

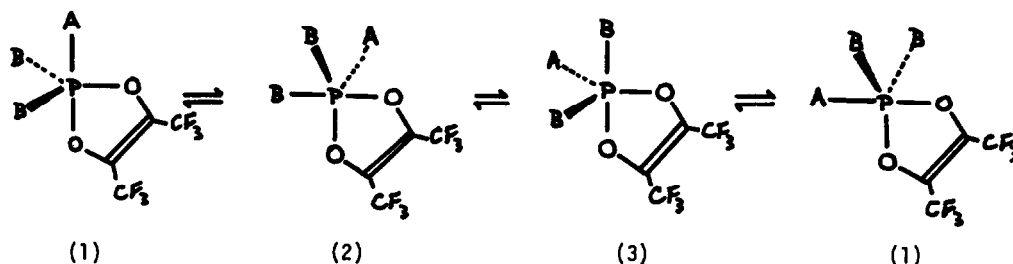
1,3,2-DIOXAPHOSPHOLENS FROM HEXAFLUOROBIACETYL AND TRIVALENT PHOSPHORUS COMPOUNDS

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Ramirez and Kugler<sup>1</sup> recently reported the formation of a stable pentacovalent 1,3,2-dioxaphosphenol (1; A, B = OPh) from hexafluorobiacetyl (HFBA) and triphenyl phosphite at  $-70^\circ$  in dichloromethane. We have independently obtained similar adducts from HFBA and a variety of trivalent phosphorus compounds and have studied their variable-temperature  $^{19}\text{F}$  n.m.r. spectra in order to gain more data on the relative apicophilicities of groups in pentacovalent phosphoranes.<sup>2</sup>



The most stable conformer of an adduct in which A is more apicophilic than B is as shown in (1). The  $\text{CF}_3$  groups become equivalent by pseudorotation via the higher energy topomers (2) and (3). The free energy of activation for this process will be a function of the difference in apicophilicity between A and B, although as a kinetic parameter it will of necessity exceed this difference. In a series of adducts with either A or B constant,  $\Delta G^\ddagger$  will vary with the apicophilicity of B or A respectively. Typical of the observed  $^{19}\text{F}$  n.m.r. spectra is that of the adduct (A = Cl; B = Ph). At room temperature this is a sharp singlet. On cooling, the signal broadens and below  $-17^\circ$  splits into two equal broad signals. These acquire fine structure as the temperature is further lowered and at  $-65^\circ$  are both quartets.

The Table contains data on a number of adducts together with the associated  $\Delta G^\ddagger$ s calculated by application of the Gutowsky-Holm equation. The apparent difference in apicophilicity between methoxy and phenoxy is reasonable in terms of bonding theory<sup>3</sup> but unexpected in view of the

Table  
Data on the 1,3,2-Dioxaphospholens (1)

		$^{19}\text{F}^{\text{b,d}}$						
A	B	$\delta_{\text{P}}^{\text{a}}$	Mass Spectrum	$\delta^{\text{c}}$	$T^{\text{c}}$ (°C)	$\Delta\nu$ (Hz)	$\Delta G^*$ (kcal mol $^{-1}$ )	
PhO	PhO	+61.3	504, 485, 411	64.9				
PhO	Me <sub>2</sub> N	+34.8	406, 387, 362, 313	65.8	-80	159	8.9	
PhO	EtS	+ 3.2	421, (M-F) 379, 347	65.1	-98	178	8.0	
MeO	Ph	+15.7	410, 391, 379	65.4	-60	174	9.8	
PhO	Ph	+18.8	472, 453, 395 379	64.9	- 4	151	12.6	
Cl	Ph	+ 4.9 <sup>d</sup>	414, 395, 379	65.4	-17	141	12.0	

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> relative to external H<sub>3</sub>PO<sub>4</sub>. <sup>b</sup> 56.4 MHz. <sup>c</sup> P.p.m. upfield relative to internal CFC1<sub>3</sub>. <sup>d</sup> In light petroleum.

observance of two isomers of the 1:1 adduct from dimethyl phenyl phosphite and benzylideneacetylacetone.<sup>4</sup> The relatively high apicophilicity of chlorine is presumably a balance between electronegativity and the presence of both 3p donor and low-lying acceptor orbitals.<sup>3</sup>

The barrier to pseudorotation in the adduct (A=OPh;B=SEt) may be due either to a difference in apicophilicity between phenoxy and ethylthio or to a barrier to rotation round the equatorial PS bonds as observed in alkylthio- and arylthio-fluorophosphoranes.<sup>5</sup> Slow rotation on the n.m.r. timescale introduces an additional energy difference between (1) and (2) since in (1) the sulphur p-orbitals will be in the equatorial plane whereas in (2) the p-orbital of the pivot sulphur will be in the apical plane. The barrier to pseudorotation in the adduct (A=OPh; B=NMe<sub>2</sub>) is probably due to a difference in apicophilicity between phenoxy and dimethylamino, in agreement with previous observations,<sup>2</sup> and not to slow PN bond rotation, as the methyls are equivalent in the <sup>1</sup>H n.m.r. spectrum at -100°.

#### References.

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