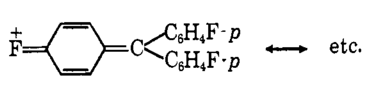
0.19. Found: C, 42.77; H, 0.24), ν_{OH} 3600 cm^{-1}, pmr (CCl_4): τ 5.82 (septuplet), $J_{HF} = 3.0$ cps [triphenylcarbinol: τ 7.23 (multiplet), $J_{HH} = 1.0$ cps].

When II was dissolved in 100% H_2SO_4 at room temperature, a pink solution formed immediately. The visible spectrum of this solution exhibited strong absorption, $\lambda_{\max}^{H_2SO_4}$ 500 mμ (log ϵ 4.63). We attribute this behavior to the presence of cation I. Triphenylmethyl cation possesses bands at 428 and 409 mμ (log ϵ 4.58).[2] Compound II is regenerated when the acid solution is poured into water. Support for the existence of the cation was found by hydride exchange with cycloheptatriene.[3] The mixture was added to water and, after extraction with carbon tetrachloride and evaporation of solvent, a white solid, tris(pentafluorophenyl)methane, $(C_6F_5)_3CH$ (III), mp 158.0–159.5° (cor) (CH_3OH), was isolated (*Anal.* Calcd for $C_{19}HF_{15}$: C, 44.38; H, 0.19. Found: C, 44.19; H, 0.44); pmr (CCl_4): τ 3.80 (multiplet), substantially deshielded with reference to $(C_6H_5)_3CH$ (τ 4.54). Compound III was also prepared in 70% yield by reaction of II with phosphorus tribromide. No halide could be isolated. The mechanism of this reaction is under study.

Cation I is very unstable in sulfuric acid solution relative to triphenylmethyl cation. In 96% H_2SO_4, the half-life of I is about 2 min at room temperature. The development of a second band at shorter wavelength is observed within a few minutes. The nature of the species being formed is under investigation.

The transiency of I makes it difficult to obtain a quantitative measure of its stability, but it appears that the alcohol is half-ionized in 93% H_2SO_4, so that the pK_{R^+} of II is about −17.5, while that of triphenylcarbinol is −6.63.[4] The instability of I reflects the increased localization of the positive charge on the methinyl carbon, due to repulsion of the charge by the C–F bond dipoles.

We have also prepared 4,4′,4′′-trifluorotriphenylcarbinol (IV), mp 91–92.5°, by reaction of ethyl *p*-fluorobenzoate with excess *p*-fluorophenylmagnesium bromide (*Anal.* Calcd for $C_{19}H_{13}OF_3$: C, 72.61; H, 4.17. Found: C, 72.86; H, 4.28). Compound IV forms a carbonium ion in sulfuric acid solution ($\lambda_{\max}$ 433 mμ) which is more stable (pK_{R^+} = −6.05) than triphenylmethyl cation. In this case, resonance stabilization by participation of the *p*-fluorine atoms (V) outweighs the destabilization due to the inductive effect.



V

In contrast, the over-all polar effect of the pentafluorophenyl group is the overwhelming factor, and resonance is of little significance.

Further studies on these and related compounds will be reported in a full paper.[5]

Acknowledgment. The authors wish to express their gratitude to the National Institutes of Health for financial support of this research under Grant GM-12146, and to the U. S. Steel Foundation for a fellowship to Michael A. McKinney.

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[2] H. H. Jaffé and M. Orchin, "Theory and Application of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p 458.

[3] H. J. Dauben, Jr., F. A. Gadecki, K. M. Harman, and D. L. Pearson, *J. Am. Chem. Soc.*, 79, 4557 (1957).

[4] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, 77, 3044 (1955); N. C. Deno, H. E. Berkheimer, W. L. Evans, and H. J. Peterson, *ibid.*, **81**, 2344 (1959).

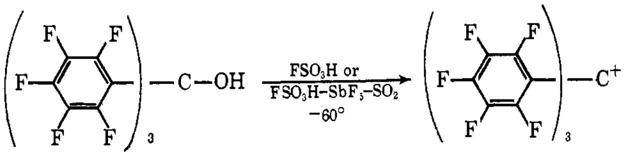
[5] NOTE ADDED IN PROOF. The method of choice for the preparation of II is the reaction of diethyl carbonate with 3 equiv of C_6F_5Li at −25°. The yield is better than 50%.

Stable Carbonium Ions. XXXV.[1] Pentafluorophenylcarbonium Ions

Sir:

Tri-, di-, and monophenylcarbonium ions are well investigated (ultraviolet, infrared, nmr, X-ray studies).[2] In extension of our previous work on fluoroalkylcarbonium ions[3] we felt it was of interest to extend our investigations to fluorophenylcarbonium ions. The fluorine nmr shifts are much larger than the pmr shifts, and therefore anisotropy and other effects influence the effect of a positive charge on chemical shifts to a lesser degree. We wish now to report the observation of the tris-, bis-, and monopentafluorophenylcarbonium ions and their nmr study.

Tris(pentafluorophenyl)carbinol[4a] gives a relatively unstable solution in sulfuric acid.[4b] It was, however, found that its solution in fluorosulfonic acid or fluorosulfonic acid–antimony pentafluoride at −60° is stable and allows the observation of the ^{19}F magnetic resonance spectrum (Figure 1) of tris(pentafluorophenyl)carbonium ion (I). In FSO_3H–SbF_5 solution the ^{19}F nmr shift of the *p*-fluorine atoms is underlying the broad Sb–F resonance. This interference can be eliminated by using neat fluorosulfonic acid as solvent. The ^{19}F resonance spectrum of ion I when compared with that of starting tris(pentafluorophenyl)carbinol (II; Table I) shows substantial deshielding of the *ortho*, *meta*, and *para* ring fluorine atoms ($\Delta\delta_{ortho}$ = 14.7 ppm, $\Delta\delta_{meta}$ = 6.21 ppm, and $\Delta\delta_{para}$ = 40.1 ppm). The largest deshielding effect (40.1 ppm) is observed in the case of the *p*-fluorine atoms. This clearly indicates the high degree of charge delocalization into *ortho* and *para* positions in ion I and the importance of resonance forms of quinoidal nature.



I

Taft's observation[5] of fluorine nmr shielding in monofluorophenyl cations in strong acid media is also in accordance with this observation.

The bis(pentafluorophenyl)carbonium ion II can

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[1] Part XXIV: G. A. Olah, J. M. Bollinger, C. A. Cupas, and J. Lukas, *J. Am. Chem. Soc.*, in press.

[2] For a summary see G. A. Olah and M. W. Meyer in "Friedel-Crafts and Related Reactions," Vol. 1, G. A. Olah, Ed., Wiley-Interscience Publishers, Inc., New York, N. Y., 1963, Chapter VIII.

[3] G. A. Olah and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **88**, 3310 (1966).

[4] (a) We are grateful to Professor R. Filler for a sample of tris(pentafluorophenyl)carbinol; (b) see R. Filler, C.-S. Wang, M. A. McKinney, and F. N. Miller, *J. Am. Chem. Soc.*, **89**, 1026 (1967), indicating half-protonation in 93% H_2SO_4.

[5] Professor R. W. Taft, Jr., personal communication.

Table I. F^{19} and H^1 Nmr Shifts of Pentafluorophenylcarbonium Ions (in ppm from CCl_3F and TMS)

	Methyl alcohol, halide				Carbonium ion			
	δ_{CH}[b]	ϕ_{ortho}[a]	ϕ_{meta}[a]	ϕ_{para}[a]	δ_{CH}	ϕ_{ortho}	ϕ_{meta}	ϕ_{para}
Tris(pentafluorophenyl)-methyl alcohol		+140.98	+161.54	+152.22		+126.25	+154.29	+112.12[c]
Bis(pentafluorophenyl)-methyl alcohol	−3.67	+144.17	+162.28	+153.69	~[−9.30]	+111.61	+153.86	+100.36[c]
Pentafluorophenyl methyl fluoride α-F: $\phi = +211.74$ $J_{HF} = 47.8$ Hz	−5.47	+143.57	+162.53	+152.27	−9.60	+103.18	+151.53	+ 74.89[d]

[a] In $CDCl_3$ at 25° from internal CCl_3F. [b] In SO_2 at −20° from TMS capillary. [c] In $FSO_3H–SbF_5–SO_2$ at 60° from CCl_3F in a separate tube (F^{19}) or TMS capillary (H^1). [d] In $SbF_5–SO_2$ at −60° from CCl_3F in a separate tube (F^{19}) or TMS capillary (H^1).

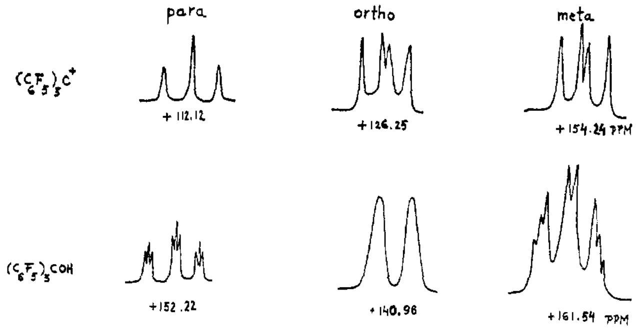
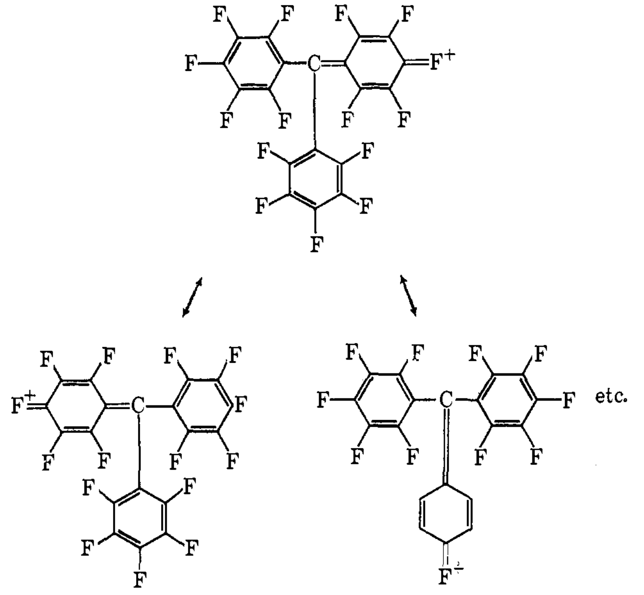
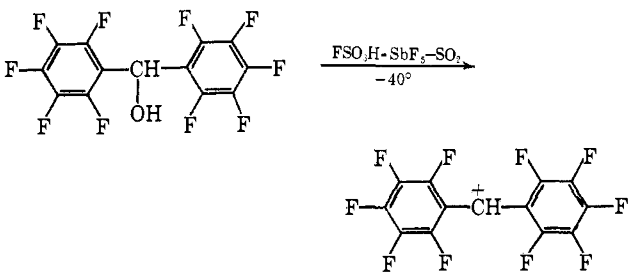


Figure 1.

be generated from bis(pentafluorophenyl)carbinol[6] in $FSO_3H–SbF_5–SO_2$ solution at −60°. Ion II is con-



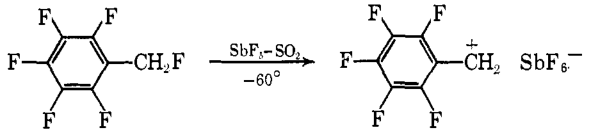
siderably less stable than ion I and cannot be obtained in stable form in neat fluorosulfonic acid. The ^1H



II

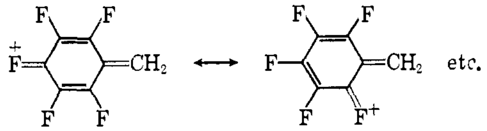
and ^{19}F nmr data of ion II together with those of the starting alcohol are summarized in Table I. The deshielding pattern of the ring fluorine atoms follows that of ion I. The aliphatic methine proton in ion II is partially masked by the solvent acid.

Pentafluorophenylcarbonium ion (III) was obtained from pentafluorobenzyl fluoride (prepared from pentafluorobenzyl bromide[6] and HgF_2) in $SbF_5–SO_2$ solution at −60°. The methylene protons in ion III are



III

at −9.60 ppm. The deshielding effect of the ring fluorine is very substantial in the *para* and *ortho* positions, which can be well explained assuming strong contributions from the quinoidal forms.



The *m*-fluorine peaks in II and III have almost identical appearances to the *m*-fluorines of I (Figure 1). The *o*- and *p*-fluorine resonances in II and III are considerable broadened, indicating long-range coupling to the α-hydrogen(s). This broadening is more noticeable for the *p*-fluorines (substantiating a stronger contribution from the *p*-quinoidal resonance forms) and, as expected, is greater for III than for II.

All nmr spectra were obtained on a Varian Model A56-60A spectrometer, equipped with a variable-temperature probe and operated at 56.4 and 60 MHz.

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(6) Obtained from Imperial Smelting Ltd., Bristol, England.

(7) National Science Foundation predoctoral research investigator.

Cyclopropanones. V. Inhibition of Polymerization and Addition of Acids[1]

Sir:

A simple, high-yield preparation of cyclopropanone (**1**) has recently been reported.[1] However **1** was found to polymerize rapidly at room temperature, and only

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(1) See N. J. Turro and W. B. Hammond, *J. Am. Chem. Soc.*, **88**, 3672 (1966), for paper IV.