

Apicophilicity of the Benzoyl Group in Five-co-ordinate Phosphoranes

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Evidence is presented from the variable-temperature ^1H n.m.r. spectrum of 5-benzoyl-2,2,3,3,7,7,8,8-octamethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (9) that the apicophilicity of the benzoyl group is comparable to those of the phenoxy- and phenylthio-groups. Benzoyldifluorodimethylphosphorane is prepared from benzoyldimethylphosphine and xenon difluoride. Its low temperature ^{19}F and ^1H n.m.r. spectra give some evidence for restricted rotation round the equatorial *P*-benzoyl bond.

ACYL groups are electronegative and π -acceptors. In terms of the analysis by Hoffmann, Howell, and Muetterties¹ of the factors determining the apicophilicity of groups in five-co-ordinate phosphoranes they would therefore be expected to be highly apicophilic. As part

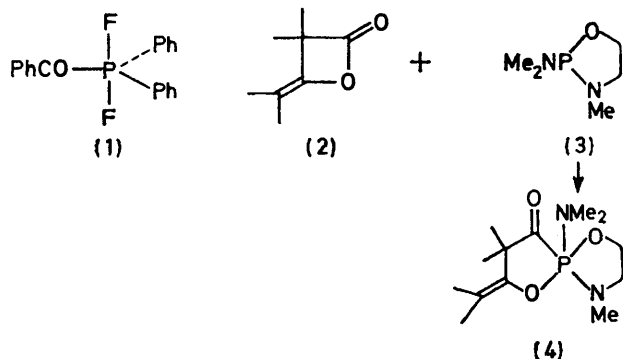
of our work² aimed at defining the relative apicophilicities of groups attached to phosphorus in five-co-ordinate phosphoranes we now report on the benzoyl group. There are two previous reports on acylphosphoranes. The benzoyldifluorophosphorane (1) was tentatively identified³ in solution (^{19}F and ^{31}P n.m.r. spectra) from the

¹ R. Hoffmann, J. M. Howell, and E. L. Muetterties, *J. Amer. Chem. Soc.*, 1972, **94**, 3047.

² E.g. S. Bone, S. Trippett, and P. J. Whittle, *J.C.S. Perkin I*, 1974, 2125; R. K. Oram and S. Trippett, *ibid.*, 1973, 1300.

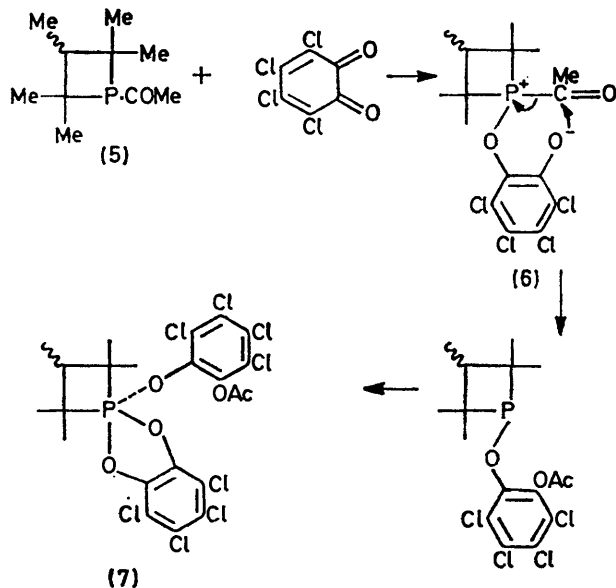
³ C. Brown, M. Murray, and R. Schmutzler, *J. Chem. Soc. (C)*, 1970, 878.

reaction of fluorodiphenylphosphine with benzoyl fluoride, whereas the spirophosphorane (4) was isolated⁴



from the reaction of dimethylketene lactone dimer (2) with the phosphorodiamidite (3).

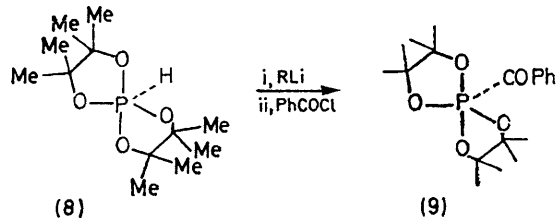
Addition reactions of acylphosphetans did not lead to acylphosphoranes because of migration of the acyl groups in dipolar intermediates. Thus the acylphosphetane (5),



a mixture of geometrical isomers, with hexafluoroacetone gave a product mixture whose acetyl signals appeared as singlets in the proton n.m.r. spectrum indicating that they were no longer attached to phosphorus. Similarly from tetrachloro-*o*-benzoquinone and (5) a mixture of isomeric 2:1 adducts was isolated which are formulated as the phosphoranes (7) formed *via* migration of the acetyl groups in the 1:1 intermediates (6).

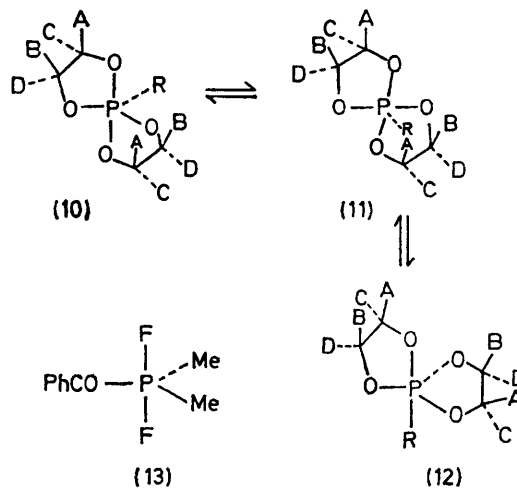
Metallation of the tetraoxyspirophosphorane (8) with *N*-lithio-*N*-cyclohexylisopropylamine followed by treatment with benzoyl chloride gave the benzoylspirophosphorane (9) in high yield. The ³¹P chemical shift (39.5

p.p.m. to high field of 85% H₃PO₄), carbonyl absorption at 1659 cm⁻¹, and mass spectrum agree with this structure. The proton n.m.r. spectrum at room temperature consists, in the methyl region, of two signals each equivalent to 12 protons, showing that, as expected, pseudorotation between the topomeric trigonal bipyramids (10) and (11; R = COPh) is rapid on the n.m.r. time-scale at this temperature. This pseudorotation makes A ≡ B and C ≡ D. The two signals coalesce reversibly at 140 °C in 1-bromonaphthalene; this corresponds to a free energy of activation for the process leading to equivalence of the methyls of 20.9 kcal mol⁻¹. The process involves pseudorotation to the phosphorane (12; R = COPh) having an apical benzoyl group and a diequatorial five-membered



ring. The analogous pseudorotation (11) ⇌ (12) when R = H (ref. 5) has Δ*G*^{*} 18.4 kcal mol⁻¹ indicating that in this system a hydrogen atom is more apicophilic than a benzoyl group. As hydrogen is known² to be more apicophilic by 3–4 kcal mol⁻¹ than phenoxy- and phenylthio-groups this implies that the benzoyl group is similar in apicophilicity to these.

Hoffmann¹ predicted that with an equatorial π-acceptor group the preferred orientation would be with the acceptor orbital in an apical plane and that this could, as with π-donor groups,^{1,6} lead to a considerable barrier to rotation round the equatorial bond. We have sought this effect in benzoylphosphoranes.



Treatment of phenyl dimethylphosphinite in trichlorofluoromethane with xenon difluoride at low temperature gave, after vigorous reaction, as the major product,

⁴ W. G. Bentrude, W. D. Johnson, and W. A. Khan, *J. Amer. Chem. Soc.*, 1972, **94**, 923.

⁵ D. Houalla, R. Wolf, D. Gagnaire, and K. B. Robert, *Chem. Comm.*, 1969, 443.

⁶ E. L. Muetterties, P. Meakin, and R. Hoffmann, *J. Amer. Chem. Soc.*, 1972, **94**, 5674.

difluorodimethylphenoxyphosphorane,⁷ identified by its ¹⁹F (doublet of septets, J_{PF} 745, J_{HF} 13 Hz, at +3.3 p.p.m. relative to $CFCl_3$) and ¹H (doublet of triplets, J_{PH} 18, J_{FH} 13 Hz, at τ 8.22) n.m.r. spectra. A similar reaction with benzoyldimethylphosphine gave one major product (85% as judged by the ¹⁹F n.m.r. spectrum of the resulting solution). This was identified as the benzoylphosphorane (13) from its ³¹P (25 p.p.m. to high field of 85% H_3PO_4), ¹⁹F (doublet of septets, J_{PF} 627, J_{HF} 13 Hz, at +29.3 p.p.m. relative to $CFCl_3$), and ¹H (doublet of triplets, J_{PH} 18, J_{FH} 13 Hz, at τ 8.0) n.m.r. spectra at room temperature.

The ¹⁹F n.m.r. spectrum of (13) was unchanged at -100 °C but the methyl signals in the ¹H spectrum showed considerable broadening at this temperature. Similarly the methyl signals in the ¹H n.m.r. spectrum of (9) were broadened considerably at -100 °C while the signals due to the benzoyl protons remained sharp. These results suggest that rotation round the equatorial *P*-benzoyl bond is slowing at -100 °C on the n.m.r. time-scale with the benzoyl group preferring to be in the equatorial plane. However the barrier to rotation must be less than 8 kcal mol⁻¹.

EXPERIMENTAL

¹⁹F N.m.r. spectra were obtained at 56.4 MHz and ³¹P n.m.r. spectra at 24.3 MHz. Positive shifts are upfield from the reference in each case.

1-Acetyl-2,2,3,4,4-pentamethylphosphetan.—Acetyl chloride (1.2 g) in light petroleum (15 ml) was added over 15 min to a stirred solution of 2,2,3,4,4-pentamethylphosphetan⁸ (2.2 g) and triethylamine (1.55 g) in ether–light petroleum (1 : 1; 30 ml) and the suspension was refluxed for 4 h. Filtration and distillation then gave 1-acetyl-2,2,3,4,4-pentamethylphosphetan (76%) as a 1.8 : 1 mixture of isomers (from integration of n.m.r. spectra), b.p. 63–65° at 0.8 mmHg, ν_{max} 1655 cm⁻¹, τ (major isomer) 7.47 (1H, m), 7.75 (3H, d, J 5 Hz), 8.62 (6H, d, J 11 Hz), 8.68 (6H, d, J 14 Hz), and 9.10 (3H, dd, J 1 and 7 Hz), ³¹P δ ($CHCl_3$) -64 p.p.m. The minor isomer had identifiable peaks at τ 7.67 (3H, d, J 6 Hz), and 9.18 (3H, dd, J 1 and 7 Hz), the others being obscured by those of the major isomer, and ³¹P δ -73 p.p.m.

Reaction of 1-Acetyl-2,2,3,4,4-pentamethylphosphetan with Tetrachloro-*o*-benzoquinone.—A solution of the quinone (2.36 g) in ether (25 ml) was added over 0.5 h to a stirred solution of the acetylphosphetan (0.8 g) in ether (20 ml), and the solution was refluxed for 1 h. Evaporation of solvent

and crystallisation of the residue from hexane gave the 2 : 1 *adduct* (7) as a 3 : 1 mixture of isomers (from integration of ¹H n.m.r. spectrum), m.p. 158–163°, ν_{max} 1794 cm⁻¹, τ (benzene; major isomer), 8.02 (3H, s), 8.72 (6H, d, J 22 Hz), 8.95 (6H, d, J 22 Hz), and 9.32 (3H, dd, J 1.5 and 7 Hz), ³¹P δ -15 p.p.m., m/e (³⁵Cl) 604 (M - 70), 561, 387, 344, and 275 (Found: C, 39.2; H, 2.9; Cl, 41.6; P, 4.8. $C_{22}H_{19}Cl_8O_5P$ requires C, 38.9; H, 2.8; Cl, 41.9; P, 4.6%).

5-Benzoyl-2,2,3,3,7,7,8,8-octamethyl-1,4,6,9-tetraoxa-5-phosphaspiro[4.4]nonane (9).—A solution of the tetraoxyphosphorane (8) (1.32 g) in tetrahydrofuran (10 ml) was added to a stirred solution of *N*-lithio-*N*-cyclohexylisopropylamine (0.735 g) in tetrahydrofuran (20 ml) at -78 °C and the mixture was kept at this temperature for 0.5 h. Benzoyl chloride (0.7 g) in tetrahydrofuran (10 ml) was then added and the solution allowed to warm to room temperature and then refluxed for 0.5 h. Solvent was removed under reduced pressure and the residue extracted with hot ether–light petroleum (1 : 1; 30 ml). Evaporation of the extract and crystallisation of the residue from light petroleum gave the *spiroposphorane* (9) (86%), m.p. 158–160°, τ 1.50–1.77 (2H, m), 2.20–2.63 (3H, m), 8.65 (12H, s), and 8.92 (12H, s), ³¹P δ (CH_2Cl_2) +39.5 p.p.m., m/e 353 (M - 15), 310, 263, 181, 147, and 105 (Found: C, 61.2; H, 7.8; P, 8.3. $C_{19}H_{29}O_5P$ requires C, 61.0; H, 7.9; P, 8.4%).

Benzoyldimethylphosphine.—Phenyl dimethylphosphinite (12 g) in toluene (10 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (5 g) in toluene (50 ml). The resulting dimethylphosphine was carried in a slow stream of nitrogen into a stirred solution of benzoyl chloride (10.95 g) and triethylamine (7.9 g) in light petroleum (50 ml). After 6 h the mixture was filtered and the filtrate distilled to give benzoyldimethylphosphine (46%), b.p. 68–72° at 1 mmHg, ν_{max} 1643 cm⁻¹, τ 2.05–2.27 (2H, m), 2.50–2.70 (3H, m), and 8.75 (6H, d, J 2 Hz).

Reaction of P^{III} Compounds with Xenon Difluoride.—Xenon difluoride (< 1 mol. equiv.) was sublimed *in vacuo* onto the inner wall of a Kel-F (polytrifluorochloroethylene) n.m.r. tube above a solution of the P^{III} compound in trichlorofluoromethane at -197 °C. The solution was allowed to warm until mobile and brought into contact with the xenon difluoride, when an immediate and vigorous reaction occurred. When reaction was complete the solution was warmed to room temperature and the tube sealed.

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[5/047 Received, 8th January, 1975]

⁷ S. C. Peake, M. J. C. Hewson, and R. Schmutzler, *Inorg. Chem.*, 1971, 10, 2723.

⁸ J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin I*, 1972, 713.