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 $\Delta F° = 0.2 \pm 0.2$ kcal, and with the azide the integration method furnished $\Delta F° = 0.0 \pm 0.2$ kcal.

Procedural flexibility is one of the principal advantages of the nmr method. In determining $\Delta F°$ 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 $\Delta F°_{R^+}$ is suggested for this purpose.

**Table I.** Relative Carbonium Ion Stabilization Energies ($\Delta F°_{R^+}$)

| Cation | $\Delta F°_{R^+}$, kcal/mole From nmr | From[a] $pK_{R^+}$ | 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 $pK_{R^+}$ data, taking $pK_{R^+}$ 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 $\sigma^+$ 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.

(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.

In general, agreement among the results obtained by the nmr method and the $pK_{R^+}$ 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 $\Delta F°_{R^+}$ 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 $\sigma^+$ values[10] of −0.256 and −0.311, respectively. Finally, we note that the nmr method readily furnishes the $\Delta F°_{R^+}$ for the 1,2,3,4-tetraphenyl-2-chlorocyclobutenium cation,[11] whose hydrolytic nonreversibility[11a] precludes stability measurements by the $pK_{R^+}$ method.

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

**Acknowledgments.** The authors are grateful to H. J. Dauben for a sample of tri-*p*-*t*-butyltrityl fluoroborate and to R. W. Taft for providing unpublished data.

(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).

**A. E. Young, V. R. Sandel, H. H. Freedman**
*The Dow Chemical Company, Eastern Research Laboratory*
*Wayland, Massachusetts*
*Received August 4, 1966*

## 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

(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).

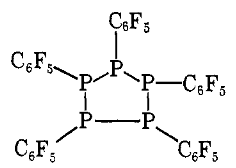
(4) W. A. Henderson, M. Epstein, and F. S. Seichter, *J. Am. Chem. Soc.*, **85**, 2462 (1963).

(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).

made by treatment of $PBr_3$ with an equimolar quantity of $C_6F_5MgBr$ and by HI cleavage of $C_6F_5P[N(CH_3)_2]_2$,[6b] respectively. Mercury acted upon $C_6F_5PBr_2$ (2-day shaking in a sealed flask at 25°) to produce a yellow oil. The reaction was completed by extraction of the oil with ether, followed by shaking with an additional portion of mercury (1 day at 25°). Isolation and evaporation of the ether solution, followed by recrystallization from 9:1 *n*-hexane–ether, resulted in a 91% yield of a white crystalline solid, mp 156–161°. *Anal.* Calcd for $C_6F_5P$: C, 36.38; F, 47.49; P, 15.64. Found: C, 36.61; P, 15.16. The mercury coupling reaction of $C_6F_5PI_2$ closely resembled that of $CF_3PI_2$.[7]

The molecular formula $(C_6F_5P)_5$ agrees with the observed molecular weight in $CH_2Br_2$ solution: found, 1005; calcd, 990. The ring structure I would be consistent with mass spectral fragments bearing more than



I

one phosphorus atom such as $(C_6F_5P)_2P_2^+$ (0.3%), $(C_6F_5P)_2P^+$ (0.2%), $(C_6F_5P)_2^+$ (13.2%), and $C_6F_5PP^+$ (70.3%), and also with infrared frequencies which could be assigned to phosphorus ring stretching.[8] The presence of $C_6F_5P$ groups was demonstrated by both the infrared and the nmr spectra of I, the latter (in diethyl ether solution) showing *ortho*, *meta*, and *para* $^{19}F$ resonances at $\phi$ = 126.41, 160.06 (triplet plus fine structure), and 149.47 ppm (approximately a triplet), respectively, relative to $CCl_3F$ as internal standard. The *ortho* resonance was wider (~150-cps width) and more complex than the others owing to coupling with the ring $^{31}P$ nuclei. The $\pi$ bonding situation in $(C_6F_5P)_5$ would appear to be about the same as in $C_6F_5P(C_6H_5)_2$ in terms of the recently published relationship[9] between the chemical shift of the *para* $^{19}F$ resonance and $\pi$ bonding in pentafluorophenylphosphine derivatives.

Dissolution and subsequent evaporation of an ether solution (or sublimation) of I led to an apparently different polymorph (see X-ray powder data in Table I). The melting behavior of I is also consistent with polymorphism. The form from *n*-hexane–ether (form A) melted at 156–161° when placed in a bath which had been preheated to 145°. However, the form from the ether solution (form B) melted immediately in the 145° bath. Upon cooling and remelting form B, it melted at 159–162°, the same range as form A. It is apparent that subsequent investigation of the $C_6F_5$–P ring system may prove it to be as complex as its phenyl counterpart.

(7) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).
(8) R. L. Amster, N. B. Colthup, and W. A. Henderson, *Spectrochim. Acta*, **19**, 1841 (1963), and *Can. J. Chem.*, **42**, 2577 (1964), have assigned the symmetric phosphorus ring stretch in the range 390–410 $cm^{-1}$ and the asymmetric ring stretch in the range 465–490 $cm^{-1}$. We found medium intensity peaks at 390 and 508 $cm^{-1}$ in the infrared spectrum of I (Nujol mull). The strong bands which we observed at 974 and 1480 $cm^{-1}$ seem to be characteristic of $C_6F_5P$ compounds; see, *e.g.*, ref 6b.
(9) M. G. Hogben, R. S. Gay, and W. A. G. Graham, *J. Am. Chem. Soc.*, **88**, 3457 (1966).

**Table I.** X-Ray Diffraction Data

| $(C_6F_5P)_5$, form A | | $(C_6F_5P)_5$, form B | |
|---|---|---|---|
| *d*, A | $I/I_0$ | *d*, A | $I/I_0$ |
| 11.05 | 0.6 | 11.79 | 0.1 |
| 10.16 | 0.8 | 9.46 | 0.3 |
| 9.36 | 0.1 | 8.76 | 0.2 |
| 7.73 | 0.1 | 8.08 | 0.1 |
| 6.86 | 0.1 | 6.84 | 0.1 |
| 6.30 | 0.2 | 6.44 | 0.1 |
| 5.81 | 0.2 | 6.03 | 0.1 |
| 5.50 | 0.5 | 5.72 | 0.1 |
| 5.20 | 0.5 | 5.36 | 0.1 |
| 4.90 | 0.4 | 5.14 | 0.2 |
| 4.77 | 0.7 | 4.80 | 1.0 |
| 4.48 | 0.3 | 4.63 | 0.5 |
| 4.33 | 0.1 | 4.18 | 0.3 |
| 4.19 | 0.1 | 4.07 | 0.2 |
| 4.07 | 1.0 | 4.00 | 0.2 |
| 3.91 | 0.2 | 3.85 | 0.8 |
| 3.61 | 0.1 | 3.47 | 0.4 |
| 3.46 | 0.2 | 3.70 | 0.5 |
| 3.34 | 0.1 | 3.37 | 0.3 |
| 3.29 | 0.5 | | |

The electron-withdrawing effect of the $C_6F_5$ group manifested itself chemically in terms of the lack of reactivity of I toward $CH_3I$. However, like all cyclopolyphosphines the phosphorus ring structure was ruptured by elemental chlorine.[1] Interestingly, we were unable to isolate the phosphorane, $C_6F_5PCl_4$, from this reaction, even when excess chlorine was employed. In fact, attempts to chlorinate $C_6F_5PCl_2$ resulted in an unstable yellow solid (presumably $C_6F_5PCl_4$) which decomposed *in vacuo* by $Cl_2$ evolution.[10] As expected[11] $SbF_3$ fluorination of $C_6F_5PCl_2$ led to $C_6F_5PF_2$ (vapor tension = 2.5 mm at 25°, P–F stretching modes at 838 and 850 $cm^{-1}$ in the infrared. *Anal.* Calcd for $C_6F_5PF_2$: C, 30.51; F, 56.36. Found: C, 30.17; F, 56.19.

**Acknowledgment.** This work was supported by the Robert A. Welch Foundation and the U. S. Public Health Service (Grant GM 12437-02). It is also a pleasure to acknowledge the help of Dr. Stanley L. Manatt of the Jet Propulsion Laboratory, Pasadena, California, who both recorded and interpreted the nmr spectra.

(10) Emeleus and Millar[6d] have managed to prepare the phosphorane $(C_6F_5)_3PCl_2$. The reason for the apparent instability of $C_6F_5PCl_4$ is not known. There would be a certain amount of structural interest in $C_6F_5PCl_4$, since the $C_6F_5$ group, being the more electronegative ligand, should occupy an axial site if the molecular geometry is trigonal bipyramidal; see an excellent review on pentacoordination by E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966), on this point.
(11) The available evidence indicates that fluorination stops at the phosphinous fluoride stage when electronegative groups are attached to the phosphorus atom: *e.g.*, A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958); J. F. Nixon, *J. Chem. Soc.*, 777 (1965); R. Schmutzler, *Chem. Ber.*, **96**, 2435 (1963); R. Schmutzler, *Inorg. Chem.*, **3**, 415 (1964); J. F. Nixon, *J. Inorg. Nucl. Chem.*, **27**, 1281 (1965).

**A. H. Cowley, R. P. Pinnell**
*Department of Chemistry, The University of Texas*
*Austin, Texas 78712*
*Received August 12, 1966*

## The Total Synthesis of Racemic Aflatoxin $B_1$

*Sir:*

The aflatoxins are a group of acutely toxic and extremely carcinogenic metabolites produced by some