Relative Apicophilicities of Alkyl and Aryl Groups in Quinquecovalent Phosphoranes

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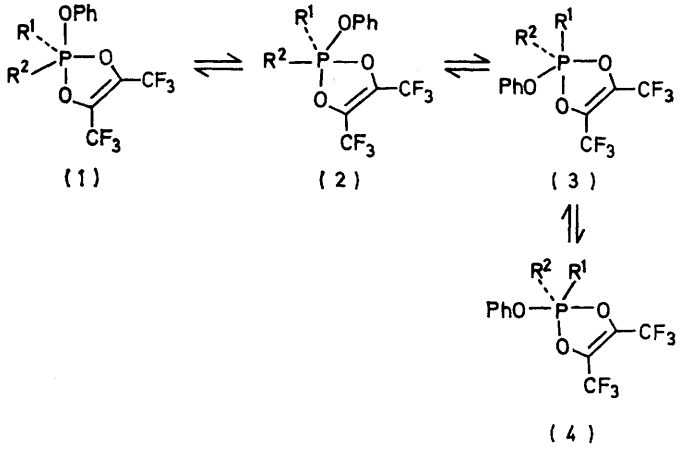
Variable temperature n.m.r. data on the perfluorobiacetyl adducts of phenyl dialkyl- and alkylaryl-phosphinites and on 6-substituted 1,5,7,11-tetraoxa-6-phosphaspiro[5.5]undecanes show that the greater compression at the apical, as opposed to the equatorial, positions in trigonal bipyramidal phosphoranes plays a large part in determining the relative apicophilicities of alkyl and aryl groups in these systems, and that the apicophilicities of methyl and phenyl groups are more similar than previous data had indicated.

OUR previous work [1] on the pseudorotation of the hexafluoroacetone adducts of 1-substituted 2,2,3,4,4-pentamethylphosphetans had indicated that methyl and isopropyl are more apicophilic than phenyl by at least 5 kcal mol^{-1}. We subsequently showed [2] that the adduct from the phenylphosphetan has essentially square-pyramidal geometry and therefore sought additional evidence on the relative apicophilicity of these groups. The present paper presents data, from systems that can be expected to have trigonal bipyramidal geometry, which indicate much smaller differences in apicophilicity, with phenyl however still the least apicophilic.

Perfluorobiacetyl Adducts of Phenyl Phosphinites.—Perfluorobiacetyl reacted rapidly with phenyl dialkyl- and alkylaryl-phosphinites at −78 °C.[3] The resulting adducts were not isolated because of their great hydrolytic sensitivity, but are formulated as the phosphoranes (1) on the basis of their ^{31}P n.m.r. chemical shifts, mass spectra, and ^{19}F n.m.r. spectra. The ^{19}F n.m.r. spectra, at low temperatures when equilibration between the lowest energy topomeric conformers (1) and (4) is slow on the n.m.r. time-scale, showed two equal signals having the fine structure of quartets. On warming, the signals lost their fine structure and eventually coalesced. The



behaviour was reversible. These changes are associated with changes, relative to the n.m.r. time-scale, in the rate of equilibration of the topomers (1) and (4) *via* the higher energy phosphoranes (2) and (3). As the alkyl and/or aryl groups R^1 and R^2 are changed, changes in the free energy of activation for the interconversion of (1) and (4) will reflect changes in the relative apicophilicity of R^1 or R^2 (whichever is the less apicophilic) together with changes in steric factors. The results are given in the Table.

N.m.r. data for the phosphoranes (1)

R^1	R^2	^{31}P [a]	^{19}F $\Delta\nu$/Hz	^{19}F T_c/°C	ΔG^*/ kcal mol^{-1} [b]
Me	Me	−8	159	−57	10.0
Et	Et	−13	184	−35	11.0
Pr^i	Pr^i	−13	151	11	13.3
Bu^t	Bu^t	−8	153	41	14.8
Me	Bu^t	−11	132	−37	11.0
Me	Ph	+5	243 [c]	−45	10.4
Ph	Ph[3]	+18.8	151	−4	12.6

[a] P.p.m. to high field of 85% H_3PO_4. [b] ±0.3 kcal mol^{-1}. Derived by using the Gutowsky–Holm equation. [c] 94.1 MHz; remainder at 56.4 MHz.

The only clearly identifiable factor in these results is a steric one. It is usually assumed that apical positions are more hindered than equatorial, for they have three nearest neighbours at 90° as opposed to two, but there has been little direct evidence on this. The contrast between the energy barriers in the case of the adducts from the dimethyl-, di-t-butyl-, and t-butylmethyl-phosphinites shows that the major part of the increase in the barrier in going from dimethyl to di-t-butyl is due to the compression on bringing two t-butyl groups into a 90° disposition with respect to one another. The other results are interpretable in similar terms and there is little room left for large differences in apicophilicity between alkyl groups, or between methyl and phenyl, in the absence of steric effects.

The adduct from the di-t-butylphosphinite is of interest in relation to the unusual chemistry of di-t-butyl phosphorus compounds. In general,[4] phosphonium or phosphoryl centres having two t-butyl groups attached to phosphorus are extraordinarily resistant to nucleophilic attack. Attack at faces containing two t-butyl groups, to give intermediates having two equatorial t-butyl groups, will be hindered by the two large groups in the early stages of the approach, whereas attack opposite a t-butyl, to give intermediates having one apical and one equatorial t-butyl group, clearly leads

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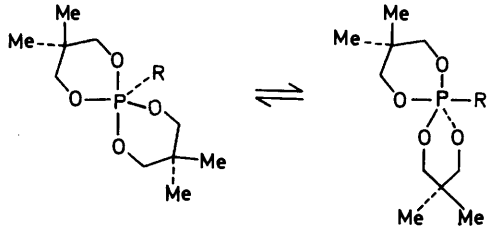
[2] J. A. Howard, D. R. Russell, and S. Trippett, *J.C.S. Chem. Comm.*, 1973, 856.
[3] J. I. Dickstein and S. Trippett, *Tetrahedron Letters*, 1973, 2203.
[4] N. J. De'ath and S. Trippett, *Chem. Comm.*, 1969, 172; A. P. Stewart and S. Trippett, *J. Chem. Soc.* (*C*), 1970, 1263.

to high-energy phosphoranes because of the increased compression between the two t-butyl groups as in (2; $R^1 = R^2 = Bu^t$).

1,5,7,11-*Tetraoxa*-6-*phosphaspiro*[5.5]*undecanes*.— We have recently [5] described the preparation of the spirophosphoranes (5; R = Me, CH_2Ph, or Ph) from 1-substituted 1,3,2-dioxaphosphorinans and 2,2-dimethyl-



(5) (6)

propane-1,3-diol in the presence of *N*-chlorodi-isopropylamine. The phosphoranes (5; R = Me or Ph) had previously been obtained in solution by the exchange route by Denney,[6] who recorded a free energy barrier to equivalence of the ring methyls in the ^1H n.m.r. spectrum of (5; R = Me) of about 12 kcal mol^{-1}. Equivalence of the methyl groups is associated with the pseudorotation (5) ⇌ (6), which places a six-membered ring diequatorial and the alkyl or aryl group apical. We find free energies of activation for these pseudorotations in the spirophosphoranes (5; R = Me, CH_2Ph, or Ph) of 12.7 (T_c −32 °C, Δν 8 Hz), 12.2 (T_c −35 °C, Δν 13 Hz), and 13.2 (T_c −15 °C, Δν 15 Hz) kcal mol^{-1}, respectively. The greater apicophilicity of the benzyl group, which relative to methyl cannot be due to steric effects, is of particular interest in connection with phosphonium salt hydrolysis where the order of leaving group ability is benzyl > phenyl > methyl. Again the difference in apicophilicity between methyl and phenyl is less than our previous experiments suggested.

We conclude (*a*) that, because of the greater crowding at the apical than at the equatorial positions, steric factors play a large and variable part in determining the relative apicophilicities of alkyl and aryl groups in trigonal bipyramidal phosphoranes, and (*b*) that the difference in apicophilicity between alkyl and aryl groups is less than data on pseudorotation of the hexafluoroacetone adducts of 1-substituted phosphetans had indicated.

EXPERIMENTAL

^1H N.m.r. spectra were determined at 60 MHz for solutions in $CDCl_3$ unless otherwise stated.

Phenyl t-Butylmethylphosphinite.— *NN*-Diethyl-t-butylmethylphosphinous amide [7] (17.5 g) and phenol (9.4 g) were heated together at 160 °C for 4 h. Distillation then gave *phenyl t-butylmethylphosphinite* (85%), b.p. 72—75° at 0.5 mmHg, τ 2.67—3.17 (5 H, m), 8.73 (3 H, d, *J* 6 Hz), and 8.95 (9 H, d, *J* 13 Hz). The phosphinite (1.96 g) and sulphur (0.32 g) were refluxed in benzene (20 ml) for ½ h. Solvent was removed and the residue chromatographed on basic alumina. Elution with ether–light petroleum gave *O-phenyl t-butylmethylphosphinothioate* (90%), b.p. 170° (oven temp.) at 0.3 mmHg, m.p. 29.5—31° (from light petroleum), τ (CCl_4) 2.67—3.17 (5 H, m), 8.25 (3 H, d, *J* 12 Hz), and 8.72 (9 H, d, *J* 17 Hz) (Found: C, 58.0; H, 7.6; P, 13.55. $C_{11}H_{17}OPS$ requires C, 57.9; H, 7.5; P, 13.6%).

Similar reactions gave phenyl dimethylphosphinite (94%), b.p. 197—200°, τ 2.53—3.17 (5 H, m) and 8.58 (6 H, d, *J* 6 Hz), identified as the phosphinothioate, m.p. 38.5—39.5° (from CCl_4–hexane; lit.,[8] m.p. 36—38°); phenyl diethylphosphinite (84%), b.p. 94—96° at 10 mmHg, τ 2.50—3.22 (5 H, m), 8.05—8.68 (4 H, m), and 8.91 (6 H, dt, *J* 14.5 and 7 Hz), identified as the *phosphinothioate*, b.p. 160° (oven temp.) at 0.5 mmHg, τ (CCl_4) 2.63—3.15 (5 H, m), 7.98 (4 H, dq, *J* 12 and 8 Hz), and 8.80 (6 H, dt, *J* 20 and 8 Hz) (Found: C, 56.0; H, 6.9; P, 14.3. $C_{10}H_{15}OPS$ requires C, 56.1; H, 7.0; P, 14.5%); and phenyl methylphenylphosphinite (82%), b.p. 116—122° at 0.4 mmHg, τ 2.30—3.35 (10 H, m) and 8.41 (3 H, d, *J* 7 Hz), identified as the *phosphinothioate*, b.p. 170° (oven temp.) at 0.2 mmHg, τ 1.88—2.30 (2 H, m), 2.33—2.70 (3 H, m), 2.75—3.25 (5 H, m), and 7.87 (3 H, d, *J* 13 Hz) (Found: C, 63.2; H, 5.3; P, 12.7. $C_{13}H_{13}OPS$ requires C, 62.9; H, 5.2; P, 12.5%).

Phenyl Di-isopropylphosphinite.—A solution of sodium phenoxide (5.8 g) in tetrahydrofuran (50 ml) was added slowly to a stirred solution of di-isopropylphosphinous chloride (7.6 g) in the same solvent (80 ml), and the mixture was refluxed for 6 h. Light petroleum (150 ml) was then added to the cooled mixture. Filtration and distillation gave phenyl di-isopropylphosphinite (77%), b.p. 76—78° at 0.3 mmHg, τ 2.32—3.08 (5 H, m), 7.70—8.24 (2 H, m), and 8.40—9.0 (12 H, m), identified as the *phosphinothioate*, b.p. 170° (oven temp.) at 0.3 mmHg, τ (CCl_4) 2.62—3.17 (5 H, m), 7.38—8.13 (2 H, m), 8.73 (dd, *J* 17 and 7 Hz), and 8.77 (dd, *J* 17 and 7 Hz) (the last two absorptions totalling 12 H) (Found: C, 59.7; H, 7.7; P, 12.8. $C_{12}H_{19}OPS$ requires C, 59.5; H, 7.85; P, 12.8%).

Reaction of Phenyl Phosphinites with Perfluorobiacetyl.— Perfluorobiacetyl (0.01 mol) was passed into a stirred solution of the phosphinite (0.01 mol) in ether (15 ml) at −78 °C, and the mixture kept at this temperature until the yellow colour was discharged. The solution was then stored at −20 °C and aliquot portions were taken for spectral analysis. In all cases the ^{19}F n.m.r. spectrum showed the presence of only one fluorine-containing species with the signal(s) at or centred at 64—65 p.p.m. to high field of internal $CFCl_3$, and the mass spectrum, after complete removal of solvent, showed the molecular ion and fragmentation expected for the phosphorane (1) (*e.g.* the adduct from phenyl t-butylmethylphosphinite showed *m/e* 390, 375, 371, 333, 297, 248, and 212).

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