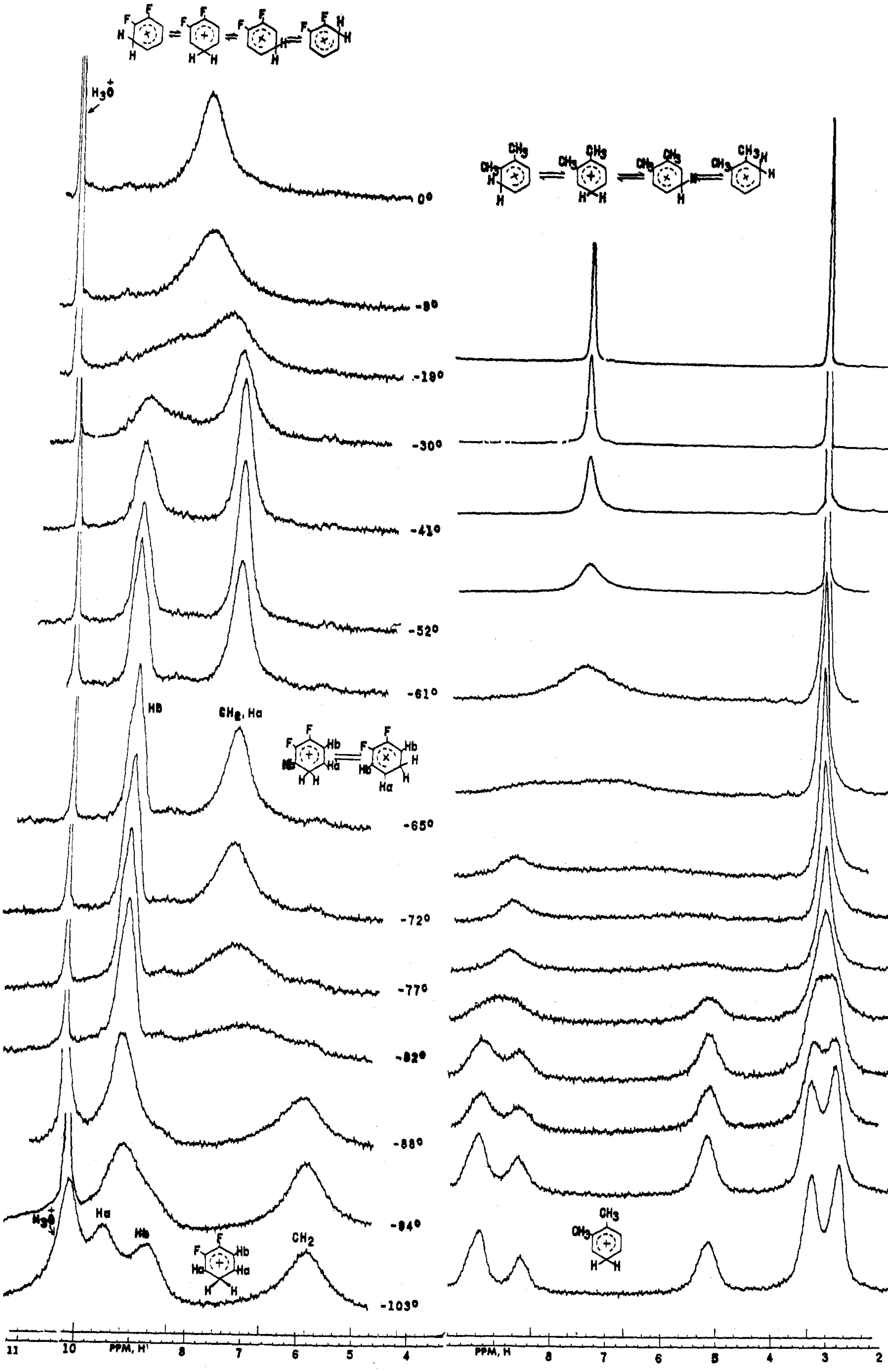


Figure 3.—Temperature-dependent pmr spectra of 3,4-difluorobenzenium ion 7 (left) and 3,4-dimethylbenzenium ion (right).

molecular nature of exchange was obtained when *o*-difluorobenzene was deuterated in DF–SbF$_5$–SO$_2$ClF solution at −78°. Deuteration was found to take place only at C-4 and C-5, as shown by the equal intensity of the two proton absorptions at δ 7.9 and 9.1 in the pmr spectrum (*vide supra*) of the d_1-3,4-difluorobenzenium ion at −61°. When the temperature of the solution was raised above −52°, the intensity of the

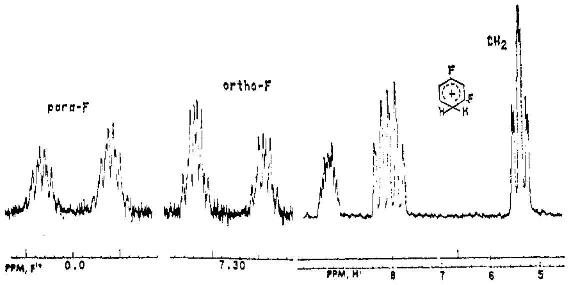
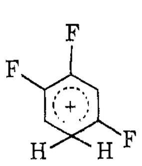


Figure 4.—^{1}H and ^{19}F nmr spectra of 2,4-difluorobenzenium ion **11**.

two resonances changed. The intensity of the more deshielded absorption decreased and that of the shielded absorption increased, reaching a ratio of 2:3. At the same time, the intensity of the acid peak (present owing to a small amount of protic acid impurity in the DF–SbF$_5$–SO$_2$ClF solution) was not affected.

m-**Difluorobenzene** (**10**) was protonated in superacid at −30° to give 2,4-difluorobenzenium ion **11**. The nmr (^{1}H and ^{19}F) spectra of ion **11** are shown in Figure 4. The methylene protons of ion **11** show a triplet of doublets at δ 5.40 (J_{HF} = 9 and J_{HH} = 2 Hz), indicating that CH$_2$ is equally coupled to the ortho and para F but the coupling is smaller than in ions **2** and **5** (11 Hz). The small coupling (2 Hz) is due to CH$_2$–ortho-H coupling. The ortho proton centered at δ 9.3 shows a complicated deshielded multiplet, owing to spin–spin interactions with CH$_2$, meta H, and F. The two meta protons show a five-line absorption from δ 7.7 to 8.3. More careful studies show that it is actually two sets of triplets. The deshielded triplet at δ 8.2 (J_{HF} = 8 Hz) is assigned to the meta H between the two fluorine atoms, caused by their joint inductive effects. The triplet at δ 7.9 (J_{HF} = J_{HH} = 8 Hz) is then assigned to the other meta H. The ^{19}F nmr spectrum of ion **11** shows two sets of doublet of multiplets at ϕ 0.0 (para F) and 7.3 (meta F). The doublet is due to the large fluorine–fluorine coupling of 80 Hz. The nmr (^{1}H and ^{19}F) spectra of ion **11** are temperature independent from −80 to −10°.

Protonation of 1,2,4- and 1,3,5-trifluorobenzenes (**12** and **13**) in superacid at −78° gave the 2,4,5- and 2,4,6-trifluorobenzenium ions **14** and **15**, respectively. The nmr (^{1}H and ^{19}F) spectra of ion **14** are shown in Figure 5. The methylene protons of ion **14** show a slightly broadened triplet at δ 5.43 (J_{HF} = 9 Hz). The proton–fluorine couplings (ortho and para) must be equal and the broadening may be due to the ortho and meta F couplings. The ortho proton of ion **14** has an eight-line multiplet at δ 8.45 and is shielded compared to that of 4-fluorobenzenium ion **2** (δ 9.93). A similar shielding effect has been observed in the 2,4-difluorobenzenium ion **5** (see previous discussion). Each of the three fluorine absorptions of ion **14** show two multiplets owing to the unusually large fluorine–fluorine coupling generally observed in fluorobenzenium ions.



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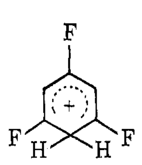


15

The pmr spectrum of ion **15** shows a quartet at δ 5.30 (CH$_2$, J_{HF} = 8 Hz) and an eight-line multiplet at δ 7.64 (meta H), indicating that methylene protons are equally coupled to the three fluorine atoms and the meta protons are coupled to all three fluorine atoms. In the ^{19}F nmr spectrum, ion **15** shows two fluorine absorptions at ϕ −7.45 (para F, triplet of quintet, J_{FF} = 70 and J_{HF} = 8 Hz) and 21.45 (ortho F, doublet of multiplet, J_{FF} = 70 Hz). The triplet of quintet of the para fluorine is due to the long-range fluorine–fluorine coupling (70 Hz) and also to the equal proton–fluorine couplings of para F–meta H and para F–CH$_2$. Both ions **14** and **15** show no temperature-dependent behavior from −80 to −10°.

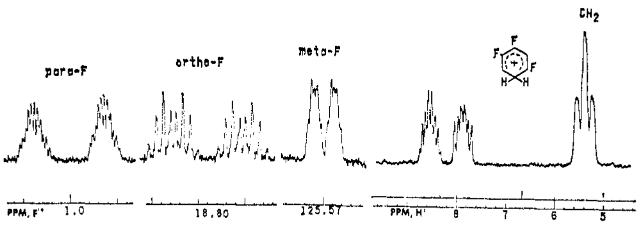
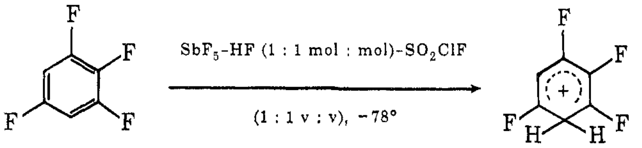


Figure 5.—^{1}H and ^{19}F nmr spectra of 2,4,5-trifluorobenzenium ion **14**.

1,2,3,5-Tetrafluorobenzene (**16**), when protonated in superacid at −78°, gave the 2,3,4,6-tetrafluorobenzenium ion **17**. The pmr spectrum of ion **17** shows two well-resolved absorptions at δ 5.62 (CH$_2$, quartet, J_{HF} = 8 Hz) and 7.78 (meta, doublet of triplets, J_{HF} = 8 and 4 Hz). The methylene protons are equally coupled to the ortho and para fluorine atoms. The meta proton apparently couples to the adjacent fluorine atoms with equal magnitude and the small coupling could be due to the meta fluorine. The ^{19}F nmr spectrum of ion **17** shows a triplet at ϕ 152.02 (J_{FF} = 20 Hz) for the meta F which is equally coupled to the ortho and para fluorine atoms. Each peak of the triplet is a multiplet with coupling constants of less than 1 Hz, presumably owing to the spin–spin interaction of meta H and the distant ortho F. There are five multiplet fluorine absorption between ϕ 12.4 and 16.6 (with an intensity corresponding to two fluorine atoms) and these can be assigned to the para F and the ortho F, which is adjacent to the meta F. Owing to a smaller inductive effect of the other ortho F, the more shielded doublet of multiplets at ϕ 53.2 (J_{FF} = 68 Hz) was assigned to the latter. The nmr (^{1}H and ^{19}F) spectra of ion **17** are again temperature independent from −80 to −10°.



16 **17**

The reaction conditions for the protonation of **1,2,3,4-tetrafluorobenzene** (**18**) are important. The ratio of superacid SbF$_5$–HF to diluent SO$_2$ClF must be 1:1 (v:v) and the acid must be at least four times in excess of the substrate 1,2,3,4-tetrafluorobenzene. The pmr spectrum of protonated 1,2,3,4-tetrafluorobenzene (**19**) is temperature dependent (Figure 6A). At −83°, a slightly broadened triplet absorption is observed at δ 5.8 (2 H, J_{HF} = 10 Hz) corresponding to the methylene proton of the benzenium ion **19**. It is assumed that the

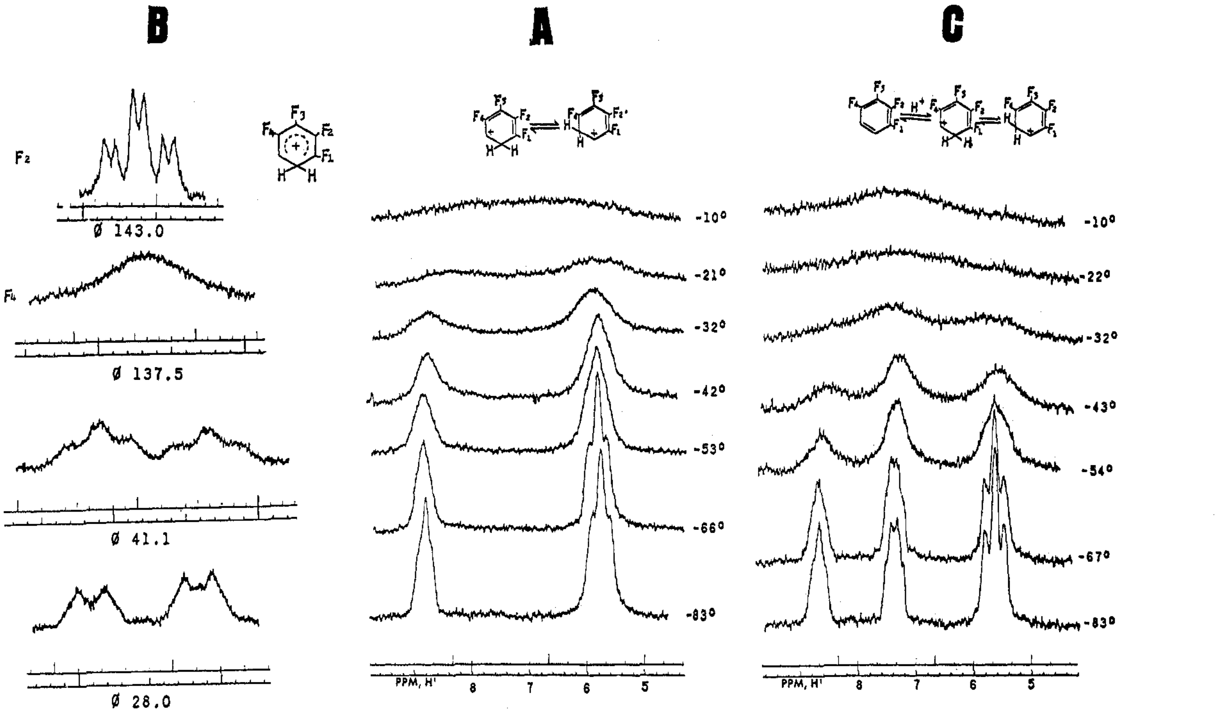
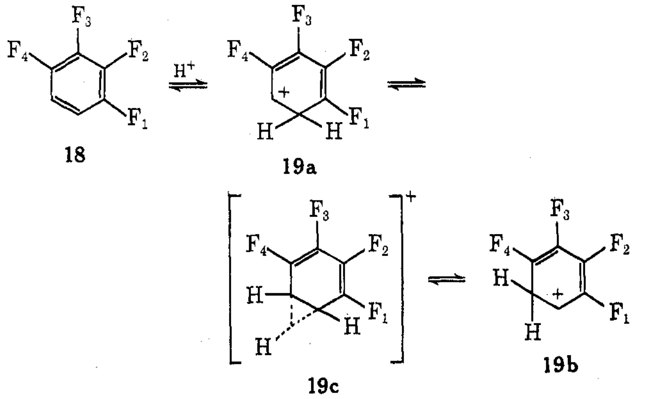


Figure 6—(A) Temperature-dependent pmr spectra of 2,3,4,5-tetrafluorobenzenium ion **19**; (B) ^{19}F nmr spectra of 2,3,4,5-tetrafluorobenzenium ion **19**; (C) temperature-dependent pmr spectra of a mixture of 1,2,3,4-tetrafluorobenzene **18** and 2,3,4,5-tetrafluorobenzenium ion **19**.

triplet is due to the CH_2 coupling with the two fluorine atoms (ortho and para). The ortho proton shows a broad absorption at δ 8.8. In the ^{19}F nmr spectrum, four fluorine absorptions were observed (Figure 6B). The most deshielded absorption at ϕ 28.0 is assigned to the para fluorine (F_3). The unusually large coupling (J_{FF} = 90 Hz) is due to the ortho,para fluorine coupling. This kind of coupling has been observed in other fluorobenzenium ions. Consequently, the ortho fluorine (F_1) is assigned to the second most deshielded fluorine absorption at ϕ 41.1. The most shielded doublet of triplet at ϕ 143.3 is assigned to the meta fluorine (F_2), since it couples to all of the fluorine atoms in ion **19** (the coupling constants of $J_{F_1-F_2}$ and $J_{F_3-F_2}$ are about equal).

As the temperature of the solution was raised (*e.g.*, $-53°$), the two-proton absorptions became broad and finally merged into the base line at $-10°$. Meanwhile, the four fluorine absorptions were also broadened and merged into the base line similarly to the pmr absorptions. In the pmr spectrum, the acid peak was also broadened and became shielded at higher temperature ($-10°$). The temperature-dependent nmr spectra of the solution of **18** are reversible. However, the ion is decomposed gradually at $-10°$. All these data indicate that both intra- and intermolecular proton exchanges of ion **19** occur. The transition state for the intramolecular hydrogen exchange again is considered to be of tetracoordinated benzonium ion nature, **19c**.

When the superacid concentration is less than 4 *M* to 1,2,3,4-tetrafluorobenzene, both parent 1,2,3,4-tetrafluorobenzene and protonated ion **19** are observed at $-83°$. The nmr (^1H and ^{19}F) spectra of this solution again show temperature-dependent nature (Figure 6C). Upon raising the temperature, the acid peak (not shown in Figure 6C) is also broadened and becomes shielded, indicating that an additional intermolecular proton exchange process also takes place (**18** + **19** $\rightleftarrows$ **19** + **18**).



1,2,4,5-Tetrafluorobenzene (**20**) was protonated in $HF-SbF_5-SO_2ClF$ solution at $-80°$ to give 2,3,5,6-tetrafluorobenzenium ion **21**. The nmr spectra of ion **21** show two broadened pmr absorptions at δ 5.8 (CH_2) and 8.7 (para H) and also two broadened fluorine resonances at ϕ 45.7 (ortho F) and 121.4 (meta F). The broadening may be due to complex couplings and the viscosity of the medium at low temperature ($-80°$). Both proton and fluorine resonances become broader and finally merge into the base line at higher temperature ($-40°$). The temperature-dependent behavior can be explained in terms of **21** undergoing intermolecular hydrogen exchange with the superacid system or/and the formation of a radical cation. Since 1,2,4,5-tetrafluorobenzene (**20**) is a highly deactivated system, an intramolecular 1,2-hydrogen shift process is very unlikely. Consequently, formation of a protonation–deprotonation equilibrium can be best considered. On the other hand, when highly fluorinated aromatics (*e.g.*, tetra-, penta-, and hexafluorobenzenes) are treated with SbF_5-FSO_3H at room temperature, radical cations are known to form.[12] This behavior is probably due to SbF_5 present in the system oxidizing the fluoroaromatic π system.

Pentafluorobenzene (22) was also protonated in $HF-SbF_5-SO_2ClF$ solution at −78° to give 2,3,4,5,6-pentafluorobenzenium ion (**23**). The pmr spectrum of ion **23** shows a multiplet at δ 5.8, indicating the methylene protons of a benzenium ion. The pmr spectrum of **22** is also a multiplet but the aromatic proton is more deshielded (δ 6.9). In the ^{19}F nmr spectrum of ion **23**, the para fluorine displays a triplet of triplets at ϕ 33.5 ($J_{FF}^{o} = 76$ and $J_{FF}^{m} = 25$ Hz) indicating that it is coupled to both ortho and meta fluorine atoms. Each peak of the triplet of triplets is slightly broadened since it also couples to the methylene protons. The ortho-fluorine absorption is less deshielded than that of para fluorine and appears as a doublet of multiplets at ϕ 47.6 ($J_{FF}^{p} = 76$ Hz). In addition, the meta fluorines show a doublet of multiplets ^{19}F nmr resonance at ϕ 146.6 ($J_{FF}^{p} = 25$ Hz). As for ion **21**, both proton and fluorine absorptions of ion **23** are broadened at higher temperature, and may be due to the same explanations.

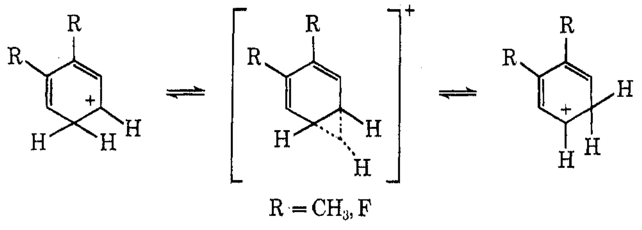
Comparison of Fluoro- and Methylbenzenium Ions.—Comparison of the nature of fluorobenzenium ions in superacids shows similarities as well as some differences to those of the corresponding methylbenzenium ions. Temperature-dependent nmr spectra of 4-fluorobenzenium ion, isomeric difluorobenzenium ions, and 2,3,4,5-tetrafluorobenzenium ion were observed in a parallel fashion with the corresponding methylbenzenium ions.

We have already discussed and compared the temperature-dependent behavior of 4-fluorobenzenium ion with 4-methylbenzenium ion. Similarly, temperature-dependent pmr spectra of 3,4-dimethylbenzenium ion were also observed, resembling closely those of 3,4-difluorobenzenium ion. Figure 3 (right) shows the temperature-dependent pmr spectra of 3,4-dimethylbenzenium ion. The degenerate 1,2-hydrogen shifts are again of intramolecular nature (within the studied temperature range). In the case of the 2,5-difluorobenzenium ion, degenerate intramolecular 1,2-hydrogen shifts were found below 0°. However, the corresponding 2,5-dimethylbenzenium ion undergoes intramolecular 1,2-hydrogen shifts only below −74°. On the other hand, both 2,4-dimethyl- and 2,4-difluorobenzenium ions show no intramolecular 1,2-hydrogen shift.

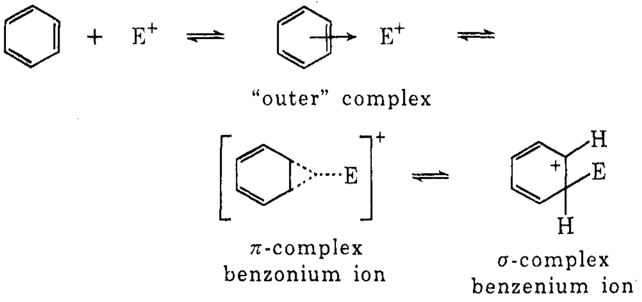
Temperature-dependent pmr spectra of 2,3,4,5-tetramethylbenzenium ion (prehnitenium ion) have been studied by Brouwer.[13] Degenerate intramolecular 1,2-hydrogen shifts similar to those of the 2,3,4,5-tetramethylbenzenium ion were also found in the 2,3,4,5-tetrafluorobenzenium ion.

Both 2,4,6- and 2,3,5-trifluoro- and the corresponding trimethylbenzenium ions show no intramolecular 1,2-hydrogen shifts. In contrast, the 2,3,4,5,6-pentamethylbenzenium ion undergoes intramolecular 1,2-hydrogen shifts while the corresponding pentafluorobenzenium ion does not. The hexamethylbenzenium ion (protonated hexamethylbenzene) also undergoes degenerate 1,2-hydrogen shifts.[13] The analog fluorine compound, hexafluorobenzene, was not found to be protonated in any superacids studied. It formed a donor–acceptor complex with antimony pentafluoride.

In none of the studied arenium ion systems was there evidence that the "frozen-out" species at low temperature are of bridged aronium ion nature. Thus presently it seems that the 1,2-hydrogen shifts in degenerate arenium ion rearrangement proceed through a relatively high-lying bridged aronium ion state involved between the two identical arenium ion intermediates. Aronium ions also play a similar role in electrophilic aromatic substitutions.



In electrophilic aromatic substitution, the electrophile (E^+) first interacts with an aromatic substrate forming a weak reagent–substrate complex ("outer" complex[14]). The formation of such complexes is reversible and does not lead to substituted products. As the reagent moves closer to bonding distance, the highest lying occupied aromatic π orbital containing an electron pair overlaps with the empty orbital of the electrophile, forming a two-electron three-center bond (π complex). The formed complex is indeed a bridged tetracoordinated carbonium ion (benzonium ion) and is identical with that involved in 1,2-hydrogen (methyl) shifts of benzenium ions. Opening the three-center bond of the benzonium ion leads to the observable trivalent benzenium ion (σ complex) intermediate.



Among the three species ("outer" complex, benzonium ion, and benzenium ion) involved in electrophilic aromatic substitutions and isomerizations, "outer" complexes and benzenium ions are directly observable. Benzonium ions, however, were not yet observed under stable ion conditions.

Experimental Section

Materials—All fluorinated benzenes were commercially available (Pennisular Chemresearch) and used without further purification.

Preparation of the Ions.—Samples of the protonated fluoro-

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[12] N. M. Bazhin, Yu. V. Pozdnyakovich, V. D. Shteingarts, and G. G. Yakobson, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 10, 2300 (1969).

[13] Reference 9, p 889.

[14] Using Mulliken's definition: R. S. Mulliken, *J. Amer. Chem. Soc.*, **72**, 600 (1950); **74**, 811 (1952); *J. Phys. Chem.*, **56**, 801 (1952).

benzenes for nmr studies were prepared by adding 0.2 g of the fluorobenzene to 2 ml of SbF_5-HF-SO_2ClF solution which had been cooled at −78°. Upon warming and stirring, clear solutions were obtained.

Nmr Studies.—A Varian Associates Model A-56-60A nmr spectrometer equipped with a variable-temperature probe was used to obtain all spectra. Capillary TMS and $CFCl_3$ were used for proton and fluorine references, respectively.

Kinetic Analysis.—The activation energies for intramolecular 1,2-hydrogen shifts in protonated *o*-difluorobenzenes were determined by nmr line shape analysis. A computer stimulation of line shape was employed based on the Gutowsky–Holm[11] equation for multiple-site exchange. Activation parameters were calculated as previously described.[1b]

All the temperature-dependent nmr spectra are reversible under the studied conditions, unless otherwise mentioned.

Acknowledgment.—Support of our work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the National Science Foundation is gratefully acknowledged.

Notes

Stable Carbocations. CLVI. Dealkylative Formation of the *tert*-Butyl Cation from Substituted *tert*-Butylbenzenes with Fluoroantimonic Acid[1]

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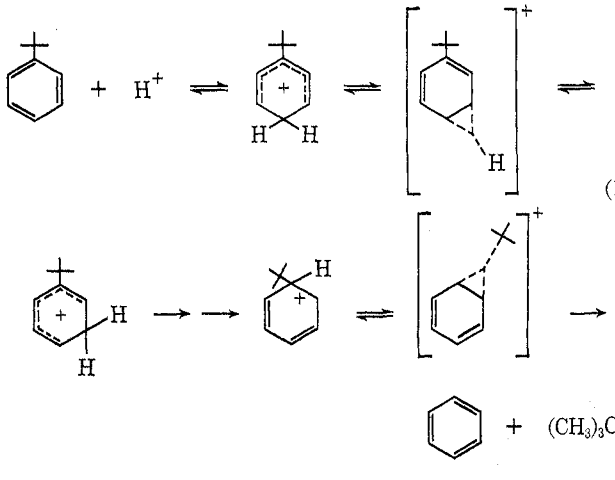
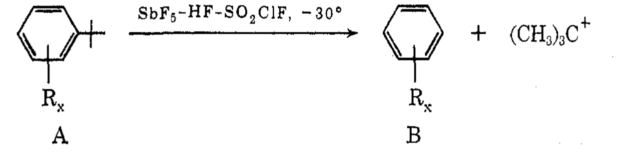
Received February 12, 1973

Under Friedel–Crafts reaction conditions, isomerization of di-*tert*-butylbenzene[2] and *tert*-butyltoluene[3] is well known. Under stable ion conditions, isomerization processes of alkylbenzenium ions[4] were also studied. In the study of protonation of alkylbenzenes, *tert*-butylbenzene was found to cleave readily to benzene and *tert*-butyl cation in superacid media even at low temperature.[4,5] The study of protonation of *tert*-butylbenzene in superacids at low temperature also provided direct experimental evidence for the formation of the *tert*-butylbenzenium ion. Raising the temperature results in intramolecular hydrogen migration as is shown by temperature-dependent nmr spectra. Eventually, the proton is attached to the carbon carrying the *tert*-butyl group (in all probability) and subsequently the *tert*-butyl cation is cleaved according to an α,β-cleavage mechanism (eq 1).



(1)

Ring-substituted alkylbenzenes, particularly with electron-withdrawing or sterically crowded groups, make formation of ring-protonated arenium ions increasingly difficult or even prevent it. In order to gain further insight into the protolytic behavior of *tert*-butylbenzenes with increasing substitution, we studied 17 substituted *tert*-butylbenzenes in SbF_5–HF–SO_2ClF solution at −30°. In all cases, *tert*-butyl cation was formed as evidenced by its pmr singlet absorption[2] at δ 4.0–4.2 (dependent on concentration and media). This peak was increased in intensity by adding a known solution of the *tert*-butyl cation. The pmr spectra of the de-*tert*-butylated benzenes are identical with those of the corresponding benzenes derivatives in the same superacid media. For example, the pmr spectrum of *p*-*tert*-butylbenzoic acid in SbF_5–HF–SO_2ClF solution is identical with that of the *tert*-butyl cation and O-protonated benzoic acid in the same superacid solution.



A B

R_x = F_5, *o*-F, *p*-F, *p*-NH_2, *m*-$CONH_2$, *o*-, *p*-NO_2, *p*-$COCH_3$, *p*-COOH, *o*-, *m*-, *p*-*tert*-butyl, 3,5-di-*tert*-butyl, 3,5-di-*tert*-butyl-4-nitro, 3,5-di-*tert*-butyl-4-bromo, 2,4,5- and 3,4,5-tri-*tert*-butyl

Owing to the electron-withdrawing groups (*e.g.*, F_5, COOH, and NO_2), protonation at ring and subsequent benzenium–benzonium–benzenium ion rearrangement leading to cleavage of the *tert*-butyl group may not be necessary. Protonation may directly involve the C_{Ar}–C_α bond *via* a three-center bonded transition state (I) (thus reacting in accordance with known protolytic behavior of neopentane derivatives).

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(1) Part CLV: G. A. Olah, D. A. Beal, and P. W. Westerman, *J. Amer. Chem. Soc.*, **95**, 3387 (1973).

(2) G. A. Olah, C. G. Carlson, and J. C. Lapierre, *J. Org. Chem.*, **29**, 2687 (1964).

(3) G. A. Olah, N. W. Meyer, and N. A. Overchuk, *J. Org. Chem.*, **29**, 2310 (1964).

(4) For a review and references see D. M. Brouwer, E. L. Mackor, and C. MacLean in "Carbonium Ions," G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 865.

(5) G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly, and G. D. Mateescu, *J. Amer. Chem. Soc.*, **94**, 2034 (1972), and references cited therein.