

Hexafluoroacetone Adducts of 1-Phenylphosphetans. The Barrier to Placing a Four-membered Ring Diequatorial in a Trigonal Bipyramid: Nuclear Magnetic Resonance Study

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Summary The variable temperature ^{19}F n.m.r. spectrum of the 1:2-adduct of 2,2,4,4-tetramethyl-1-phenylphosphetan and hexafluoroacetone leads to a free energy of activation for placing the phosphetane ring diequatorial of $20.1 \text{ kcal mol}^{-1}$.

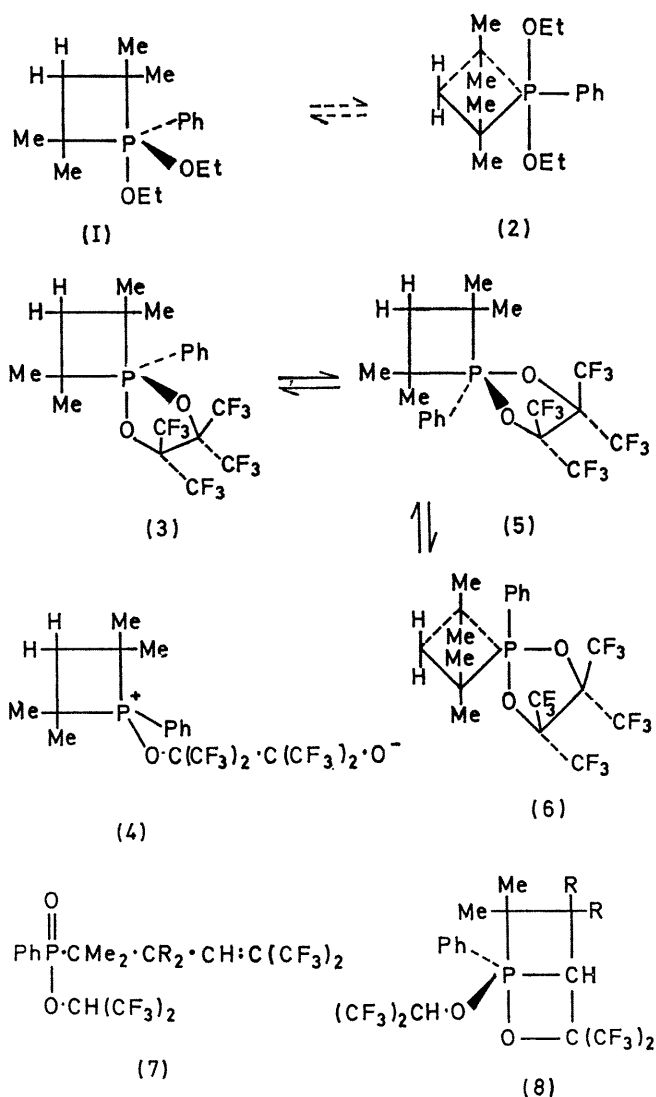
In pentaco-ordinate trigonal bipyramids, isolable or postulated as intermediates in nucleophilic substitutions at phosphorus and in which the phosphorus is part of a four-membered ring, there is conflict between the desire of the ring to occupy an apical-equatorial as opposed to a diequatorial position (strain factor) and the preference of electronegative groups for apical positions (stereoelectronic factor). The retention of configuration observed¹ in substitutions at phosphorus involving such intermediates implies that the strain factor is the larger and calculations reported by Mislow² support this view. Denney and his co-workers³ have recently reported on the variable temperature ^1H n.m.r. spectrum of the diethoxyphosphorane (1). The signals due to the diastereotopic hydrogens of the ethoxy-groups coalesce at 30° due to a process which involves placing the four-membered ring diequatorial as in (2). Here the strain factor is opposed by the stereoelectronic factor associated with replacing the apical CMe_2 by an apical ethoxy-group. We now report on a case in which the same strain factor is not partly offset by the movement of a highly electronegative group.

2,2,4,4-Tetramethyl-1-phenylphosphetan gives with hexafluoroacetone a stable 1:2-adduct (3), m.p. $89-91^\circ$ (from MeOH), ^{31}P -2.5 p.p.m., τ $1.7-2.6$ (5H, m), 8.3 (6H, d, $J_{\text{PH}} 16$ Hz), $7.7-8.4$ (1H, m), 8.5 (6H, d, $J_{\text{PH}} 20$ Hz), and $8.8-9.5$ (1H, m). The ^1H n.m.r. spectrum is unchanged from -60° to 160° . At room temperature and below the ^{19}F n.m.r. spectrum in *o*-dichlorobenzene consists of two signals of equal intensity at $+3.17$ and $+6.01$ p.p.m. (relative to PhCF_3 as internal standard) showing fine structure. Above 120° these signals broaden and finally coalesce at 155° . The process is reversible with no decomposition and the coalescence temperature is unchanged in 1-bromonaphthalene and in ethylene glycol. This rules out a process of equivalence *via* the betaine (4).

The data imply a pseudorotation, rapid on the n.m.r. time scale down to -60° , between the equivalent structures (3) and (5). At higher temperatures equivalence of the CF_3 groups, but not of the CH_3 groups, is achieved *via* the high energy trigonal bipyramid (6) having a four-membered ring spanning a diequatorial position.† The free energy of activation for this process at 155° is $20.1 \text{ kcal mol}^{-1}$.

Mislow's calculations suggest that structures such as (2) and (6) are transition states and not intermediates between trigonal bipyramids having four-membered rings apical-equatorial. If so, $20.1 \text{ kcal mol}^{-1}$ is the energy required to

move the ring from an apical-equatorial to a diequatorial position minus a small stereoelectronic factor due to the difference in electronegativity between CMe_2 and phenyl.



Denney's data lead to a corresponding energy of about 15 kcal mol^{-1} for the same process involving movement of an ethoxy-group. The 5 kcal difference between these free energies is a measure of the difference in the preferences of the phenyl and the ethoxy-group for the apical position.

Similar stable 1:2-adducts have been obtained from

† Placing the five-membered ring diequatorial would make the pairs of α -methyls equivalent without producing equivalence of the CF_3 groups.

2,2-dimethyl-2,2,3,3-tetramethyl,[‡] and the two isomers of 2,2,3,4,4-pentamethyl-1-phenylphosphetan.[§] Their variable temperature n.m.r. spectra are qualitatively similar to, but of necessity more complicated than, those of the 2,2,4,4-tetramethyl isomer. In the preparation of those adducts

having CH₂ attached to phosphorus the oxides (**7**; R = H or Me) were also obtained, presumably *via* the oxaphosphetans (**8**).⁴ However, these adducts were still stable at 160° in *o*-dichlorobenzene.

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[‡] In this case the intermediate 1,3,5-dioxaphospholan could be isolated.

[§] The isomeric adducts are not interconverted at 160°, again showing that the five-membered ring does not become diequatorial.

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² K. Mislow, *Accounts Chem. Res.*, 1970, **3**, 321.

³ D. Z. Denney, D. W. White, and D. B. Denney, *J. Amer. Chem. Soc.*, 1971, **93**, 2066.

⁴ F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, 1968, **33**, 3787.