# Hexafluoroacetone Adducts of Phosphines containing a Group Susceptible to Nucleophilic Attack

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The betaines formed by attack of the tervalent phosphorus compounds R_2PX (X = NCO, NCS, or CH:CH$_2$) on the oxygen atom of hexafluoroacetone (HFA) cyclise to give ylides which react further with HFA to give bicyclic phosphoranes. A 1,3,2-oxazaphosphetan is formed from the phosphoramidite $(PhO)_2P \cdot NHPh$ and HFA.

THE initial reaction between hexafluoroacetone (HFA) and phosphines is thought to be formation of the betaine (1) by attack of phosphorus on the carbonyl oxygen atom.[1,2] Further addition to a second molecule of HFA followed by cyclisation gives either the kinetically favoured 1,3,4-dioxaphospholan (2) or the more stable 1,3,2-dioxaphospholan (3). In many cases compound (2) appears to be formed at low temperatures and rearranges at room temperature to give (3). With a secondary phosphine,[2] proton transfer in the betaine (1; R^3 = H) gives a phosphinite ester (4), isolated as the phosphinate after oxidation, while with a tertiary phosphine containing an α-hydrogen atom [3,4] proton transfer in the betaine (1; R^3 = R^{4}CH$_2$) leads to the

ylide (5), which with a further molecule of HFA gives the 1,2-oxaphosphetan (6). In some cases the 1,3,2-

dioxaphospholans (3) rearrange on heating to form the 1,2-oxaphosphetans (6). This paper reports the re-
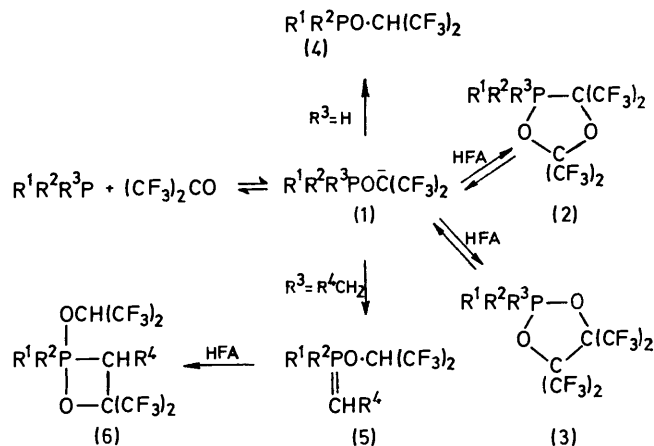
[1] F. Ramirez, C. P. Smith, J. F. Pilot, and A. S. Gulati, *J. Org. Chem.*, 1968, **33**, 3787.
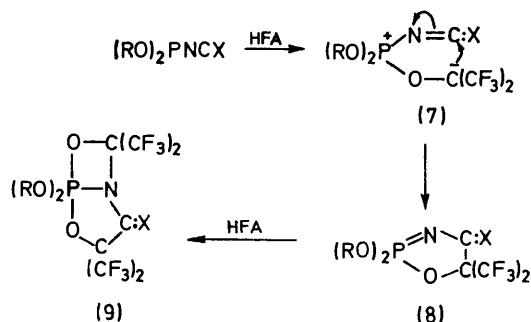
[2] R. F. Stockel, *Chem. Comm.*, 1968, 1594.

[3] F. Ramirez, C. P. Smith, and J. F. Pilot, *J. Amer. Chem. Soc.*, 1968, **90**, 6726.

[4] Mazhar-Ul-Haque, C. N. Caughlan, F. Ramirez, J. F. Pilot, and C. P. Smith, *J. Amer. Chem. Soc.*, 1971, **93**, 5229.

actions of HFA with phosphines containing a group susceptible to nucleophilic attack and with an amino-phosphine.

Diethyl phosphoroisocyanatidite and diethyl phosphoroisothiocyanatidite with HFA gave crystalline 1 : 2 adducts rapidly hydrolysed by moisture and formulated
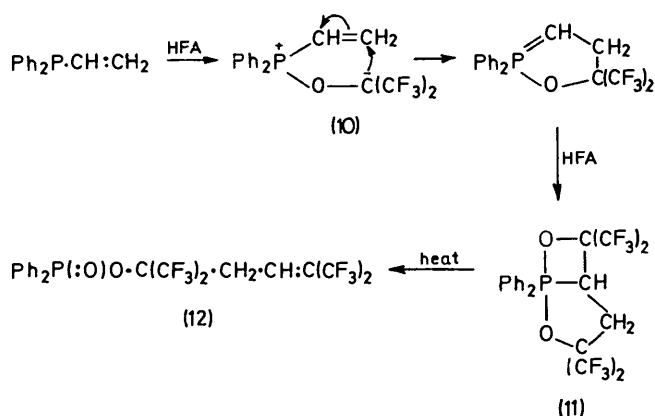
as the bicyclic phosphoranes (9; R = Et, X = O or S). Both adducts showed positive ^{31}P chemical shifts,

of the NCX groups were absent and compound (9; R = Et, X = O) showed the expected carbonyl absorption at 1780 cm^{-1}. The corresponding adduct from diphenyl phosphoroisocyanatidite, *i.e.* (9; R = Ph, X = O), was hydrolytically more stable and gave the expected molecular ion peak in its mass spectrum. The major fragmentation involved loss of HFA, and heating compound (9) led to loss of HFA rather than to intramolecular imine formation.

The bicyclic phosphoranes (9) are presumably formed by cyclisation of the initial betaines (7) followed by reaction of the resulting stabilised ylides (8) with a second molecule of HFA. Strain in the trigonal bipyramidal phosphoranes is minimised by having both rings apical-equatorial and the nitrogen equatorial.

Diphenylvinylphosphine with HFA gave a stable 1 : 2 adduct formulated as the bicyclic phosphorane (11), formed *via* cyclisation of the intermediate vinylphosphonium salt (10). The mass and n.m.r. spectra were as expected for structure (11) except for coincidence of two of the four expected ^{19}F signals. At 160° the adduct smoothly underwent the final stage of a Wittig olefin synthesis and gave the phosphinate (12).

The phosphoramidite (PhO)$_2$P·NHPh with HFA gave a stable 1 : 2 adduct formulated as the 1,3,2-oxazaphosphetan (14), formed *via* the nitrogen ylide (13). The mass and n.m.r. spectra were in agreement with this structure. At 130 °C compound (14) gave the phosphate (15) and the imine (16), together with HFA and the ylide (13) from which the phosphoramidate (17) was obtained after chromatography.

Previous examples of cyclisation of the betaines formed from phosphines and electrophiles include the reactions of diphenyl-(α-phenylvinyl)phosphine[5] and methylenaminophosphines[6] with electrophilic olefins and the reactions of diethyl phosphoroisocyanatidite with aldehydes[7] and with ethyl pyruvate.[8]
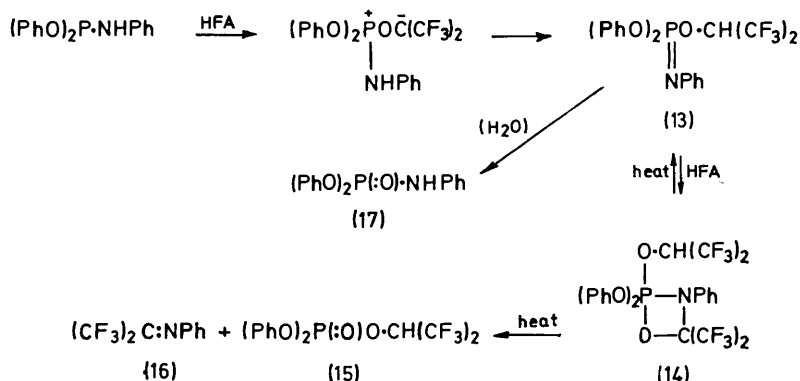
equivalent ethoxy-groups in their ^{1}H n.m.r. spectra, and two singlets of equal intensity in their ^{19}F n.m.r. spectra. Furthermore the characteristic i.r. absorptions

EXPERIMENTAL

^{19}F N.m.r. chemical shifts are quoted relative to internal PhCF$_3$; ^{31}P n.m.r. shifts were recorded for solutions in

[5] M. P. Savage and S. Trippett, *J. Chem. Soc. (C)*, 1968, 591.
[6] A. Schmidpeter and W. Zeiss, *Angew. Chem. Internat. Edn.*, 1971, **10**, 396; W. Zeiss and A. Schmidpeter, *Tetrahedron Letters*, 1972, 4229.

[7] R. I. Tarasova, N. M. Kislitsyna, and A. N. Pudovik, *J. Gen. Chem. (U.S.S.R.)*, 1971, **41**, 1989.
[8] A. N. Pudovik, I. V. Gur'yanova, and V. P. Kakurina, *J. Gen. Chem. (U.S.S.R.)*, 1971, **41**, 1993.

ether and are quoted relative to external 85% H_3PO_4. Shifts to high field are positive.

Reaction of Phosphines with Hexafluoroacetone.—Hexafluoroacetone (40 mmol) was condensed into a solution of the phosphine (10 mmol) in dichloromethane, light petroleum, or ether (10 ml) at $-78°$. The mixture was kept at $-78°$ for 0·5 h and allowed to warm to room temperature with a solid carbon dioxide–acetone condenser in place. Solvent was then removed under reduced pressure and the residue was crystallised from light petroleum.

Diethyl phosphoroisocyanatidite gave 5,5-*diethoxy*-3,3,7,7-*tetrakistrifluoromethyl*-4,6-*dioxa*-1-*aza*-5-*phosphabicyclo*-[3.2.0]*heptan*-2-*one* (9; R = Et, X = O) (81%), m.p. 40—50° (decomp.), $\nu_{max.}$ 1780, 1720, 1450, 1210, and 1040 cm^{-1}, τ 5·65 (4H, dq, J 10 and 8 Hz) and 8·56 (6H, dt, J 2 and 8 Hz), δ (^{19}F) +11·4 (6F, s) and +14·4 p.p.m. (6F, s), δ (^{31}P) +36 p.p.m. (Found: C, 26·65; H, 2·1; F, 45·6. $C_{11}H_{10}F_{12}NO_5P$ requires C, 26·65; H, 2·2; F, 46·0%).

Diethyl phosphoroisothiocyanatidite gave 5,5-*diethoxy*-3,3,7,7-*tetrakistrifluoromethyl*-4,6-*dioxa*-1-*aza*-5-*phosphabicyclo*[3.2.0]*heptane*-2-*thione* (9; R = Et, X = S) (88%), m.p. below room temp., $\nu_{max.}$ 1424, 1220, 1042, 974, 800, and 723 cm^{-1}, τ 5·62 (4H, dq, J 10 and 8 Hz) and 8·6 (6H, dt, J 2 and 8 Hz), δ (^{19}F) +12·1 (6F, s) and +13·5 p.p.m. (6F, s), δ (^{31}P) +30 p.p.m. (Found: C, 25·5; H, 2·05; F, 44·65. $C_{11}H_{10}F_{12}NO_4PS$ requires C, 25·8; H, 1·95; F, 44·6%).

Diphenyl phosphoroisocyanatidite gave 5,5-*diphenoxy*-3,3,7,7-*tetrakistrifluoromethyl*-4,6-*dioxa*-1-*aza*-5-*phosphabicyclo*[3.2.0]*heptan*-2-*one* (9; R = Ph, X = O) (85%), m.p. 94—95°, $\nu_{max.}$ 1789, 1590, 1490, 1458, 1224, 890, 832, and 722 cm^{-1}, δ (^{19}F) +11·3 (6F, s) and +14·4 p.p.m. (6F, s), δ (^{31}P) +49 p.p.m., *m/e* 591, 572, 522, and 348 (Found: C, 38·35; H, 1·7; F, 38·8. $C_{19}H_{10}F_{12}NO_5P$ requires C, 38·6; H, 1·85; F, 38·6%). At 100° for 10 min the adduct lost 26·3% of its weight but no pure compound could be isolated from the residue.

Diphenylvinylphosphine gave 1,1-*diphenyl*-3,3,6,6-*tetrakistrifluoromethyl*-2,7-*dioxa*-1-*phosphabicyclo*[3.2.0]*heptane* (11) (92%), m.p. 32—33°, $\nu_{max.}$ 1450, 1372, 1340, 1315, 1208, 1138, 1100, 954, 879, 820, and 720 cm^{-1}, τ 1·5—2·3 (4H, m), 2·4—2·75 (6H, m), 4·8—5·75 (1H, m), and 6·9—8·25 (2H, m), *m/e* 544, 475, 378, 307, 217, and 201, δ (^{19}F) +9·08 (3F, q,

J 16 Hz), +13·35 (6F, m), and +14·45 p.p.m. (3F, q, J 16 Hz), δ (^{13}P) +17 p.p.m. (Found: C, 44·1; H, 2·5; F, 42·2. $C_{20}H_{13}F_{12}O_2P$ requires C, 44·2; H, 2·5; F, 41·9%). On heating to 160° for 0·5 h the adduct gave 5,5,5-*trifluoro*-1,1,4-*tristrifluoromethylpent*-3-*enyl* *diphenylphosphinate*, m.p. 48—50° (from light petroleum), $\nu_{max.}$ 1720, 1460, 1375, 1220, 1160, 730, and 690 cm^{-1}, τ 1·75—2·8 (10H, m), 2·8—3·15 (1H, m), and 6·25—6·6 (2H, m), δ (^{19}F) −3·51 (3F, q, J 13·2 Hz), +2·35 (3F, q, J 1·32 Hz), and +11·19 p.p.m. (6F, s), δ (^{31}P) −35 p.p.m. *m/e* 544, 523, 473, 394, 306, 217, and 201.

Diphenyl *N*-phenylphosphoramidite gave 2-(2,2,2-*trifluoro*-1-*trifluoromethylethoxy*)-2,2-*diphenoxy*-3-*phenyl*-4,4-*bistrifluoromethyl*-1,3,2-*oxazaphosphetan* (14), m.p. 72·5—73·5° (from ethanol), δ (^{19}F) +10·25 (6F, d, J 6 Hz) and +12·8 p.p.m. (6F, s), δ (^{31}P) +63·7 p.p.m., *m/e* 622 (M − F), 548, 475, and 400 (Found: C, 45·0; H, 2·65; F, 35·3; N, 2·35. $C_{24}H_{16}F_{12}NO_4P$ requires C, 44·95; H, 2·5; F, 35·55; N, 2·2%). The oxazaphosphetan was heated at 150° for 1 h and volatile products were trapped at −78°. The trap contained hexafluoroisopropylideneaniline (16), $\nu_{max.}$ 1590, 1250, and 1175 cm^{-1}, δ (^{19}F) −1·16 (3F, m), and +6·97 p.p.m. (3F, m), *m/e* 241, 222, and 172 which appeared to dimerise during 1 week at −20° (*m/e* then 463 and 394). The residue showed *m/e* 475 (13) and 400 (15) with no 325 (17) and an ^{19}F spectrum consisting of two doublets of about equal intensity. Chromatography of the residue (1 g) on silica and elution with benzene gave 2,2,2-*trifluoro*-1-*trifluoromethylethyl diphenyl phosphate* (15) (0·3 g), m.p. and mixed m.p. with an authentic sample prepared from hexafluoropropan-2-ol and diphenyl phosphorochloridate in the presence of triethylamine 34·5—36·5° (from dichloromethane–light petroleum), τ 2·78 (10H, m), and 4·45 (1H, m, J 6 Hz), δ (^{19}F) +11·4 p.p.m. (d, J 6 Hz), δ (^{31}P) +13 p.p.m., *m/e* 400, 381, 3307, and 233 (Found: C, 45·0; H, 3·0. $C_{15}H_{11}F_6O_4P$ requires C, 45·0; H, 2·8%). Elution with methanol gave diphenyl *N*-phenylphosphoramidate (0·5 g), m.p. and mixed m.p. 126—129°.