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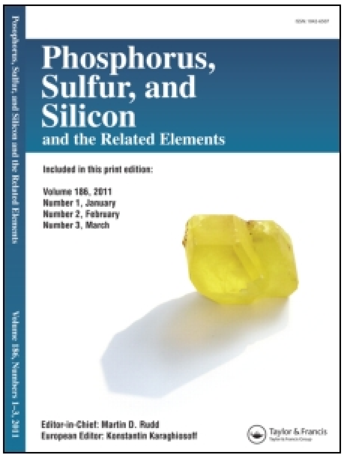

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THE RELATIVE APICOPHILICITIES OF PSEUDOHALOGEN SUBSTITUENTS IN FIVE CO-ORDINATE PHOSPHORANES

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THE RELATIVE APICOPHILICITIES OF PSEUDOHALOGEN SUBSTITUENTS IN FIVE-CO-ORDINATE PHOSPHORANES

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Variable temperature nmr spectroscopy on the 1 : 1-adduct of cyanodiphenylphosphine and perfluorobiacetyl and on the phosphoranes formed from tetrachloro-*o*-benzoquinone and various 2-substituted 4,4,5,5-tetramethyl-1,3,2-dioxaphospholans has led to an order of relative apicophilicity in these phosphoranes of CN > Cl ~ NCO ~ NCS > N_3 > OPh. Hexafluoroacetone and 2-(2′,4′,6′-trimethylbenzoyl)-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan gave the oxide (**8**).

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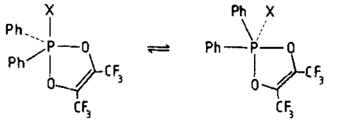
Continuing our investigations[1] on the relative apicophilicities of substituents in five-co-ordinate phosphoranes, we report here on some pseudohalogen groups.

CYANO

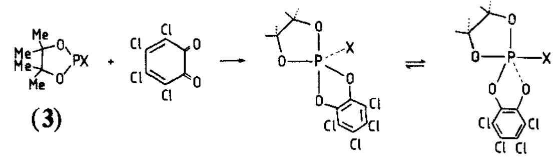
Cyanodiphenylphosphine condensed with perfluorobiacetyl[2] to give the phosphorane (**1**; X = CN). The two equal intensity ^{19}F nmr signals of (**1**; X = CN) coalesced reversibly at 30 ± 1°C giving a free energy of activation for the pseudorotation (**1**; X = CN) $\rightleftharpoons$ (**2**; X = CN)[2] of 13.9 ± 0.1 kcal mol^{-1}. This value compares with that of 12.3 kcal mol^{-1} for the corresponding chlorophosphorane and shows that, in this system, the cyano group is more apicophilic than the chlorine atom.



(**1**) (**2**)

Confirmation of this was obtained from a study of the spirophosphoranes (**4**) derived from tetrachloro-*o*-benzoquinone. The cyanophosphorane (**4**; X = CN) was obtained from condensation of the *P*-cyano-1,3,2-dioxaphospholan (**3**; X = CN) with tetrachloro-*o*-benzoquinone and from the *P*-chlorophosphorane (**4**; X = Cl)[3] and silver cyanide in acetonitrile. It showed only weak absorption in the infra-red at 2210 cm^{-1} but had ^{31}P −38.9 ppm (CH_2Cl_2) and the expected mass spectrum. The two equal intensity signals (Δν 8 Hz) in the ^1H nmr spectrum of (**4**; X = CN) in CCl_4, due to the four methyl groups, coalesced reversibly at 46 ± 2°C corresponding to ΔG* for the pseudorotation (**4**; X = CN) $\rightleftharpoons$ (**5**; X = CN) of 16.9 ± 0.1 kcal mol^{-1}. This compares with ΔG* for the corresponding pseudorotation of (**4**; X = Cl) of 17.8 kcal mol^{-1}.[3]

The high relative apicophilicity of the cyano-group must be due to its electronegativity and its π-acceptor properties.[4]



(**3**) (**4**) (**5**)

ISOCYANATO AND ISOTHIOCYANATO

The 1,3,2-dioxaphospholans (**3**; X = NCO or NCS) were obtained from the corresponding chlorophosphite on refluxing in acetonitrile with the appropriate sodium salt. Addition of tetrachloro-*o*-benzoquinone then gave the spirophosphoranes (**4**; X = NCO or NCS). These were not obtained crystalline but the physical data leave no doubt about their structures. The ^1H nmr spectrum of (**4**; X = NCO) in CCl_4 showed two equal intensity signals (Δν 6 Hz) which coalesced reversibly at 53°C corresponding to ΔG* for the pseudorotation (**4**; X = NCO) $\rightleftharpoons$ (**5**;

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X = NCO) of 17.5 ± 0.2 kcal mol^{-1}. The similar spectrum of (**4**; X = NCS) in 1,1,2,2-tetrachloroethane (T_c 57°C; $\Delta\nu$ 5 Hz) led to a value of 17.8 ± 0.1 kcal mol^{-1} for the free energy of activation of the pseudorotation (**4**; X = NCS) $\rightleftharpoons$ (**5**; X = NCS).

The isocyanato and isothiocyanato groups are therefore very similar in apicophilicity to the chlorine atom.

AZIDO

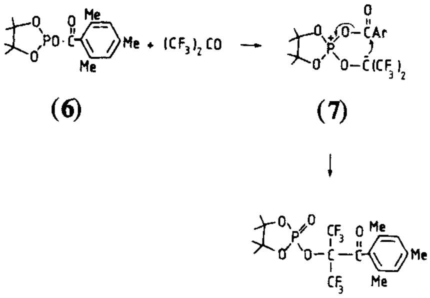
The azidophosphorane (**4**; X = N_3) was obtained from the corresponding chlorophosphorane and sodium azide in acetonitrile at room temperature. The ^{31}P nmr chemical shift (+7.8 ppm) was unexpectedly high but the mass and infra-red spectra were in favour of the structure (**4**; X = N_3). The ^1H nmr spectrum in 1,1,2,2-tetrachloroethane showed two equal intensity signals ($\Delta\nu$ 3 Hz), due to the methyl groups, which coalesced reversibly at 76 ± 2°C leading to a value of 19.3 ± 0.1 kcal mol^{-1} for the free energy of activation of the pseudorotation (**4**; X = N_3) $\rightleftharpoons$ (**5**; X = N_3). In this system the azido group is therefore less apicophilic than the chlorine atom but more apicophilic than the phenoxy group[3] for which the corresponding ΔG^* is 20.5 kcal mol^{-1}.

MISCELLANEOUS

Among the potentially highly apicophilic groups for which evidence on relative apicophilicity is so far lacking are the acyloxy groups RCO.O. We have tried, unsuccessfully, to prepare phosphoranes that would give data on the 2,4,6-trimethylbenzoyloxy group, chosen in order to minimize the possibility of acyl migration in intermediate betaines.[5]

No phosphorane formation was observed in the ^{31}P nmr spectrum when perfluorobiacetyl was treated with diphenyl-2,4,6-trimethylbenzoyloxyphosphine obtained from chlorodiphenylphosphine and 2,4,6-trimethylbenzoic acid in the presence of triethylamine. Similarly no phosphoranes were formed from perfluorobiacetyl and diphenyltrimethylsilylphosphine or diphenyltrifluoromethylphosphine. The latter was obtained from diphenyltrimethylsilylphosphine and trifluoroiodomethane in ether at −78°C, a more convenient route than those reported.[6]

The chloro-1,3,2-dioxaphospholan (**3**; X = Cl) with 2,4,6-trimethylbenzoic acid and triethylamine gave the phosphite (**6**). With tetrachloro-*o*-benzoquinone this did not give a phosphorane while with hexafluoroacetone a 1:1-adduct was formed in high yield to which the formula (**8**) is assigned on the basis of its ^{31}P nmr chemical shift of +3.0 ppm, the sharp singlet in its ^{19}F nmr spectrum even at low temperature, and its infra-red absorption at 1730 cm^{-1}. (**8**) is presumably formed *via* the betaine (**7**) despite the *o*-methyl groups.



(**6**) (**7**) (**8**)

With tetrachloro-*o*-benzoquinone, the trimethylsiloxy-1,3,2-dioxaphospholan (**3**; X = $OSiMe_3$) gave a crystalline spirophosphorane (**4**; X = $OSiMe_3$). However, the four ring-methyl groups of the adduct showed only a single absorption in the ^1H nmr spectrum in all solvents investigated.

EXPERIMENTAL

^{19}F nmr spectra were determined at 94.1 MHz and chemical shifts are relative to internal $PhCF_3$. ^{31}P nmr spectra were obtained at 24.3 MHz; chemical shifts are relative to external 85% H_3PO_4. Positive shifts are downfield from the reference in both cases. ^1H nmr spectra were obtained at 60 MHz in $CDCl_3$ solution unless otherwise stated.

P-*Cyano*-P,P-*diphenyl-4,5-bistrifluoromethyl-1,3,2-dioxaphospholene* (1; X = CN)

Anhydrous silver cyanide (0.05 mol) and chlorodiphenylphosphine (0.05 mol) in xylene (25 ml) were refluxed for 16 h and filtered. Distillation then gave cyanodiphenylphosphine (56%), bp 180–182° at 1.5 mmHg (literature[7] bp 187–188° at 13.5 mmHg). Because of the very weak absorption at 2190 cm^{-1} the cyanophosphine was characterized as the sulphide, mp 49–50° (literature[8] mp 50–52°), ν_{max} 2180 cm^{-1}.

Hexafluorobiacetyl (5 mmol) was distilled into a solution of the cyanophosphine (5 mmol) in dichloromethane (5 ml) at −78°C under a dry-ice condenser. The mixture was allowed to come to room temperature over 0.5 h and the solvent evaporated. Extraction of the residue with light petroleum (bp 30–40°C) and removal of the solvent gave (**1**; X = CN), δ_P (CH_2Cl_2) −43.6, δ_F (CH_2Cl_2) −10.31 (3F, m) and −13.06 (3F, m), ν_{max} 2200 cm^{-1}, *m*/*e* 405, 384, 379, 342, 327, 298, 260, and 201.

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2-Cyano-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (**3**; X = CN)

A stirred mixture of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (0.1 mol), silver cyanide (0.1 mol), and acetonitrile (50 ml) was heated under reflux for 6 h. Filtration and distillation then gave (**3**; X = CN) (50%), bp 74–78° at 0.75 mmHg, δ_{H} 1.34 (6H, s) and 1.50 (6H, s), δ_{P} 174.6, *m/e* 173, 149, 147, 122, 106, and 83, ν_{max} 2095 cm^{-1}.

Similar reactions using sodium cyanate and sodium thiocyanate gave the 2-isocyanato-compound (**3**; X = NCO, 56%), bp 95–97° at 1.3 mmHg, δ_{H} 1.40 (s), δ_{P} ($CDCl_3$) 175.2, *m/e* 189, 149, 147, 124, 122, 106, 85, and 83, ν_{max} 2240 cm^{-1}, and the 2-isothiocyanato-compound (**3**; X = NCS, 40%), bp 115–118° at 1.3 mmHg, δ_{H} 1.28 (6H, s), and 1.40 (6H, s), δ_{P} ($CDCl_3$) 127.6, *m/e* 205, 190, 147, 122, 107, 100, 89, and 83, ν_{max} 2000 cm^{-1}.

Preparation of Spirophosphoranes using Tetrachloro-o-benzoquinone

Tetrachloro-*o*-benzoquinone (5 mmol) in ether (20 ml) was added slowly to a stirred solution of the tervalent phosphorus compound (**3**; 5 mmol) in ether (5 ml) and the solution set aside until the colour was discharged. Evaporation and extraction of the residue with ethyl acetate–light petroleum gave the following. 2-Trimethylsiloxy-4′,4′,5′,5′-tetramethyl-tetrachloro-1,3,2-benzodioxaphosphole-2-spiro-2′-1′-3′-2′-dioxaphospholan (**4**; X = $OSiMe_3$), mp 171–172°, δ_{H} 0.34 (9H, s) and 1.49 (12H, s), δ_{P} ($CDCl_3$) −35.9 (Found: C, 37.75; H, 4.2. $C_{15}H_{21}O_5Cl_4PSi$ requires c, 37.35; H, 4.4%). The 2-cyanophosphorane (**4**; X = CN), δ_{H} 1.43, δ_{P} −38.9, *m/e* 423, 421, 419, and 417, ν_{max} 2210 cm^{-1}. The 2-isocyanatophosphorane (**4**; X = NCO), δ_{H} 1.42, δ_{P} −14.5, *m/e* 439, 437, 435, and 433, ν_{max} 2270 cm^{-1}. The 2-isothiocyanatophosphorane (**4**; X = NCS), δ_{H} (CCl_4) 1.40 (6H, s) and 1.46 (6H, s), δ_{P} −42.7, *m/e* 455, 453, 451, and 449, ν_{max} 2000 cm^{-1}.

2-Azido-4′,4′,5′,5′-tetramethyl-tetratrachloro-1,3,2-benzodioxaphosphole-2-spiro-2′-1′,3′,2′-dioxaphospholan (**4**; X = N_3)

The 2-chlorophosphorane (**4**; X = Cl, 10 mmol)[3] in acetonitrile (30 ml) was stirred with sodium azide (10 mmol) at room temperature for 2 days. Filtration, evaporation below room temperature, and extraction of the residue with cold ethyl acetate gave (**4**; X = N_3), δ_{H} 1.49, δ_{P} 7.8, *m/e* 439, 437, 435, and 433, ν_{max} 2180 cm^{-1}. A similar procedure using silver cyanide gave the 2-cyanophosphorane (**4**; X = CN) described above.

2-Trimethylsiloxy-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan (**3**; X = $OSiMe_3$)

Chlorotrimethylsilane (0.25 mol) was added slowly to a stirred solution of 4,4,5,5-tetramethyl-1,3,2-dioxaphospholan 2-oxide[9] (0.15 mol) and triethylamine (0.25 mol) in benzene (150 ml) and the mixture heated under reflux for 1 h. Filtration and distillation gave (**3**; X = $OSiMe_3$) (70%), bp 50–55° at 0.05 mmHg, δ_{H} 0.20 (9H, s), 1.22 (6H, s), and 1.36 (6H, s), δ_{P} 126.9, *m/e* 236, 210, 155, 149, 122, and 106, characterized as the sulphide, mp (from light petroleum) 50–53°, δ_{H} 0.30 (9H, s), 1.32 (6H, s), and 1.40 (6H, s), δ_{P} (CH_2Cl_2) 54.6 (Found: C, 40.65; H, 7.55; P, 11.85. $C_9H_{21}O_3PSSi$ requires C, 40.3; H, 7.85; P, 11.55%.)

Diphenyltrifluoromethylphosphine

Trifluoroiodomethane (0.02 mol) was condensed into a stirred solution of diphenyltrimethylsilylphosphine[10] (0.02 mol) in ether (20 ml) at −78°C. The mixture was then allowed to warm to room temperature and distilled to give diphenyltrifluoromethylphosphine (78%), bp 150–160° at 15 mmHg (literature[6] bp 255–257°), δ_{F} (CH_2Cl_2) 7.83 (d, *J* 72 Hz).

Diphenyl-2,4,6-trimethylbenzoyloxyphosphine

2,4,6-Trimethylbenzoic acid (0.05 mol) in ether (50 ml) was added slowly to chlorodiphenylphosphine (0.05 mol) and triethylamine (0.05 mol) in ether (150 ml) at 0°C. The mixture was then refluxed for 1 h, cooled and filtered, and the filtrate evaporated. Crystallization of the residue from ethyl acetate–light petroleum gave diphenyl-2,4,6-trimethylbenzoyloxyphosphine (87%), mp 112–114°, δ_{H} 2.25 (6H, s), 2.35 (3H, s), 6.90 (2H, s), and 7.3–8.2 (10H, m), δ_{P} (CH_2Cl_2) 103.2, *m/e* 348, 325, 319, 293, 262, 219, and 201, ν_{max} 1745 cm^{-1} (Found: C, 75.45; H, 6.0; P, 8.9. $C_{22}H_{21}O_2P$ requires C, 75.85; H, 6.1; P, 8.9%). The corresponding sulphide had mp 115–116°, δ_{P} (CH_2Cl_2) 77.1 (Found: C, 69.6; H, 6.0; P, 8.7. $C_{22}H_{21}O_2PS$ requires C, 69.45; H, 5.6; P, 8.4%).

A similar reaction gave (**6**), bp 180–185° at 0.45 mmHg, δ_{H} 1.31 (6H, s), 1.40 (6H, s), 2.29 (3H, s), 2.36 (6H, s), and 6.80 (2H, s), δ_{P} (CH_2Cl_2) 135.6, *m/e* 310, ν_{max} 1710 cm^{-1}.

Reaction of (**6**) *with Hexafluoroacetone*

Hexafluoroacetone (22 mmol) was condensed into a solution of (**6**; 10 mmol) in ether (30 ml) at −78°C. After 0.5 h the solution was allowed to warm to room temperature. Evaporation and crystallization of the residue from ethyl acetate-light petroleum gave 2[1′,1′,1′,3′,3′,3′-hexafluoro-2′-(2″, 4″,6″-trimethylbenzoyl)isopropoxy]-4,4,5,5-tetramethyl-1,3,2-dioxaphospholan 2-oxide (**8**; 98%), mp 120.5–121°, δ_{H} 1.11 (6H, s), 1.43 (6H, s), 2.24 (6H, s), 2.30 (3H, s), and 6.94 (2H, s), δ_{P} (CH_2Cl_2) 3.0. δ_{F} ($CDCl_3$) −3.23 (s), *m/e* 476, 395, 377, 321, 296, 280, 227, 211, and 169, ν_{max} 1730 cm^{-1} (Found: C, 48.0; H, 4.85; P, 6.5. $C_{19}H_{23}O_5F_6P$ requires C, 47.9; H, 4.85; P, 6.5%).

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