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 (R₀) compound, it is feasible and even desirable to vary (within limit) the solvent, temperature, R₀ moiety, and X or Y⁻ in R and R₀, 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. Follow-

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

	ΔF	ΔF°_{R} +, kcal/mole		
	From	From ^a	From ¹	
Cation	nmr	pK _R +	emf	
Triphenylcyclopropenium	12.9	13.30		
Tri-p-methoxytrityl	11.3	10.2°	11.9	
9-(<i>p</i> -Methoxyphenyl)- xanthylium	9.1	11.10	8.6	
Di-p-methoxytrityl	8.2	7.4°	8.6	
9-Phenylxanthylium	8.0	17.50	7.4	
<i>p</i> -Methyl- <i>p</i> '-methoxytrityl	5.7			
Tri-p-methyltrityl	4.6	4.2°	4.7	
p-Methoxytrityl	4.5	4.40	5.0	
Tri-p-t-butyltrityl	4.4	0.5°		
Di-p-methyltrityl	3.2	3.0 ^d	3.3	
Mono-p-methyltrityl	1.6	1.7,ª 1.9°	1.8	
Mono-m-methyltrityl	0.8		0.7	
Di-p-methoxydiphenylmethyl	0.5	1.25°		
Trityl	(0.0)	(0.0)	(0.0)	
<i>m</i> -Methyl- <i>p</i> '-chlorotrityl	-0.2	-0.2	-0.1	
<i>m</i> -Methyl- p' , p'' -dichlorotrityl	-0.8	-0.7*		
1,2,3,4-Tetraphenyl-2-chloro- cyclobutenium	-1.8	••••		

^a Calculated from reported pK_{R} + data, taking pK_{R} + for trityl = -6.6 at 25° (from ref 1b). ^bR. 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. ^e R. A. Diffenbach, Thesis, The Pennsylvania State University, 1966.

ing Taft,² the free energy of the cations have all been related to unsubstituted trityl cation (eq 1, R_0 = trityl) and the symbol $\Delta F^{\circ}_{R^+}$ is suggested for this purpose.

(7) Presumably exchange takes place via an SE2 process rather than the much more rapid SN1 exchange⁴ 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 $pK_{\rm R}^+$ 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 $\Delta F^{\circ}_{\rm R}^+$ value for which has ranged from $0.5^{\rm 1b}$ to $2.9^{\rm 9}$ kcal. The nmr value of $4.4 \pm$ 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^+ values¹⁰ of -0.256 and -0.311, respectively. Finally, we note that the nmr method readily furnishes the $\Delta F^{\circ}_{\rm R^+}$ for the 1,2,3,4-tetraphenyl-2-chlorocyclobutenium cation,¹¹ whose hydrolytic nonreversibility^{11a} precludes stability measurements by the $pK_{\rm R^+}$ method.

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

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(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 compounds⁵ 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.

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

(6) Previous reports of C_6F_6P 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 PBr₃ with an equimolar quantity of C₆F₅MgBr and by HI cleavage of C₆F₅P[N(CH₃)₂]₂,^{6b} respectively. Mercury acted upon C₆F₅PBr₂ (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 C₆F₅PI: C, 36.38; F, 47.49; P, 15.64. Found: C, 36.61; P, 15.16. The mercury coupling reaction of C₆F₅PI₂ closely resembled that of CF₃PI₂.⁷

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



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 C₆F₅P groups was demonstrated by both the infrared and the nmr spectra of I, the latter (in diethyl ether solution) showing ortho, meta, and para ¹⁹F resonances at $\phi = 126.41$, 160.06 (triplet plus fine structure), and 149.47 ppm (approximately a triplet), respectively, relative to CCl₃F as internal standard. The ortho resonance was wider (\sim 150-cps width) and more complex than the others owing to coupling with the ring ³¹P nuclei. The π 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 relationship⁹ between the chemical shift of the para ¹⁹F resonance and π 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 C₆F₅-P ring system may prove it to be as complex as its phenyl counterpart.

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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 ₆ F ₅ P) ₅ ,	$(C_6F_5P)_5$, form B		
<i>d</i> , A	I/I_0	<i>d</i> , 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				
3.91 3.61 3.46 3.34 3.29	0.2 0.1 0.2 0.1 0.5	3.85 3.47 3.70 3.37	0.8 0.4 0.5 0.3		

The electron-withdrawing effect of the C_6F_5 group manifested itself chemically in terms of the lack of reactivity of I toward CH₃I. 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_5 -PCl₄) which decomposed *in vacuo* by Cl₂ evolution.¹⁰ As expected¹¹ SbF₃ 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.

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The Total Synthesis of Racemic Aflatoxin B₁

Sir:

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

⁽¹⁰⁾ Emeleus and Millar^{8d} have managed to prepare the phosphorane $(C_{\delta}F_{\delta})_{\delta}PCl_{2}$. The reason for the apparent instability of $C_{\delta}F_{\delta}PCl_{4}$ is not known. There would be a certain amount of structural interest in $C_{\delta}F_{\delta}PCl_{4}$, since the $C_{\delta}F_{\delta}$ group, being the more electronegative ligand b, 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.