

One Co-ordinate Phosphorus Compounds: 1,3-Dipolar Cycloadditions with 2,2-Dimethylpropylidynylphosphine

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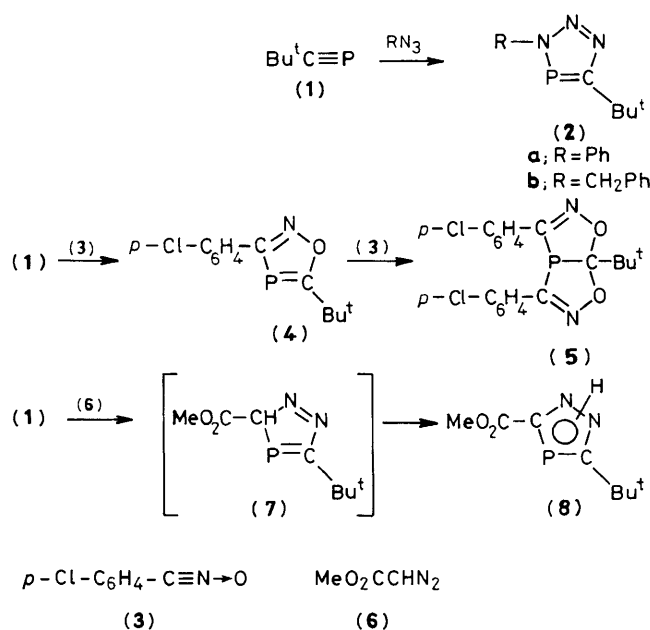
1,3-Dipolar cycloadditions of azides, *p*-chlorobenzonitrile oxide, and methyl diazoacetate with 2,2-dimethylpropylidynylphosphine occur regiospecifically yielding cyclic 'aromatic' monoadducts: triaza-, oxaza-, and diaza-phospholes and the oxazaphosphole can react further with *p*-chlorobenzonitrile oxide to give a symmetrical [3.3.0] phosphorus heterocycle.

Since Gier's synthesis of phosphaethyne,¹ some other phospho-alkynes have been prepared² but the 2,2-dimethylpropylidynylphosphine,³ (1) is the only one described as stable and obtained on a preparative scale at room temperature. If the reactivity of this compound with organometallic derivatives⁴ has been investigated, very few facts concerning its behaviour particularly in cycloaddition reactions are known. Only Märkl *et al.*⁵ suppose the formation of $\text{PhC}\equiv\text{P}$ followed by a Diels-Alder addition to explain the obtention of phosphabenzene in the reaction of $\text{Ph}(\text{Me}_3\text{Si})\text{C}=\text{P}\text{Cl}$ with cyclopentadienones and α -pyrones in the presence of KF and 18-crown-6 ether. The primary cycloadducts have not been isolated.

Compound (1) reacts (CH_2Cl_2 , 12 h) with azides (room temp.), *p*-chlorobenzonitrile oxide (3) (-20°C , >2 equiv.), and methyl diazoacetate (6) (room temp.) giving the stable adducts (2), (5), and (8) (Scheme 1). The reaction is regiospecific and almost quantitative (analysis of crude product by ^{31}P n.m.r. spectroscopy). The adducts (2), (5), and (8) were isolated and had spectroscopic characteristics, mass spectra data, and elemental analyses in agreement with the proposed structures. The structure of the adducts, hence the regiospecificity of reaction, has been established by n.m.r. spectroscopy.† Triazaphospholes (2a): m.p. $50\text{--}51^\circ\text{C}$ (SiO_2 chromatography, CH_2Cl_2); yield‡ 52%; ^{31}P n.m.r. δ 169 p.p.m.; ^{13}C n.m.r. δ 198.6 ($^1J_{\text{PC}}$ 56 Hz, $\text{P}=\text{C}$). (2b): m.p. $71\text{--}72^\circ\text{C}$ (sublimation); yield‡ 24%; ^{31}P n.m.r. δ 170 p.p.m.;

^1H n.m.r. δ 5.65 ($^3J_{\text{PH}}$ 6.8 Hz, CH_2); ^{13}C n.m.r. δ 198.5 ($^1J_{\text{PC}}$ 56 Hz, $\text{P}=\text{C}$).

The assignment of the structure is based on the following facts: (i) for (2b), the value of the coupling constant between P and CH_2 bound to the nitrogen atom is in accordance with $^3J_{\text{PH}}$. If the orientation of the addition of the dipole was inverse, we would have a $^4J_{\text{PH}}$ coupling constant whose value



† Solvent for ^1H and ^{31}P n.m.r. spectroscopy: CH_2Cl_2 ; for ^{31}P downfield shift positive relative to 85% H_3PO_4 .

‡ Isolated pure product. Non optimized yield.

Scheme 1

is expected to be smaller (<2 Hz, as for example in diazaphospholes⁶). (ii) The similar chemical shifts of the ^{31}P n.m.r. and of the cyclic carbon in (2a) and (2b) suggests the same kind of ring arrangement for (2a) and (2b); besides in (2a), a coupling constant of 7 Hz between phosphorus and the *o*-phenyl carbon (δ 122.3 p.p.m.) is more likely to be a $^3J_{\text{PC}}$ than a $^4J_{\text{PC}}$.

The oxazaphosphole (4), obtained with one equivalent of (3), is characterized only in solution by n.m.r. spectroscopy [^{31}P δ 66 p.p.m.; ^{13}C : the two cyclic carbon atoms (δ 226.9 and 176.5) are directly linked to the phosphorus atom as shown by the large coupling constants (63 and 60 Hz)]. This indicates a $^1J_{\text{PC}}$ interaction. The $^2J_{\text{PC}}$ which would be observed, if the orientation of the addition was inverse, would be smaller (diazaphosphole, $^2J_{\text{PC}} < 10$ Hz⁶). With an excess of (3), (5) is obtained as the result of a cycloaddition on (4) [m.p. 224–225 °C (C_6H_6 –EtOH, 1:4); yield‡ 47%; ^{31}P n.m.r. δ –5 p.p.m. (trico-ordinated phosphorus atom)]. The ^1H and ^{13}C n.m.r. data show the symmetry of the molecule. The chemical shifts and the coupling constant in the ^{13}C n.m.r. results confirm the structure [δ 154.0 ($^1J_{\text{PC}}$ 43 Hz, $\text{C}=\text{N}$), 128.8 ($^1J_{\text{PC}}$ 20 Hz, $\text{P}-\text{C}$)].

Diazaphosphole (8) results from the 'aromatization' of the primary cycloadduct (7) [m.p. 140–141 °C (SiO_2 chromatography, CH_2Cl_2 – Et_2O 2:1 or sublimation); yield‡ 52%; ^{31}P n.m.r. δ 96 p.p.m.; ^{13}C n.m.r. δ 192.8 and 164.2 ($^1J_{\text{PC}}$ 62 and 52 Hz)]. The n.m.r. characteristics confirm the structure as discussed for (4).

Compound (1) reacts with 2,3-dimethylbutadiene giving an adduct [2 mol (1)—1 mol 2,3-dimethylbutadiene as deter-

mined by mass spectrometry] with two non equivalent phosphorus atoms [^{31}P n.m.r. δ –211 and –166 p.p.m. (J_{PP} 148 Hz, AB pattern)].

Added in proof: 1,3-dipolar cycloadditions with (1) have been carried out simultaneously by Regitz *et al.* (*Angew. Chem.*, 1984, in the press), personal communication.

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