head), 1.90 → 1.40 and 1.20 → 0.70 (m, each 2 H, ring methylene protons).

7-(2′-Ethylidenyl)bicyclo[2.2.1]hept-2-enyl 3,5-Dinitrobenzoate (15b): mp 81–82°; nmr δ 9.10 (s, 3 H, aromatic), 6.28 (m, 2 H, ring vinyl), 4.95 (m, 3 H, $-CH_2O$ + single vinyl proton), 3.55 and 3.15 (bs, each 1 H, bridgehead), 2.00 → 1.60 and 1.30 → 1.00 (m, each 2 H, ring methylene protons). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.13; H, 4.32; N, 8.55.

7-*anti*-Vinyl-7-*syn*-hydroxybicyclo[2.2.1]hept-2-ene (17a) and 7-*syn*-vinyl-7-*anti*-hydroxybicyclo[2.2.1]hept-2-ene (18a) were preparedas a mixture of isomers by the vinyllithium reduction of bicyclo[2.2.1]hept-2-en-7-one: bp 70–120° (20 mm); yield 58%. The mixture contained 75% **17a** and 25% **18a** which were separated by preparative glc on a 30 ft × $^3/_8$ in. metal column packed with 30% Carbowax 20M on 30–60 Chromosorb W at 145° with helium carrier gas flow of 120 ml/min. The anti-OH isomer **18a** had shorter retention time and was collected as a colorless liquid and **17a** was a white solid: mp 55–57°; nmr **17a**: δ 6.25, ∼6.05, 5.98, and 5.82 (s, 1 H, single vinyl), 6.05 (t, 2 H, 2 ring vinyl protons, J = 2 Hz), 5.53 (d), 5.22 (t), 5.02 (d, 2 H, terminal vinyl CH_2), 2.90 (s, 1 H, hydroxyl), 2.52 (m, 2 H, 2 bridgehead protons), 1.95 → 1.60 and 1.10 → 0.75 (m, each 2 H, ring methylene protons). Nmr **18a**: δ 6.62, 6.45, 6.34, and 6.15 (s, 1 H, single vinyl), 6.02 (t, 2 H, 2 ring vinyl protons, J = 2 Hz), 5.42, 5.20, and 5.00 (d, 2 H, terminal vinyl CH_2), 2.50 (m, 2 H, 2 bridgehead protons), 2.30 (s, 1 H, hydroxyl), 2.30 → 1.90 and 1.20 → 0.85 (m, each 2 H, 4 ring methylene protons).

7-*anti*-Vinylbicyclo[2.2.1]hept-2-enyl 7-*syn*-3,5-Dinitrobenzoate (17b): mp 129–130°; nmr δ 9.10 (s, 3 H, aromatic), 6.55, 6.37, 6.25, and ∼6.10 (s, 1 H, single vinyl), 6.10 (t, 2 H, 2 ring vinyl protons, J = 2 Hz); 5.63 and 5.48 (d), 5.32 (m, 2 H, terminal vinyl CH), 3.45 (m, 2 H, 2 bridgehead protons), 2.05 → 1.67 and 1.27 → 0.95 (m, each 2 H, 4 ring methylene protons). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.25; H, 4.38; N, 8.39.

7-*syn*-Vinylbicyclo[2.2.1]hept-2-enyl 7-*anti*-3,5-Dinitrobenzoate (18b): mp 150–151°; nmr δ 9.10 (s, 3 H, aromatic), 6.49, 6.31, 6.20, and ∼6.08 (s, 1 H, single vinyl), 6.05 (t, 2 H, 2 ring vinyl protons, J = 2 Hz), 5.45 → 5.25 and 5.10 (m, 2 H, terminal vinyl CH_2), 3.23 (m, 2 H, 2 bridgehead protons), 2.15 → 1.75 and 1.45 → 1.02 (m, each 2 H, 4 ring methylene protons). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.26; H, 4.38; N, 8.39.

2-Carbethoxymethylenebicyclo[2.2.1]hept-5-ene. Bicyclo[2.2.1]-hept-5-en-2-one, prepared by the method of Bartlett and Tate,[30] was used in the synthesis: bp 116–117 (12 mm); yield 55%; nmr δ 6.30 → 5.48 (complex, 3 H, 3 vinyl protons), 4.15 and 3.93 (d, 2 H, CH_2 of ethyl, J = 7 Hz further split J = 2 Hz), 3.25 and 3.05 (bs, each 1 H, bridgehead protons), 2.60 → 1.20 (complex, 4 H, bridge and C(3) methylene), 1.25 (t, 3 H, CH_3 of ethyl, J = 7 Hz further split, J = 2 Hz).

2-(2′-Hydroxyethylidene)bicyclo[2.2.1]hept-5-ene (16a): bp 79–81° (1.2 mm); yield 70%; nmr δ 5.95 (s, 2 H, 2 ring vinyl protons), 5.35 (m, 1 H, single vinyl proton), 3.90 (t, 2 H, $-CH_2O$, J = 7 Hz), 3.40, 3.05, and 2.90 (bs, total 2 H, bridgehead protons from the two isomers present), 3.00 (s, 1 H, hydroxyl), 2.15 and 1.65 (d, 2 H, protons at C(3), J = 15 Hz), 1.55 and 1.35 (d, 2 H, bridge protons, J = 8 Hz).

2-(2′-Ethylidenyl)bicyclo[2.2.1]hept-5-enyl 3,5-Dinitrobenzoate (16b): mp 80–81°; nmr δ 9.10 (s, 3 H, aromatic), 6.10 (m, 2 H, 2 ring vinyl protons), 5.60 (m, 1 H, single vinyl proton), 4.90 (t, (2 H, $-CH_2O$, J = 8 Hz), 3.65, 3.15, and 3.05 (bs, total 2 H, bridgehead protons from the two isomers present), 2.38 and 1.92 (d, 2 H, protons at C(3), J = 14 Hz), 1.67 and 1.47 (d, 2 H, bridge protons, J = 8 Hz). *Anal.* Calcd for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27; N, 8.48. Found: C, 58.40; H, 4.35; N, 8.40.

2-*exo*-Vinyl-2-*endo*-hydroxybicyclo[2.2.1]hept-5-ene (22) was prepared by the vinylmagnesium bromide method: bp 77–59° (15 mm); yield 65%; nmr δ 6.40 → 5.80 (complex, 3 H, 2 ring vinyl protons + single vinyl), 5.30 (d), 5.10 (t), 4.82 (d, 2 H, terminal vinyl CH_2), 2.90 → 2.52 (m, 2 H, bridgehead protons), 1.70 (s, 1 H, hydroxyl), 2.05 → 0.90 (complex, 4 H, protons at bridge and C(3)).

2-*endo*-Vinyl-2-*exo*-hydroxybicyclo[2.2.1]hept-5-ene (21) was obtained by glc separation of the products from the solvolysis of **16b**: nmr 6.40 → 5.65 (3 H, complex consisting of a multiplet at 6.10 for the endocyclic vinyl proton (2 H), and four singlets for the single vinyl proton), 5.38, 5.13, and 4.93 (d, 2 H, terminal vinyl CH_2), 3.00 and 2.66 (bs, each 1 H, the bridgehead protons), 2.30 → 1.35 (complex, 4 H, bridge protons and CH_2 β to the vinyl group).

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[30] P. D. Bartlett and B. E. Tate, *J. Amer. Chem. Soc.*, **78**, 2473 (1956).

Perfluoroaromatics. Tris(polyfluoroaryl) Carbocations

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Abstract: A series of polyfluorinated triarylmethanols has been synthesized, and the effects of fluorine substitution on the stability of carbenium ions, generated in concentrated sulfuric acid, have been evaluated. An interesting additive effect of the *o*-, *m*-, and *p*-fluoro substituents is observed. A satisfactory correlation is found between carbenium ion stability, as measured by pK_{R^+} values, and Hammett σ^+ constants for a number of para-substituted cations. The experimentally determined pK_{R^+} and pK_a values of three polyfluorinated triarylmethanols and the corresponding hydrocarbons provide a linear correlation and suggest a method for estimating one from the other.

Since the observation of the first stable, long-lived triphenylmethyl cations,[1] extensive studies have been carried out[2] on mono-, di-, and triaryl carbenium ions by ultraviolet, infrared, X-ray, and nmr techniques. Olah and coworkers[3] studied the influence of substitution of heteroatoms such as fluorine on the stability of carbenium ions. They observed that, in contrast to

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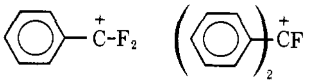
[1] F. Kehrmann and F. Wentzel, *Chem. Ber.*, **34**, 3815 (1901); **35**, 622 (1902).

[2] For an extensive review, see G. A. Olah, *Science*, **168**, 1298 (1970).

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

the hydrocarbon cations, the heteroatom-substituted ions are strongly stabilized by electron donation from the unshared electron pairs of the heteroatoms adjacent to the cationic carbon center. Thus, in phenyldifluorocarbenium ion and diphenylfluorocarbenium ion, it is suggested that fluorine is particularly effective in stabiliz-



ing the ions *via* back-coordination of its unshared electron pairs into the vacant p orbital of the methyl carbon. Since such direct overlap between the vacant p orbital of methyl carbon and the unshared electron pairs of fluorine substituted on the phenyl rings is not possible, it was of considerable interest to study the effect of substituents in a series of selected symmetrically fluorinated carbinols. The measurement of pK_{R^+} values for the carbinols provides a reliable measure of the stability of carbenium ions. In our earlier work[4] on tris(4-fluorophenyl)carbinol, we observed that the corresponding cation, generated in sulfuric acid solution, was more stable than triphenylmethyl cation. It was also noted that the cation derived from tris(pentafluorophenyl)carbinol was very unstable in sulfuric acid relative to trityl cation. These observations were interpreted in the terms of the competitive effectiveness of resonance stabilization *vs.* the overall polar effect or inductive destabilization. The presence of similar competing effects was also indicated in the simultaneously published studies of Olah and Comisarow.[5] One of the objectives of this work was to gain a better understanding of the contribution of each of these factors to the stability of the cations.

The pK_{R^+} values of triarylmethanols were determined according to the method suggested by Deno, *et al.*[6,7] We have used the general acidity function, H_R, determined by these authors from the study of the dependence of the positions of alcohol–carbenium ion equilibria on sulfuric acid concentration. The H_R value at the point of half-protonation represents the pK_{R^+} value for the triarylmethanol. The concentration of cations is determined spectroscopically.

Experimental Section

The preparation of tris(4-fluorophenyl)methanol and tris(pentafluorophenyl)methanol has been reported.[4] The routes to the other carbinols are summarized below. The details have been described elsewhere.[8a,b]

Tris(3,5-difluorophenyl)methanol. Freshly distilled diethyl carbonate in anhydrous ether was added dropwise to a Grignard reagent formed from 3,5-difluoroiodobenzene and magnesium turnings in a minimum amount of ether. After the mixture was refluxed for 2 hr, the solvent was replaced by benzene and the mixture refluxed for an additional 6 hr in order to drive the reaction to completion. The mixture was then hydrolyzed with a saturated solution of ammonium chloride, extracted with ether, and dried over anhydrous magnesium sulfate. A yellow oil, sparingly soluble in *n*-hexane, was chromatographed on an acidic aluminum oxide column which was eluted successively by hexane and benzene.

The benzene eluate gave crude carbinol (30%), which was repeatedly recrystallized to give pure carbinol, mp 93–95°. *Anal.* Calcd for $C_{19}H_{10}F_6O$: C, 61.96; H, 2.73; F, 30.95. Found: C, 62.34; H, 2.82; F, 30.49.

Tris(2,6-difluorophenyl)methanol. Diethyl carbonate in anhydrous ether was added to the mixture of *m*-difluorobenzene and *n*-butyllithium at −70°. When reaction was complete, the mixture was hydrolyzed with 10% hydrochloric acid and extracted with ether. On removal of the solvent, a yellow oil was obtained which was chromatographed on an acidic aluminum oxide column. Repeated chromatography and recrystallizations gave pure carbinol, mp 95–96°. *Anal.* Calcd for $C_{19}H_{10}F_6O$: C, 61.96; H, 2.73; F, 30.95. Found: C, 62.19; H, 2.81; F, 30.78.

Tris(para-substituted tetrafluorophenyl)methanols were synthesized by treating *para*-substituted tetrafluorophenyllithium with the corresponding ethyl (para-substituted)tetrafluorobenzoate (method A) in ether at −25° or by the reaction of 3 equiv of para-substituted tetrafluorophenyllithium with 1 equiv of diethyl carbonate (method B). Two representative procedures are described below.

Method A. Ethyl 4-Methyl-2,3,5,6-tetrafluorobenzoate. 4-Methyl-2,3,5,6-tetrafluorobenzoic acid was prepared according to the procedure described by Tamborski and Soloski[9] by carbonation of 4-methyl-2,3,5,6-tetrafluorophenyllithium. The acid was then added to absolute ethanol containing concentrated sulfuric acid (5% by volume) and heated under reflux for 24 hr. The reaction mixture was cooled, poured into water, and extracted with ether. The ether layer was washed with 5% sodium bicarbonate solution and dried over sodium sulfate. Removal of ether gave a 75% yield of crude ethyl 4-methyl-2,3,5,6-tetrafluorobenzoate, which was used in the next step without further purification.

Tris(4-methyltetrafluorophenyl)methanol. To the solution of 30.5 mmol of 2,3,5,6-tetrafluorotoluene in 100 ml of ether at −70° was added dropwise 30.5 mmol of *n*-butyllithium in hexane, under an atmosphere of nitrogen. The mixture was stirred for 2 hr. After 15.2 mmol of ethyl 4-methyltetrafluorobenzoate was added, the temperature was allowed to warm to −25° and maintained at that temperature for 3 hr. The reaction mixture was allowed to warm to room temperature and then hydrolyzed with 100 ml of 6 *N* hydrochloric acid. The mixture was extracted with ether, washed with saturated sodium chloride, and dried over anhydrous sodium sulfate. On removal of ether, a yellow oil, which was completely soluble in *n*-hexane, was obtained. After freezing the *n*-hexane solution, filtration, and washing the white precipitate with ice cold *n*-hexane, 3.2 g (40%) of tris(4-methyltetrafluorophenyl)methanol, mp 119–120°, was obtained. *Anal.* Calcd for $C_{22}H_{10}F_{12}O$: C, 50.98; H, 1.94. Found: C, 50.92; H, 2.13.

Method B. Tris(4-trifluoromethyltetrafluorophenyl)methanol. The solution of 23.0 mmol of 4-trifluoromethyl-2,3,5,6-tetrafluorobenzene[9] in 100 ml of ether was stirred under an atmosphere of nitrogen for 2 hr after dropwise addition of *n*-butyllithium at −70°. About 7.7 mmol of freshly distilled diethyl carbonate was added to the mixture which was allowed to warm to −25° (CCl_4–Dry Ice). The mixture was maintained at that temperature for 3 hr, allowed to warm to room temperature, hydrolyzed with 100 ml of 6 *N* hydrochloric acid, and extracted with ether. The ether layer was washed with a saturated solution of sodium chloride and dried over sodium sulfate. Removal of ether left a yellow oil which crystallized on addition of *n*-hexane. Recrystallization from ether–hexane gave a 67% yield of tris(4-trifluoromethyltetrafluorophenyl)methanol, mp 122–123°. *Anal.* Calcd for $C_{22}HF_{22}O$: C, 38.84; H, 0.15. Found: C, 39.2; H, 0.29.

Tris(4-methoxytetrafluorophenyl)methanol was prepared by method A, mp 94–96°, 53%. *Anal.* Calcd for $C_{22}H_{10}F_{12}O_4$: C, 46.66; H, 1.78. Found: C, 46.68; H, 1.78.

Tris(pentafluorophenyl)methanol. This compound has been prepared previously.[4] Method B also gave a satisfactory yield (51%).

Tris(2,3,5,6-tetrafluorophenyl)methanol. Some difficulty was encountered in the synthesis of this compound. In order to obtain this compound, 4-bromo-2,3,5,6-tetrafluorophenylhydrazine was prepared, according to the method of Tamborski and Soloski.[9] The hydrazine was oxidized with copper sulfate[10] to 2,3,5,6-tetrafluorobromobenzene, which was then treated with *n*-butyllithium and subsequently with freshly distilled diethyl carbonate. On hydrolysis of the mixture, a yellow oil was obtained which was in-

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[4] R. Filler, C. S. Wang, M. A. McKinney, and F. N. Miller, *J. Amer. Chem. Soc.*, **89**, 1026 (1967).

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

[6] N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *ibid.*, 77, 3044 (1955).

[7] N. C. Deno and A. Schriesheim, *ibid.*, 77, 3051 (1955).

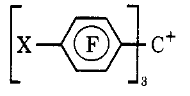
[8] (a) R. Schure, Ph.D. Thesis, Illinois Institute of Technology, 1967; (b) S. V. Kulkarni, Ph.D. Thesis, Illinois Institute of Technology, 1969.

[9] C. Tamborski and E. J. Soloski, *J. Org. Chem.*, **31**, 746 (1966).

[10] J. M. Birchall, R. N. Haszeldine, and A. R. Parkinson, *J. Chem. Soc.*, 4966 (1962).

soluble in *n*-hexane. The mixture was passed through a column containing acidic aluminum oxide and eluted successively with hexane and benzene. A low yield (3%) of the alcohol, mp 118–120°, was obtained. *Anal.* Calcd for $C_{19}H_4F_{12}O$: C, 47.92; H, 0.85. Found: C, 47.49; H, 0.96. Further elution of the column with diethyl ether gave 2 g of an alcohol (identified by its infrared spectrum), melting in the range 120–148°, whose structure was not determined.

Spectroscopic Measurements. The visible spectra of the carbenium ions were obtained on a Cary-14 recording spectrophotometer with a stoppered quartz cell of 10-cm path length. All the spectra were measured against a reference of the same solvent as used in the sample cell. The temperature in all cases was maintained at 25 ± 2°. Owing to the relative instability of the cations in concentrated sulfuric acid, all the extinction coefficients (ϵ) were obtained in 30% oleum by measuring the optical density at the absorption maxima for the cations. It was noticed that, with the exception of tris(4-methoxytetrafluorophenyl)methyl cation, all the other cations were more stable in 30% oleum and afforded a fairly accurate determination of extinction coefficients.



The different concentrations of sulfuric acid used in these experiments were determined by titrating weighed samples of the acid with standard 1 *N* sodium hydroxide solution.

In a typical experiment, the alcohol was dissolved in glacial acetic acid to give a concentration of about 1 mg/ml. Solutions of known concentration of the alcohol for spectroscopic measurements were prepared by adding 50-μl aliquots of the stock solution to 50 ml of sulfuric acid of desired concentration. The sample was immediately transferred to the cell and the spectrum of the cation recorded. Replicate measurements of optical density using the same stock solution and the same concentration of sulfuric acid were precise to better than 0.01 absorbance unit in all cases.

The pK_{R^+} values for the polyfluorinated methanols were obtained by determining the optical densities of the cations at the time of mixing at several concentrations of sulfuric acid at 25 ± 2°, and by plotting log Q (where $Q = [C_{R^+}]/[C_{ROH}]$) against the acidity function H_R. Experimentally measured values of pK_{R^+} for various cations are given in Table I.

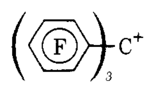
Table I. pK_{R^+} Values of Fluorinated Trityl Cations

Cation	pK_{R^+}	Ref
Triphenylmethyl	−6.63	7, this work
Tris(4-fluorophenyl)methyl	−6.05	4, this work
Tris(2,6-difluorophenyl)methyl	−11.12	This work
Tris(3,5-difluorophenyl)methyl	−14.2	This work
Tris(3-fluorophenyl)methyl	−10.72	This work, 13
Tris(pentafluorophenyl)methyl	−17.7	This work, 4
Tris(4-methyltetrafluorophenyl)-methyl	−14.3	This work
Tris(4-methoxytetrafluorophenyl)-methyl	−11.3	This work
Tris(4-hydrotetrafluorophenyl)-methyl	−17.1	This work
Tris(4-trifluoromethyltetrafluoro-phenyl)methyl	*ca.* −25.8	This work[a]

[a] Extrapolated value; see Discussion.

Results and Discussion

Filler, *et al.*,[4] observed the formation of tris(pentafluorophenyl)methyl cation (**1**) by dissolving tris(pentafluorophenyl)methanol in 100% sulfuric acid. The visible spectrum of the cation solution exhibited very strong absorption, $\lambda_{\text{mxa}}^{\text{H}_2\text{SO}_4}$ 500 nm (log ϵ 4.63). Although the cation is not very stable (half-life of *ca.* 2 min), the pK_{R^+} of the alcohol was estimated to be −17.7, with half-protonation in 93% sulfuric acid. In 100% sulfuric acid or in 30% oleum, only one band (507 nm) is observed, which is attributed to **1**. Figure 1 shows the visible spectra of tris(pentafluorophenyl)-methanol in varying concentrations of sulfuric acid. As the concentration of sulfuric acid decreases, a second band, which is absent in the unprotonated alcohol, appears at shorter wavelength (400 nm). We ascribe the development of this new absorption to the formation of the quinone dimethane (perfluorofuchsone) **2**. In the case of all other (including halogen-substituted) triarylmethanols, the corresponding cations generated in strong acid revert back to the alcohols on addition of water. However, the red-violet colored cation **1**, generated in 100% sulfuric acid, was found to undergo a gradual irreversible transformation on addition of water, as reported earlier by Soviet workers.[11] This reaction is accompanied by elimination of fluoride ion. On the basis of elemental analysis, infrared and visible spectra, and the chemical reactions of the yellow product, Gerasimova, *et al.*,[11] concluded that the material was perfluorofuchsone (**2**). In the studies of the preparations of various substituted fuchsones, Becker[12] observed a common strong absorption band for these species near 400 nm. This band corresponds very well with the secondary peak observed in Figure 1. Moreover, Figure 1 indicates that the intensity of the 400-nm band increases with increasing dilution of sulfuric acid. A proposed mechanism for this transformation is shown in Scheme I.



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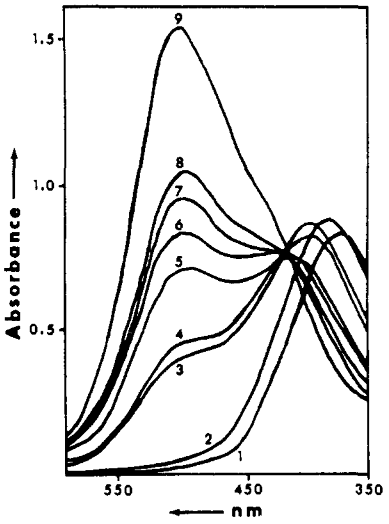

Figure 1. Visible spectra of tris(pentafluorophenyl)methanol in various concentrations of sulfuric acid at equilibrium: 1, 74.73%; 2, 85.07%; 3, 92.18%, 4, 92.8%; 5, 94.72%; 6, 95.53%; 7, 96.59%; 8, 97.22%; 9, 100.55%.

As mentioned before, no hypsochromic shifts or the development of secondary peaks were observed for the other fluorinated methanols. The rationale that only tris(pentafluorophenyl)methyl cation undergoes this transformation is based on three competing factors: *viz.* (a) the presence of a powerful electron acceptor like fluorine in the para position increases the positive

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(11) T. N. Gerasimova, E. G. Lokshina, V. A. Barkhash, and N. N. Vorozhtsov, Jr., *Zh. Obshch. Khim.*, 37, 1296 (1967).

(12) H. Dieter Becker, *J. Org. Chem.*, 32, 2943 (1967).

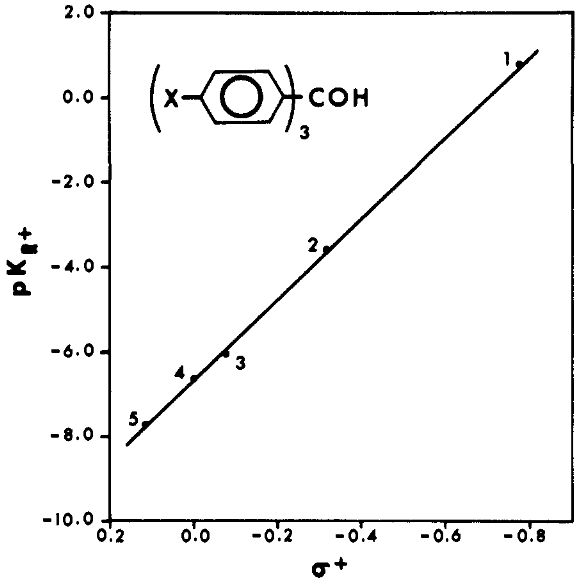
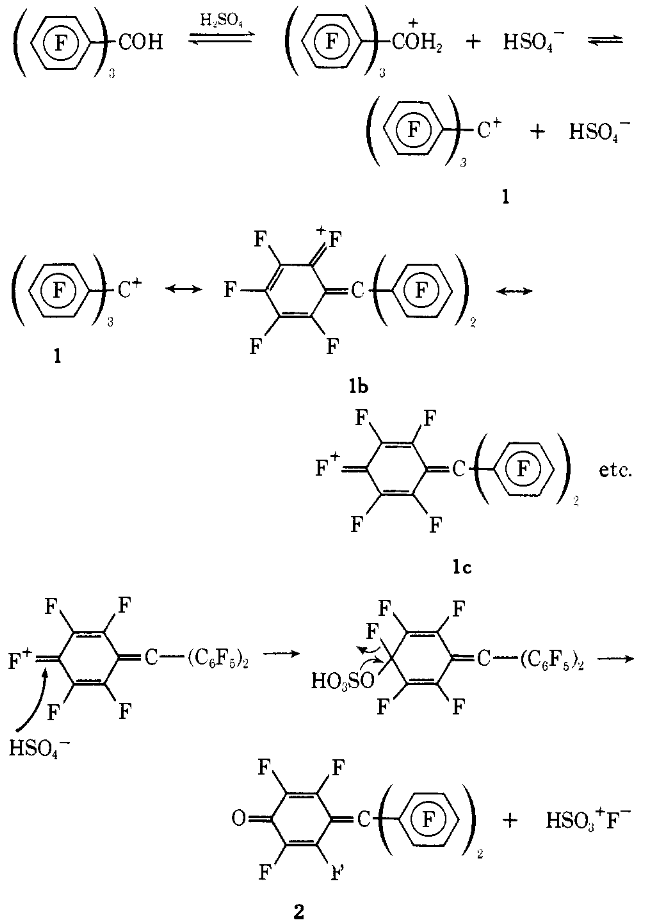


Figure 2. Plot of pK_{R^+} values *vs.* σ^+ constants for tris(4-substituted phenyl)methanols. X = (1), OCH_3, (2), CH_3, (3), F, (4), H, (5), Cl.

Scheme I



charge at C-4, thus facilitating nucleophilic attack at that position; (b) the instability of the cation **1**; and (c) steric considerations which prevent the attack of the nucleophile on the methyl or ortho carbons.

When tris(4-methoxytetrafluorophenyl)methanol was dissolved in concentrated sulfuric acid, a deep violet color developed immediately, in contrast to the red color of the other cations. The rate of decomposition of this methoxy-substituted cation was slower in 100% sulfuric acid than in 30% oleum. The enhanced stability of the cation in 100% sulfuric acid and the rapid rate of decomposition in 30% oleum suggest that the methoxy group is also protonated at the higher acid concentration. A time scan at the absorption maximum (588 nm) at both acid concentrations and extrapolation to the time of mixing gave the same value (log ϵ 4.90), indicating that at both acid concentrations alcohol is completely converted to the corresponding cation. The spectral data for the several tris(4-substituted tetrafluorophenyl)methanols is given in Table II.

Table II. Spectral Data for Tris(4-Substituted tetrafluorophenyl)methyl Cations

4-Substituent	λ_{max}, nm	Log ϵ
$—OCH_3$	588	4.90
$—CH_3$	511	4.80
—H	488	4.74
—F	507	4.61
$—CF_3$	487	4.61

Deno, *et al.*,[7] attempted to correlate pK_{R^+} values of a series of substituted triphenylmethyl cations with appropriate Hammett σ constants. They observed such a correlation for only four triarylmethanols, *viz.*, triphenyl-, tris(3-methylphenyl)-, tris(3-chlorophenyl)-, and tris(4-nitrophenyl)methanol. There was poor correlation with other ring substituents. The common feature of the four compounds which showed a correlation is the lack of a substituent which can carry a positive charge.[7]

In our earlier work,[4] we observed that tris(4-fluorophenyl)methyl cation is more stable than triphenylmethyl cation. The inductive effect of the para fluorine should destabilize the ion, while the resonance contribution, due to p–π back-bonding from the lone pairs on fluorine, would significantly stabilize the cation. Comparison of the pK_{R^+} values of tris(4-fluorophenyl)methanol (−6.05) and triphenylmethanol (−6.63) indicates that resonance stabilization somewhat outweighs the inductive destabilization. This rationale led us to attempt a correlation between observed pK_{R^+} values and σ^+ constants. Figure 2 depicts the linear relationship obtained for a series of tris(4-substituted phenyl)methyl cations, with the correlation equation

$$pK_{R^+} = -9.58\sigma^+ - 6.63 \qquad (1)$$

According to previous studies,[13a] the σ^+ value for the dimethylamino group is −1.7. By using this value and eq 1, we calculate pK_{R^+} of tris(4-dimethylaminophenyl)methanol to be 9.66 units, compared with the experimentally determined value of 9.36.[7]

Assuming that all the three aryl rings contribute equally to the delocalization of the positive charge in these symmetrically substituted triarylmethyl cations, the equation may be reduced to a form

$$pK_{R^+} = -3.19n\sigma^+ - 6.63 \qquad (\text{where } n = 0, 1, 2, \text{ or } 3) \quad (2)$$

In the case of the triarylmethyl cations with one or two

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(13) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962: (a) p 90; (b) p 101.

phenyl rings substituted in the para position, eq 2 may be used with the appropriate value of *n*. For example, the pK_{R^+} of tris(4-methylphenyl)methanol is calculated to be −3.65, with an experimentally determined pK_{R^+} of −3.56. For 4-methyltriphenylmethanol ($n = 1$), the calculated pK_{R^+} is −5.64 compared with the experimental value of −5.24. Considering that we have neglected the additional effects that may be introduced by the loss of symmetry in the cation, the concordance is fairly good. Good agreement between calculated and experimental values was also found for 4-methoxy-, 4,4′-dimethoxy-, and 4,4′,4′′-trimethoxytriphenylmethanols. The *p*-nitro group, as well as other substituents with electron-withdrawing properties due to resonance, is not expected to be governed by this correlation.[14]

Additivity Relations in Fluorinated Trityl Cations. During their studies on the conformational equilibria and interconversion of triphenylcarbenium ions, Colter, *et al.*,[15] obtained pK_{R^+} values for 3-fluoro-, 3,3′-difluoro, 3,3′,3′′-trifluoro-, 4-fluoro-, 4,4′-difluoro-, and 4,4′,4′′-trifluorotriphenylmethanols. These workers calculated pK_{R^+} values by using a modified equation of Yukawa and Tsuna. The calculated and experimentally determined values were in excellent agreement. From ^{19}F magnetic resonance studies,[15] it was observed that progressive para fluorine substitution was accompanied by a constant upfield shift, whereas progressive meta fluorine substitution caused a nearly constant downfield shift. The effect of progressive addition of para fluorine on the pK_{R^+} values of the cations is very nearly additive. It was concluded that substitution of one fluorine atom for hydrogen in the para position in triphenylmethyl cation stabilizes the cation by approximately 0.16 pK_{R^+} unit. On the other hand, substitution of a fluorine atom in the meta position was estimated to destabilize the cation by 1.32 pK_{R^+} units. On this basis, the calculated pK_{R^+} for tris(3,5-difluorophenyl)methanol is $[-6.63 + 6(-1.32)] = -14.55$, in close agreement with our experimentally determined value of −14.2.

Unfortunately, reliable estimates of the substituent constants for ortho substituents in a similar system are not available. Moreover, Martin and Smith[16] have presented compelling experimental evidence to indicate the important role of steric effects on the pK_{R^+} values of triarylmethanols. Although it may be difficult to evaluate the effect of progressive addition of ortho fluorine atoms on the stability of triphenylmethyl cations, it is possible to single out the effect of six ortho fluorine substituents in tris(2,6-difluorophenyl)methyl cation by comparing its pK_{R^+} value with that of unsubstituted triphenylmethyl cation. The overall influence of the six ortho fluorine atoms, including steric, resonance, and polar effects, appears to be one of destabilization, to the extent of −4.49 pK_{R^+} units.

If we consider the combined stabilizing effect of three para fluorine atoms ($-6.05 + 6.63 = 0.58$ pK_{R^+} units), the destabilizing effects of six meta fluorine atoms ($-14.2 + 6.63 = -7.57$ pK_{R^+} units), and the destabilizing effect of six ortho fluorine atoms ($-11.12 + 6.63 = -4.49$ units), we can estimate the pK_{R^+} value of tris(pentafluorophenyl)methyl cation to be $0.58 - 7.57 - 4.49 - 6.63 = -18.11$, in quite good agreement with the experimentally determined value of −17.7 for tris(pentafluorophenyl)methyl cation. The lower value observed experimentally may be due to the saturation effect.[13b] According to this argument, the two identical substituents influence a given species less than twice as much as one group. Considering the large number of fluoro substituents in tris(pentafluorophenyl)methyl cation, the agreement between estimated and observed pK_{R^+} is excellent.

The foregoing reasoning, as well as the molecular orbital calculations for the resonance stabilization energies of triarylmethyl cations, suggested by Streitwieser,[17] indicates that tris(4-hydrotetrafluorophenyl)methyl cation should be less stable than tris(pentafluorophenyl)methyl cation. However, the experimentally determined pK_{R^+} value (−17.1) of the former is contrary to this expectation. The possible deviation from the expected value for tris(4-hydrotetrafluorophenyl)methyl cation may be due to the presence of other carbinols as impurities. The yield of this alcohol, as mentioned earlier, was extremely low after a somewhat circuitous synthetic route.

Effects in Tris(polyfluoroaryl) Carbocations. The structure of triphenylmethyl cation has been studied by various physical methods such as X-ray crystallography[18] and ultraviolet,[19] infrared,[20] and nuclear magnetic resonance spectroscopy,[13] with the conclusion that the coplanar geometry required for maximum resonance stabilization is hindered by steric interactions between ortho hydrogens on neighboring rings. The best model, which embodies a compromise between the conflicting requirements of minimum steric strain and maximum resonance stabilization, is a propeller conformation. Electron spin resonance studies[21] of tris(2,6-difluorophenyl)methyl radical and triphenylmethyl radical in toluene solution indicate that there is no significant change in the spin density distribution in the phenyl rings when six ortho fluorines replace six ortho hydrogens. This conclusion was drawn by comparing the hyperfine coupling constants of meta and para protons in the esr spectra of the two radicals. Electron spin density calculations for triphenylmethyl radical by McLachlan and Hückel molecular orbital calculations are apparently quite sensitive to the angle of twist between the phenyl rings and the methyl carbon.[22] Even if we assume that there are slight changes in the conformation due to the substitution by six ortho fluorines in triphenylmethyl cation, there is no obvious reason to believe that the conformation of tris(4-substituted tetrafluorophenyl)methyl cations would vary from one substituent to another. Indeed, a reasonably good linear correlation is observed between pK_{R^+} of tris(4-substituted tetrafluorophenyl)methyl cations and

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[14] Use of eq 1 and σ^- (instead of σ^+) for p-NO$_2$ in tris(4-nitrophenyl)methyl cation gives a pK_{R^+} value of −18.8 compared with an experimentally determined value of −16.27.

[15] I. I. Schuster, A. Colter, and R. J. Kurland, *J. Amer. Chem. Soc.*, 90, 4679 (1968).

[16] J. C. Martin and R. G. Smith, *ibid.*, **86**, 2252 (1964).

[17] A. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, N. Y., 1962, p 362.

[18] A. H. Gomes de Mesquita, C. H. McGillarry, and K. Eriks, *Acta Crystallogr.*, **18**, 437 (1965).

[19] S. F. Mason and R. Grinter, "Steric Effects in Conjugated Systems," G. W. Grey, Ed., Academic Press, New York, N. Y., 1958, p 52.

[20] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, 674 (1957).

[21] S. V. Kulkarni and C. Trapp, *J. Amer. Chem. Soc.*, **91**, 191 (1969).

[22] (a) M. Karplus and G. K. Fraenkel, *J. Chem. Phys.*, **35**, 1312 (1961); (b) S. V. Kulkarni and C. Trapp, *J. Amer. Chem. Soc.* **92**, 4801 (1970).

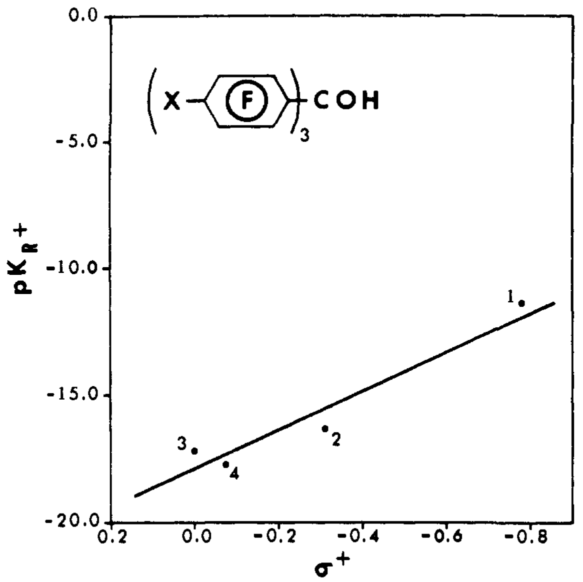

Figure 3. Plot of pK_{R^+} values *vs.* σ^+ constants for tris(4-substituted tetrafluorophenyl)methanols. X = (1), OCH_3; (2), CH_3; (3), H; (4), F.

the respective σ^+ values. (Figure 3). This approach also affords the only available method to reasonably estimate pK_{R^+} for compounds such as tris(4-trifluoromethyltetrafluorophenyl)methanol, which cannot be obtained experimentally, since the cation can only be generated in 30% oleum. This is outside of the range of H_R values, indicating that pK_{R^+} for this cation is more negative than -20. A somewhat better estimate of pK_{R^+} for this alcohol may be obtained by extrapolating to the corresponding σ^- value[13a] for the para CF_3 group (Figure 3). We may expect a correspondence similar to that for tris(4-nitrophenyl)methyl cation. The deviation from the linearity in the correlation (Figure 3) for the highly fluorinated cations is much more pronounced than that observed in Figure 2. As discussed earlier, this may be due to the saturation effect. Secondly, the overall small effect of para substituents is also overshadowed by the large destabilizing effect of six ortho and six meta substituents.

Relationship between pK_{R^+} and pK_a's. Breslow, *et al.*,[23,24] suggested an empirical method to determine pK_a values of hydrocarbons from the available pK_{R^+} values of corresponding carbinols. In the reaction sequence A the experimentally observable parameter

$$R{-}OH \underset{1}{\overset{H^+}{\rightleftharpoons}} R^+ \underset{2}{\overset{e^-}{\rightleftharpoons}} R\cdot \underset{3}{\overset{e^-}{\rightleftharpoons}} R^- \underset{4}{\overset{H^+}{\rightleftharpoons}} RH \qquad (A)$$

for step 1 is pK_{R^+} for the cation, whereas pK_a values represent step 4. In this laboratory[21,22b,25] we have been able to establish all these steps for several polyfluorotrityl hydrocarbons. From the experimentally available pK_{R^+} and pK_a[26] values for three polyfluorinated systems, *viz.* tris(4-methoxytetrafluorophenyl)methyl, tris(4-methyltetrafluorophenyl)methyl, and tris(pentafluorophenyl)methyl, a linear correlation (eq 3)

$$pK_a = 0.534pK_{R^+} + 25.35 \qquad (3)$$

is found between the pK_a's of the hydrocarbons and pK_{R^+}'s of the corresponding carbinols. In order to establish the generality of this relationship, it would be desirable to determine pK_a and pK_{R^+} for several additional pairs in the series, including the tris(4-nitrotetrafluorophenyl)methyl and tris(4-dimethylaminotetrafluorophenyl)methyl compounds.

This correlation also leads to another significant conclusion regarding the polyfluoro analogs of triphenylmethyl cations, radicals, and carbanions. As discussed earlier, our esr studies suggest that substitution of fluorine for hydrogen in the ortho positions of the aryl rings does not affect the geometry or angle of twist of the phenyl rings around the central methyl carbon. Moreover, there is no conformational change in the conversions of the cation to the radical to the carbanion, a conclusion which is consistent with the correlation discussed above.

(23) R. Breslow and K. Balasubramanian, *J. Amer. Chem. Soc.*, **91**, 5182 (1969).

(24) R. Breslow and W. Chu, *ibid.*, **92**, 2165 (1970).

(25) S. V. Kulkarni, A. E. Fiebig, and R. Filler, *Chem. Ind. (London)*, **11**, 364 (1970).

(26) R. Filler and C. S. Wang, *Chem. Commun.*, 287 (1968).