Primary α-Dichloromethylphosphine; a Precursor of Unhindered *C*-Chlorophosphaethylene and Synthetic Equivalent of Phospha-acetylene

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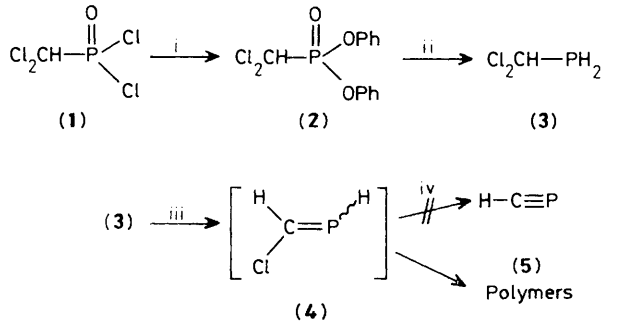
α-Dichlorophosphine (**3**), easily obtained by chemoselective phosphonate reduction, is a precursor of the unhindered *C*-chlorophosphaethylene (**4**) and a synthetic equivalent of the phospha-acetylene (**5**).

Recent research demonstrated that λ^3-phospha-alkynes bearing bulky substituents are stable at room temperature and have synthetic potential,[1] as they react with 1,3-dipoles,[1,2] 1,3-dienes,[3] or silylenes[4] and can be bound in transition metal complexes.[5] Furthermore, dimerization or trimerization within the co-ordination sphere was observed.[1b,6] However, the simplest members are stable at low temperature only, and with the exception of the parent compound HCP,[7,8] no efficient synthetic route is yet available.

We have recently shown that unhindered phospha-alkenes including the parent compound CH_2=PH can be easily formed by dehydrochlorination of the corresponding α-chloroalkyl-



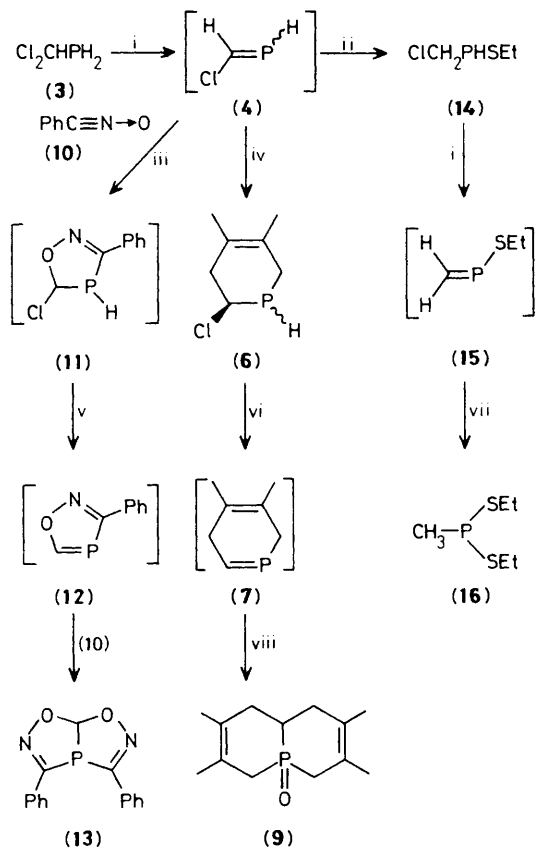
Scheme 1. *Reagents and conditions*: i, PhOH, Et_3N, CH_2Cl_2; ii, $AlHCl_2$, tetraglyme or Et_2O; iii, DABCO, tetrahydrofuran, −80 °C; iv, Lewis base.

phosphine.[9] We now describe the synthesis of the primary α-dichlorophosphine (**3**) and show that this species is a precursor of the unstabilized *C*-chlorophospha-alkene (**4**) and a synthetic equivalent of the phospha-acetylene (**5**).

Esterification of (**1**) with phenol led to the dichlorophosphonate (**2**) in 77% yield (Scheme 1). The major problem was to determine the specific conditions for the chemoselective reduction of (**2**). Reduction *in vacuo* using AlH_3 in tetraglyme, according to the procedure recently described for the preparation of α-chloromethylphosphine,[10] gave only analytical samples of (**3**). Attempts to extend this reaction to the gram-scale produced mainly polymers. However, a preparative approach succeeded using $AlHCl_2$ in diethyl ether at low temperature,† with removal of most of the solvent by trap-to-trap distillation at the end (yield 88%). No product due to the reduction of the C–Cl or C–P bonds was detected [^{31}P n.m.r.; δ −79.8 (J_{P-H} 200, J_{H-C-P} 6.8 Hz); ^1H n.m.r., δ 4.00 (dd, 2H, $J_{H-C-P-H}$ 7.0 Hz), 6.10 (dt, 1H); ^{13}C n.m.r., δ 61.6 (J_{C-P} 26.8 Hz)] (Scheme 1). α-Dichloromethylphosphine (**3**) slowly polymerizes at room temperature but can be kept for several weeks in the presence of a small amount of hydroquinone.

The low temperature HCl elimination (−85 °C) of (**3**) with 1,4-diazabicyclo[2.2.2]octane (DABCO) in a 1/2.2 molar ratio led only to polymeric products. The expected phospha-alkene (**4**) or phospha-alkyne (**5**) were not observed by low temperature ^{31}P n.m.r. experiments. Since (**5**) is stable below −20 °C,[7] the polymers probably originate from (**4**). In the presence of an excess of dimethylbutadiene, no cycloadduct was observed even at low temperature. However, we were able to control the reactivity using a weaker base. The expected cycloadduct (**6**) slowly formed at room temperature (12 h) in pyridine as evidence by monitoring the reaction with ^{31}P n.m.r. [2 stereoisomers: ^{31}P n.m.r., δ −58.4 p.p.m. (J_{P-H} 190.4 Hz), −72.7 p.p.m. (J_{P-H} 185.6 Hz); ^1H n.m.r., δ 1.60 (br. s, 6H, 2 Me), 2.50 (br. s, 2H, CH_2), 2.65 (br. s, 2H, CH_2), 4.10 (m, 1H, CH), P–H not observed]. Further HCl elimination occurred by heating the solution overnight at 60 °C. The transient dihydrophosphorine (**7**) was trapped by dimethylbutadiene leading to the diadduct (**8**) (^{31}P n.m.r., δ −63.5 p.p.m.) and after oxidation to (**9**), [^{31}P n.m.r., δ 46.0 p.p.m.; *m/z* 224.1330 (calc.), 224.1338 (found)].

† For the preparation of $AlHCl_2$ in diethyl ether see E. C. Ashby and J. Prather, *J. Am. Chem. Soc.*, 1966, **88**, 729. After cooling the mixture at −80 °C, the phosphonate (**2**) was introduced and the temperature allowed to warm to −20 °C then water added (2 equivs. with respect to $LiAlH_4$). For use of $AlHCl_2$ as specific reducing agent of phosphonates bearing a functional group in α-position see J. L. Cabioch and J. M. Denis, to be published.



Scheme 2. *Reagents and conditions*: i, Pyridine, 20 °C; ii, EtSH, 20 °C; iii, 20 °C; iv, 20 °C, CH_2=CMeCMe=CH_2; v, pyridine; vi, 60 °C, pyridine; vii, EtSH; viii, CH_2=CMeCMe=CH_2, followed by oxidation.

The *C*-chlorophospha-alkene intermediate (**4**) also reacts with benzonitrile oxide (**10**) in pyridine. The primary cycloadduct (**11**) could not be isolated. A further HCl elimination occurred leading, *via* the transient phosphole (**12**), to the symmetrical bis-adduct (**13**) in good yield. The orientation of the cycloaddition was confirmed by ^1H and ^{31}P n.m.r.; the spectroscopic data were in good agreement with those of an authentic sample recently synthesised by Regitz in a bis [3 + 2] cycloaddition of the dipole (**10**) with HCP[8] (Scheme 2).

Finally, the unhindered phospha-alkene (**4**) was chemically trapped in a nucleophilic addition. In the presence of ethanethiol, the monoadduct (**14**) was first observed {^{31}P n.m.r., δ −27.3 p.p.m. (J_{P-H} 214.9, J_{P-C-H} 7.3 Hz): ^1H n.m.r., δ 1.25 (t, 3H, *J* 7.5 Hz); 2.50 (m, 2H), 3.72 [m(d + dd), 1H, d; *J* 5.8, dd; *J* 5.3 and 6.6 Hz]: ^{13}C n.m.r., δ 19.1; 19.7; 38.2 (J_{C-P} 29.3 Hz)}. Isolation of this product was tedious, and a second competing elimination led to the bis-adduct (**16**) [^{31}P n.m.r., δ 69.5 p.p.m. (J_{P-C-H} 9.8 Hz)].

Both HCl eliminations from α-dichlorophosphine (**3**) are selective. The first elimination occurred with a weak Lewis base leading to the reactive *C*-chlorophospha-alkene (**4**) which was trapped in a [4 + 2] and [3 + 2] cycloaddition or in a nucleophilic addition. The second HCl elimination occurred only from the primary adduct. The intermediates (**7**), (**12**), and (**15**) can be considered as the adducts of the corresponding diene, dipole, or nucleophile with HCP respectively. The potential of this sequence is also important for new synthetic routes to various heterocycles bearing substituents in a well

defined position as in nucleophilic addition reactions. Similar cycloaddition or nucleophilic addition reactions with *C*-substituted derivatives are in progress.

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