"α-effect" contribution from the breaking of the C–H$_\alpha$ bond.

Although the general trend has been noted before, this is the first example of a reaction that shifts cleanly from rate-determining attack on the tight ion pair to rate-determining formation of the solvent separated ion pair on changing from ethanol–water to TFE–W solvent. It is also the first example in which the stereochemistry of the elimination and substitution reactions from the tight and solvent separated ion pairs is observed for the same reactant. The correlation of these results with α-*d* and β-*d* effects on the rates and product ratios is very satisfying.

Experimental Section

Deuterated Cyclopentyl Brosylates. Cyclopentanol, cyclopentanol-*1-d*, *cis*-cyclopentanol-*2-d*, *trans*-cyclopentanol-*2-d*, and cyclopentanol-*2,2,5,5-d*$_4$ were prepared by previously published methods.[11,14] The deuterium contents were established by mass spectrometry and were better than 93% in all cases. The purity of alcohols was better than 98% in all cases according to glpc analysis (10% Ucon). The corresponding brosylates were prepared by the usual Tipson procedure.[12]

Kinetic Measurements. The titrimetric rates were obtained employing the automatic potentiometric titration method using the pH-Stat Radiometer, SBR-2/TTT11, Copenhagen, maintaining a constant pH of 6.8. The concentration of brosylate esters was about 0.0015 *M* (10 mg in 20 ml of solvent) in all kinetic experiments. The samples of esters titrated were taken at random in order to minimize the influence of the temperature variation, or any other variations, on the rate of solvolysis. The double jacketed titrimetric cell with solvent was allowed to stabilize 20 min at the corresponding temperature prior to addition of ester. At least eight measurements were conducted for each of the esters in the particular solvent and temperature. The rate constants were calculated from the standard integrated first-order law using a nonlinear least-squares program. No trend was observed in the rate constants between 20 and 80% of reaction completion.

The rate measurements needed to detect a possible common ion rate depression effect were performed as described above with added sodium brosylate in concentrations from 0.0025 to 0.03 *M*. Only one rate measurement for the corresponding salt concentration was taken.

The possibility of the special salt effect was tested by addition of lithium perchlorate (from 0.025 to 0.03 *M*) into the reaction mixture.

Product Study. In a typical experiment, cyclopentyl brosylate (64.4 mg) and 1 ml of 80 vol % E–W were sealed in an ampoule (2 ml) and heated at 40° for 2.7 hr (10 half-lives of the reaction). The ampoule was opened and a small quantity of sodium bicarbonate and magnesium sulfate was added in order to neutralize the acid and to remove most of the water from the solvent. After 1 hr the solution was injected into the gas chromatograph (Varian 1800) equipped with a digital integrator (Varian 480). The column was 10 ft long with 10% Ucon on Chromosorb P 45/60. The temperature was changing from 70 (3.3 min) to 110° (20° per min). Peak areas obtained were multiplied by the correction number calculated from the chromatogram of the mixture containing known quantities of pure samples of each product.

The product study of each compound in a particular solvent was conducted in two ampoules in an identical way. From each sample at least three injections into a gas chromatograph were performed giving a total of six injections for each of the compounds in a particular solvent.

The products were proven to be stable under the solvolytic conditions as well as on the glpc column. Samples of the separate pure products with an adequate quantity of *p*-bromobenzoic acid added were treated in the same way as samples in the product study. The gas chromatogram revealed in all cases only the compound tested.

Nmr Study. In a typical experiment, *cis*-cyclopentyl-2-*d* brosylate (3 g) was solvolyzed for 3.3 hr (10 half-lives) in 50 ml of 70 wt % TFE–W mixture at 30°. After 3.3 hr (10 half-lives) the resulting acid was neutralized ($NaHCO_3$) and dried ($MgSO_4$). Cyclopentanol-*2-d* was separated from the mixture by means of glpc (Autoprep A-700) at 170° using a 20-ft column with 20% Carbowax 20 M on Chromosorb P 60/80. By repeating the separation procedure twice, 200 mg of 99.8% pure product was obtained. Cyclopentanol-*2-d* ($\sim$6 mg) was added into the nmr tube containing 0.4 ml of CCl_4 and $\sim$14 mg of tris(dipivalomethanato)praseodymium(III) complex. The spectra were recorded on a JEOL 100-MHz nmr spectrometer.

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Fluorine Magnetic Resonance Spectra of Some *p*-Fluorophenylcarbonium Ions. A Possible Solvation Entropy Effect[1]

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Abstract: The fluorine magnetic resonance spectra of a number of tertiary *p*-fluorophenylcarbonium ions have been determined. The chemical shifts fall into three main groups: acyclic at lowest field, monocyclic at intermediate field, and bicyclic at highest field. The total range is 8 ppm, representing about 6 kcal energy difference. A possible interpretation in terms of steric restriction of rotation by solvation is discussed.

In earlier papers we presented some evidence in support of the intuitively reasonable proposal that the para proton nuclear magnetic resonance chemical shift of phenylcarbonium ions (**1**) could serve as a measure of the π-electron demands of the carbonium ion center.[2] Although a linear correlation of the chemical shift values with the log of the calculated delocalization energies was observed over a range of carbonium ion stabilities, the chemical shift was too insensitive to energy differences to be useful (in the

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(1) This work was supported by the National Science Foundation under Grant GP 10734.

(2) D. G. Farnum, *J. Amer. Chem. Soc.*, **86**, 934 (1964); **89**, 2970 (1967).

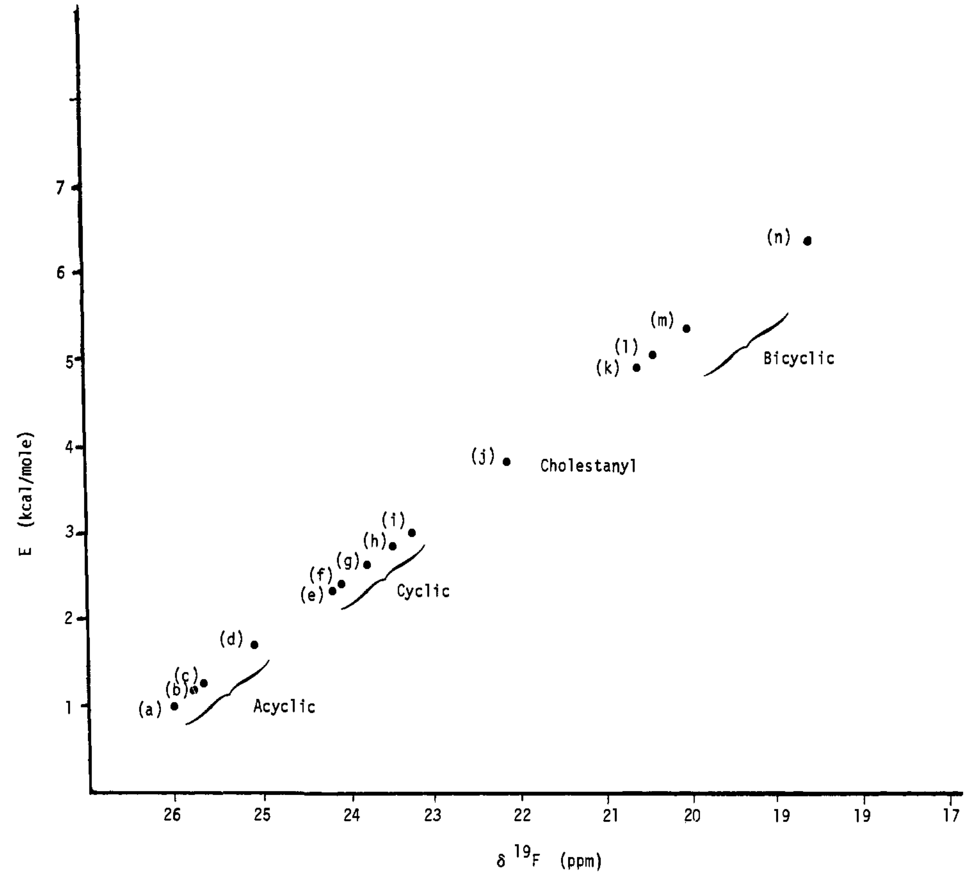
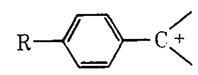


Figure 1. A display of ^{19}F chemical shifts of a number of tertiary *p*-fluorophenylcarbonium ions on a line of slope 0.75 kcal/ppm. Chemical shifts are determined as δ ^{19}F in ppm downfield from tris-*p*-fluorophenylcarbonium ion. Carbonium ions $R_1R_2C^+C_6H_4F$ plotted are as follows (R_1, R_2 given): (a) diethyl, (b) methyl, ethyl, (c) dimethyl, (d) methyl, isopropyl. Monocyclic ions $R_c{}^+C_6H_4F$ are as follows: (e) *trans*-2,5-dimethylcyclopentyl, (f) 2-methylcyclopentyl, (g) 2-methylcyclohexyl, (h) cyclohexyl, (i) cyclopentyl and *trans*-2,5-dimethylcyclohexyl. Polycyclic ions are as follows: (j) 3-cholestanyl, (k) 6-bicyclo[3.2.1]octyl, (l) 2-bicyclo[2.2.2]octyl, (m) 2-adamantyl, (n) 2-norbornyl.

neighborhood of 1 ppm/100 kcal[3]). Therefore, we decided to explore the applicability of Taft's ^{19}F chemical shift correlation[4] for some *p*-fluorophenylcarbonium ions (**2**) in view of its orders of magnitude greater sensitivity to electron demands (1 ppm/0.75 kcal), and comparative insensitivity to magnetic anisotropies of the solvent and molecule.



1, R = H
2, R = F

Table I. ^{19}F Chemical Shifts of Some *p*-Fluorophenylcarbonium Ions in Fluorosulfonic Acid at −30°

Carbonium ion	^{19}F chemical shift[a]
Acyclic: $R_1R_2C^+C_6H_4F$	
(a) $R_1 = R_2 = C_2H_5$	26.0
(b) $R_1 = CH_3$; $R_2 = C_2H_5$	25.8
(c) $R_1 = R_2 = CH_3$	25.7
(d) $R_1 = CH_3$; $R_2 = i\text{-}C_3H_7$	25.1
Monocyclic: $R_c{}^+C_6H_4F^b$	
(e) R_c = *trans*-2,5-dimethylcyclopentyl	24.2
(f) R_c = 2-methylcyclopentyl	24.1
(g) R_c = 2-methylcyclohexyl	23.8
(h) R_c = cyclohexyl	23.5
(i) R_c = cyclopentyl and *trans*-2,5-dimethylcyclohexyl	23.3
Polycyclic:	
(j) 3-Cholestanyl	22.2
(k) 6-Bicyclo[3.2.1]octyl	20.7
(l) 2-Bicyclo[2.2.2]octyl	20.5
(m) 2-Adamantyl	20.1
(n) 2-Norbornyl	18.7

[a] Ppm downfield from tris-*p*-fluorophenylcarbonium ion. [b] R_c = cyclic alkyl group.

Results and Discussion

The ^{19}F chemical shifts were determined for solutions of the carbonium ions in fluorosulfonic acid at −30° prepared from the carbinols or olefins. The chemical shift data are tabulated in Table I, and displayed in Figure 1 as a function of stabilization energy by placing the points on a line of slope 1 ppm/0.75 kcal. Note that the energies of these carbonium ions were not determined, but are simply assumed for the purposes of the display. There is also no reason to suppose that the linearity observed by Taft for the several triarylcarbonium ions[4] will survive the long extrapolation (18–26 ppm downfield) to cover our carbonium ions. In fact, the linearities which we obtained for para proton chemical shifts, and Taft obtains for ^{19}F chemical shifts, are probably the fortuitous result of observing the central region of an "s"-shaped curve, since the

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(3) D. G. Farnum and G. Mehta, *J. Amer. Chem. Soc.*, **91**, 3256 (1969).
(4) R. W. Taft and L. D. McKeever, *ibid.*, **87**, 2488 (1965).

chemical shifts should asymptotically approach a limiting low field value for an unstabilized carbonium ion, and a limiting high field value for a carbonium ion in which the charge is completely dispersed and makes no demands on the π electrons of the benzene ring. In spite of these limitations, we still use Figure 1 as a convenient means of displaying the data and as a way of suggesting the order of magnitude of the energy differences which might exist among these carbonium ions. Using the slope of Taft's plot (1 ppm/0.75 kcal) the energy spread is 6 kcal, while the chemical shift spread is an easily detected 7-8 ppm.

The carbonium ions were chosen to represent a range of structural types including acyclic, cyclic, and bicyclic, with varying degrees of alkyl substitution on the acyclic and cyclic ones. We were limited, however, to tertiary carbonium ions since less substituted ones did not survive in fluorosulfonic acid at the temperatures used. From Figure 1 it is immediately evident that the ^{19}F chemical shifts of the ions fall into three main groups. The acyclic systems cluster around 22.5 ± 0.5 ppm downfield from the standard (tris-*p*-fluorophenylcarbonium ion), the cyclic systems cluster around 23.75 ± 0.5 ppm, and the bicyclic ones over a wider range around 18.5-21 ppm.

Although steric and inductive effects may influence the ^{19}F chemical shifts (indeed, probably do), they cannot be the main structural features which result in the observed grouping of chemical shifts, since there is no correlation between extent of alkyl substitution and chemical shift. However, there is a gross correlation of chemical shifts with rigidity of the molecule, the most rigid, bicyclic systems appearing at highest field, and the least rigid, acyclic ones at lowest field. This qualitative correlation also holds well within the bicyclic ions, which seem to follow the expected order, the most rigid norbornyl at highest field, and the least rigid bicyclooctyl at lowest field. Furthermore, when this idea was tested with the 3-*p*-fluorophenylcholestanyl cation, of rigidity intermediate between the bicyclic and monocyclic ions, the cation chemical shift fell at a nicely intermediate point at 22.2 ppm.

Although the range of chemical shifts is small in terms of energy differences, and the number of examples limited, the structural correlation seems dramatic enough to warrant an attempted rationalization. We suggest that the results displayed in Figure 1 are easily explained as a solvation entropy effect. Thus, coordination of a cation with solvent molecules would result in restriction of rotation in a freely rotating, acyclic cation, giving a negative entropy effect. It would not cost as much to solvate an already restricted cyclic cation, and would cost still less to solvate a rigid bicyclic cation. Therefore the more rigid, more highly solvated cations would make less electron demands on the fluorophenyl substituents, which would result in less downfield shift of the fluorine, as observed. The energy spread of some 6 kcal (if the Taft correlation is extrapolated) is also reasonable for solvation entropy effects.[5]

The very high field position of the norbornyl system deserves comment because of the special nature of this system. It is unlikely that there is any nonclassical participation in the fluorophenylnorbornyl cation[3,6,7] since proton nmr,[3,6,7] ^{13}C nmr,[6] and laser Raman[6] spectroscopy all indicate that the 2-phenylnorbornyl cation is completely classical. Therefore, there must be some classical characteristic of the norbornyl system which results in the observed stability by comparison with other bicyclic systems. Whether this characteristic is the rigidity resulting in the suggested solvation entropy effect, or some other feature of the system, it probably also makes its contribution to the rate of solvolysis of the system as well.

Experimental Section

General. All carbonium ion precursors were characterized by their melting point or boiling point, ir, ^{19}F and ^{1}H nmr, and mass spectra. Spectroscopic data were determined on a Varian A-56-60 nmr spectrometer, a Perkin-Elmer Infracord infrared spectrophotometer, and a Perkin-Elmer Hitachi RMU-6 mass spectrometer. Melting points and boiling points are uncorrected. Carbonium ion solutions were made up to approximately 5% concentration by the addition of a solution of the carbinol or olefin precursor in Freon 114B to vigorously stirred fluorosulfonic acid at −70°. The fluorosulfonic acid layer was drawn off and used for the nmr determination. Both proton and fluorine nmr spectra were determined for the carbonium ion solutions referenced against internal tetramethylammonium fluoroborate (τ 6.87) or tris-*p*-fluorophenylcarbonium ion.[4] In all cases, the proton spectra were as expected for the carbonium ion structures.[2,3,7,8]

Preparation of the *p*-Fluorophenylcarbinols. The following general procedure was used. A 250-ml, three-necked flask equipped with two dropping funnels, one with a drying tube and the other with a septum cap, a low temperature thermometer, and provision for magnetic stirring was thoroughly flushed with nitrogen introduced *via* the septum. In the flask was placed 1.26 equiv of *p*-bromofluorobenzene and 5 ml of anhydrous ether. In the dropping funnel equipped with drying tube was placed 1.00 equiv of the ketone (usually about 5 g) dissolved in 25 ml of anhydrous ether. Into the dropping funnel equipped with a septum was introduced 1.20 equiv of 15% *n*-butyllithium in hexane *via* syringe. The *p*-bromofluorobenzene solution was cooled to −30° *via* a Dry Ice-2-propanol bath. The *n*-butyllithium solution was then added over about 5 min maintaining the reaction temperature at about −30°. The organolithium solution was then allowed to warm to 0° over 10 min and then recooled to −10°. The ketone solution was added over 5 min maintaining a reaction temperature of −10°. The resulting solution was allowed to warm to 0° over a 10-min period. The mixture was then poured onto 300 ml of cold water. Ammonium chloride (solid) was added to aid in separation of layers. The layers were separated and the aqueous phase was extracted with two 100-ml portions of ether. The combined organic extracts were washed once with 100 ml of water and once with 100 ml of saturated salt solution. The organic solution was dried over anhydrous magnesium sulfate and the drying agent was removed by filtration. The filtrate was concentrated by distillation at atmospheric pressure. The residue was either vacuum distilled or recrystallized from hexane.

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