the course or rate of reaction were noted when either potassium fluoride, rubidium fluoride, or cesium fluoride was employed as a catalyst. However, when the reaction between either $CF_3C(O)F$ or $(CF_3)_2C{=}O$ and fluorine was carried out in the complete absence of metal fluorides, no formation of the fluoroxy derivatives was observed. In fact, no reaction was noted at −78°. Although the role of the metal fluoride is not known with certainty, it is likely that an ionic intermediate such as $XYCFO^-$ is the active species involved in the fluorination. Support for this assumption was obtained by fluorination of the salt, $CsOCF_3$,[6] under similar conditions. Fluoroxytrifluoromethane was produced in quantitative yield.

Several attempts were made to extend the catalytic fluorination procedure to other carbonyl derivatives. When phosgene was allowed to react with fluorine in equimolar quantities at −78°, the following reaction was observed. Half of the phosgene initially charged

$$COCl_2 + 2F_2 \longrightarrow CF_3OF + Cl_2$$

was recovered unchanged. Fluorination of $HCF_2C(O)F$ over cesium fluoride at 0° produced an unstable material which was contaminated with small amounts of COF_2, HCF_3, and CF_4. Attempted purification of this product by vacuum line fractionation resulted in spontaneous and often violent decomposition. The ^{19}F nmr spectrum of the crude product in CF_3Cl consisted of an unresolved broad singlet at ϕ −131, an unresolved singlet at ϕ 99.9, and a doublet at ϕ 136.4, $J_{HF} = 56$ cps. The relative area ratios of the peaks are 1:2.1:1.9. This spectrum is consistent with the formulation of the product as HCF_2CF_2OF if it is assumed that coupling between the CF and OF fluorines is not observed.[7] The infrared spectrum shows no carbonyl absorptions other than trace amounts of carbonyl fluoride and has a weak band in the fluoroxy region[2] which is not present in the starting material. Due to the instability of the product no elemental analyses were obtained.[8]

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(6) M. E. Redwood and C. J. Willis, *Can. J. Chem.*, **43**, 1893 (1965).

(7) The ^{19}F nmr spectrum of C_2F_5OF consists of three groups of bands at ϕ −139.4 (OF), +97.9 (CF_2), and 82.1 (CF_3).

(8) Caution should be exercised in working with fluoroxy compounds since they are potentially dangerous.

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A Nuclear Magnetic Resonance Method for Relative Carbonium Ion Stabilization Energies

Sir:

Quantitative determination of carbonium ion stabilities is a cornerstone in the construction of a compatible structure–reactivity relationship for reactions involving cationic intermediates. In principle, a direct measure of relative carbonium ion stabilities is derived from the equilibrium amounts of a stable carbonium ion in equilibrium with its un-ionized precursor. In practice, useful data have been obtained from carbinol–carbonium ion ionization equilibrium data in strongly acidic media[1] and from the reversible electrode potential reduction method, recently developed by Taft.[2] To these pK_{R^+} and emf methods we now add a convenient nmr technique which promises to be of broad application.

When equimolar amounts of a stable carbonium ion salt (R^+Y^-) and an appropriate carbonium ion precursor (R_0X) are combined in a suitable solvent, rapid exchange of Y^- and X occurs (as shown in eq 1) to yield an equilibrated mixture in which the relative amounts of R^+ and R_0^+ are a direct measure of their free-energy difference (ΔF_0). For convenient analysis of

$$R^+Y^- + R_0X \rightleftharpoons RX + R_0^+Y^- \qquad (1)$$

the equilibrium mixture by nmr it is necessary that the maximum difference in concentration of R^+ and R_0^+ be ~19:1 ($\Delta F° \cong 3.5$ kcal) and that at least one of the components have a single, sharp resonance line, the chemical shift of which is sufficiently different in the covalent and cationic components.[3] The latter requirement is best fulfilled by a methyl or methoxyl substituent, though others (fluoro, dimethylamino, etc.) should prove equally advantageous.

The stability data obtained from (1) are substantially independent of the nonnucleophillic anion (Y^-) and we have found $SbCl_6^-$, BF_4^-, and ClO_4^- to be equally useful. However, the technique for quantitatively estimating the relative amounts of R^+ and R_0^+ depends on the nature of the group X. When the covalent component is a halide (X = Cl or Br) the expected rapid S_N1 exchange occurs between R^+Y^- and RX and between $R_0^+Y^-$ and R_0X, leading to time-averaged resonance lines whose chemical shift is proportional to the mole fraction of each component.[4] For example: mono-*p*-methyltrityl and di-*p*-methyltrityl chlorides in methylene chloride solution display their methyl protons at 139.8 and 138.3 cps[5] while the methyl protons of their respective hexachloroantimonates appear at 164.9 and 163.8 cps. An equimolar mixture of either chloride with the other carbonium ion equilibrates to give lines at 158.0 (six methyl protons) and 145.0 cps (three methyl protons). From these data it is readily calculated that the ratio of di-*p*-methyltrityl to mono-*p*-methyltrityl cations is 78 ± 1:22 ± 1 and that, therefore, $\Delta F° = 1.6 \pm 0.1$ kcal at 40°.

With carbonium ions of $pK_{R^+} > 1$, the halides are partly or completely ionized in solvents which dissolve the carbonium salts and are no longer suitable for exchange (1).[6] However, this by no means limits the utility of the nmr method since we have found that a number of covalent carbonium ion precursors readily participate in the required exchange process (1). Suitable groups (X in RX or R_0X) include methoxy, azide, acetate,

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(1) (a) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Org. Chem.*, **19**, 155 (1954); (b) N. C. Deno, J. J. Jaruzelski, and A. Schriesheim, *J. Am. Chem. Soc.*, 77, 3044 (1955); (c) N. C. Deno and A. Schriesheim, *ibid.*, 77, 3051 (1955); (d) N. C. Deno and W. L. Evans, *ibid.*, **79**, 5804 (1957).

(2) E. D. Jensen and R. W. Taft, *ibid.*, **86**, 116 (1964); R. W. Taft and L. D. McKeever, *ibid.*, 87, 2489 (1965).

(3) Identification of the components of the equilibrium mixture is best accomplished by prior assignment of the resonance lines of the individual species, or, on occasion, by low-temperature techniques.

(4) H. H. Freedman, A. E. Young, and V. R. Sandel, *J. Am. Chem. Soc.*, **86**, 4722 (1964).

(5) Downfield from internal TMS; A-60 spectrometer at 40°.

(6) An nmr investigation of the ionization of such halides is currently under investigation.

and benzoate, all of which (unlike hydride) equilibrate instantaneously in acetonitrile or methylene chloride in the presence of a carbonium ion salt to yield a thermodynamic distribution of products. In contrast to the halides, rapid exchange (on the nmr time scale) of the covalent and ionic species does not occur,[7] and, in the absence of time-averaged spectra, quantitative determination of the components may be accomplished by conventional methods of integration. The virtual equivalence of the two nmr procedures is demonstrated by the exchange between tri-*p*-*t*-butyltrityl cation and either tri-*p*-methyltrityl chloride or azide; with the time-averaged chloride, the chemical shift procedure gave $\Delta F^\circ = 0.2 \pm 0.2$ kcal, and with the azide the integration method furnished $\Delta F^\circ = 0.0 \pm 0.2$ kcal.

Procedural flexibility is one of the principal advantages of the nmr method. In determining ΔF° of an unknown (R) *vs.* a known (R_0) compound, it is feasible and even desirable to vary (within limit) the solvent, temperature, R_0 moiety, and X or Y^- in R and R_0, and to approach equilibrium from either direction. Preliminary results obtained by exploring the above variations suggest that solvent and entropy effects are minimal, in agreement with the conclusions of Taft.[2,8]

The relative stabilization energies of five different classes of carbonium ions are listed in Table I. Following Taft,[2] the free energy of the cations have all been related to unsubstituted trityl cation (eq 1, R_0 = trityl) and the symbol $\Delta F^\circ_{\mathrm{R}^+}$ is suggested for this purpose. In general, agreement among the results obtained by the nmr method and the $\mathrm{p}K_{\mathrm{R}^+}$ and emf methods is satisfactory despite the diverse nature of the techniques employed. Of particular interest is the tri-*p*-*t*-butyltrityl cation, the reported $\Delta F^\circ_{\mathrm{R}^+}$ value for which has ranged from 0.5[1b] to 2.9[9] kcal. The nmr value of 4.4 ± 0.2 kcal, obtained from three independent experiments in which the solvent, anion, and cation were varied, is more in accord with the expected electronic similarity of *p*-*t*-butyl and *p*-methyl, as revealed by their comparable σ^+ values[10] of -0.256 and -0.311, respectively. Finally, we note that the nmr method readily furnishes the $\Delta F^\circ_{\mathrm{R}^+}$ for the 1,2,3,4-tetraphenyl-2-chlorocyclobutenium cation,[11] whose hydrolytic nonreversibility[11a] precludes stability measurements by the $\mathrm{p}K_{\mathrm{R}^+}$ method.

Table I. Relative Carbonium Ion Stabilization Energies ($\Delta F^\circ_{\mathrm{R}^+}$)

Cation	$\Delta F^\circ_{\mathrm{R}^+}$, kcal/mole From nmr	From[a] $\mathrm{p}K_{\mathrm{R}^+}$	From[f] emf
Triphenylcyclopropenium	12.9	13.3[b]	...
Tri-*p*-methoxytrityl	11.3	10.2[c]	11.9
9-(*p*-Methoxyphenyl)-xanthylium	9.1	11.1[g]	8.6
Di-*p*-methoxytrityl	8.2	7.4[c]	8.6
9-Phenylxanthylium	8.0	17.5[g]	7.4
p-Methyl-*p*′-methoxytrityl	5.7	...	...
Tri-*p*-methyltrityl	4.6	4.2[c]	4.7
p-Methoxytrityl	4.5	4.4[c]	5.0
Tri-*p*-*t*-butyltrityl	4.4	0.5[c]	...
Di-*p*-methyltrityl	3.2	3.0[d]	3.3
Mono-*p*-methyltrityl	1.6	1.7,[d] 1.9[c]	1.8
Mono-*m*-methyltrityl	0.8	...	0.7
Di-*p*-methoxydiphenylmethyl	0.5	1.25[c]	...
Trityl	(0.0)	(0.0)	(0.0)
m-Methyl-*p*′-chlorotrityl	−0.2	−0.2[e]	−0.1
m-Methyl-*p*′,*p*′′-dichlorotrityl	−0.8	−0.7[e]	...
1,2,3,4-Tetraphenyl-2-chlorocyclobutenium	−1.8	...	...

[a] Calculated from reported $\mathrm{p}K_{\mathrm{R}^+}$ data, taking $\mathrm{p}K_{\mathrm{R}^+}$ for trityl = −6.6 at 25° (from ref 1b). [b] R. Breslow, J. Lockhart, and H. W. Chang, *J. Am. Chem. Soc.*, **83**, 2375 (1961). [c] Reference 1b. [d] W. N. White and C. A. Stout, *J. Org. Chem.*, **27**, 2915 (1962). [e] Estimated from σ^+ values cited in ref 10 with $\rho = -4.5$. [f] Private communication from R. W. Taft and L. D. McKeever. [g] R. A. Diffenbach, Thesis, The Pennsylvania State University, 1966.

Further extension of the nmr method for the determination of $\Delta F^\circ_{\mathrm{R}^+}$ will be given in the full paper.

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[7] Presumably exchange takes place *via* an SE2 process rather than the much more rapid SN1 exchange[4] of the halides. A preliminary report on the bimolecular exchange of carbonium ions with their benzoate precursors has been given: A. E. Young, H. H. Freedman, and V. R. Sandel, preprints of papers, 150th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1965, p 77S.

[8] At the suggestion of Professor Taft, we are currently investigating the possibility that steric factors are important in the practical application of eq 1.

[9] N. N. Lichtin and P. D. Bartlett, *J. Am. Chem. Soc.*, **73**, 5530 (1951). See also: E. Price and N. N. Lichtin, *Tetrahedron Letters*, **No. 18**, 10 (1960); N. N. Lichtin, *Progr. Phys. Org. Chem.*, **1**, 88 (1963).

[10] H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **80**, 4979 (1958).

[11] (a) H. H. Freedman and A. M. Frantz, Jr., *ibid.*, **84**, 4165 (1962); (b) R. F. Bryan, *ibid.*, **86**, 733 (1964).

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The Pentafluorophenyl–Phosphorus Ring System

Sir:

Recent interest in phenyl-substituted phosphorus ring systems has been stimulated by their structural complexity.[1] X-Ray crystallographic studies[2,3] indicate that both five- and six-membered rings are capable of existence in the crystalline state. Two apparently oligomeric forms have also been reported,[3,4] and the six-membered ring system is known to crystallize in at least four different forms.[3]

As part of a continuing interest in homocyclic group V compounds[5] we have attempted the synthesis of the corresponding pentafluorophenyl–phosphorus ring system with a view to determining its structural properties, and also because of the relative paucity of information regarding pentafluorophenyl–phosphorus derivatives in general.[6]

The new phosphinous halides $C_6F_5PBr_2$ (bp 64–65° at 1.1 mm) and $C_6F_5PI_2$ (bp 110–12° at 0.7 mm) were

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[1] For reviews see A. H. Cowley, *Chem. Rev.*, **65**, 617 (1965); and A. H. Cowley and R. P. Pinnell, "Topics in Phosphorus Chemistry, in press.

[2] J. J. Daly and L. Maier, *Nature*, **203**, 1167 (1964); **208**, 383 (1965); J. J. Daly, *J. Chem. Soc.*, 6147 (1964); 4789 (1965).

[3] L. Maier, *Helv. Chim. Acta*, **49**, 1119 (1966).

[4] W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963).

[5] A. H. Cowley and R. P. Pinnell, *Inorg. Chem.*, **5**, 1459, 1464 (1966); A. H. Cowley, A. B. Burg, and W. R. Cullen, *J. Am. Chem. Soc.*, **88**, 3179 (1966).

[6] Previous reports of C_6F_5P compounds seem confined to (a) L. A. Wall, R. E. Donadio, and W. J. Pummer, *ibid.*, **82**, 4846 (1960); (b) D. D. Magnelli, G. Tesi, J. U. Lowe, Jr., and W. E. McQuiston, *Inorg. Chem.*, **5**, 457 (1966); (c) H. G. Ang and J. M. Millar, *Chem. Ind.* (London), 944 (1966); (d) H. J. Emeléus and J. M. Millar, *J. Inorg. Nucl. Chem.*, **28**, 662 (1966).