## $4\pi + 2\pi$ Cycloadditions to *P*-Chlorobis(trimethylsilyl)methylenephosphine: New Cyclic Compounds with a >C=P– Double Bond

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The reaction of *P*-chlorobis(trimethylsilyl)methylenephosphine with several 1,3-dipoles and two dienes gives cycloadducts regiospecifically; these will eliminate Me<sub>3</sub>SiCl at low temperatures if the resulting compound is of an 'aromatic' type, leading to new cyclic >C=P- double bond derivatives.

The reactivity of the recently synthesised<sup>1</sup> open chain phospha-alkenes with 1,3-dipoles and dienes has been studied in a few cases. Niecke *et al.*<sup>2</sup> have reported the reaction of 2,2-dimethyldiazopropane with a *P*-aminophospha-alkene and very recently Van der Knapp *et al.*<sup>3</sup> have reported 1,3 dipolar cycloadditions of triarylphospha-alkenes. Meriem *et al.*<sup>4</sup> and Appel *et al.*,<sup>5</sup> have studied the reactions of 2,3dimethylbutadiene with a *C*-aminophospha-alkene and several *C*-trimethylsilylphospha-alkenes with OR or -N=groups on phosphorus.

The results of the cycloaddition reactions of compound (1) with several 1,3-dipoles and dienes are described in this communication. Compound (1) is obtained in 65% yield, b.p. 30-32 °C/0.05 Torr† following the procedure of Appel *et al.*<sup>6</sup> Some of the primary cycloadducts eliminate Me<sub>3</sub>SiCl on heating leading to 'aromatic' phosphorus heterocycles.

$$(Me_3Si)_2C=P-Cl$$
(1)

Compound (1) reacts almost quantitatively (followed by n.m.r. spectroscopy) with azides (1 equiv.) (Scheme 1) at low temperature ( $CH_2Cl_2$ , -40 °C, R = PhCH<sub>2</sub>; -80 °C, R = Ph) to give the primary cycloadducts dihydro-1,2,3,4-



† Lit.6 yield 57%; b.p. 31 °C/0.0001 Torr.

triazaphospholes (2) which are unstable. Without additives, (2a) slowly eliminates Me<sub>3</sub>SiCl (even at -40 °C, 3 days, 90%, followed by n.m.r. spectroscopy). The thermal reaction of (2b) is much more complicated and many unidentified products are formed (<sup>31</sup>P n.m.r. spectroscopy). Compounds (2) and (3) were characterized in solution by n.m.r. spectroscopy only [(2a) <sup>31</sup>P<sup>±</sup> δ 104 p.p.m. (<sup>3</sup>J<sub>PH</sub> 13 Hz); <sup>13</sup>C, δ 91.2  $({}^{1}J_{PC}79 \text{ Hz}), 51.7 ({}^{2}J_{PC}7 \text{ Hz}, \text{CH}_{2}); (2b) {}^{31}P, \delta 94 \text{ p.p.m.}; {}^{13}C,$  $\delta$  90.6 (<sup>1</sup>J<sub>PC</sub> 78 Hz), 139.6 (<sup>2</sup>J<sub>PC</sub> 11 Hz, quaternary phenyl carbon), 119.8 ( ${}^{3}J_{PC}$  10 Hz, *o*-phenyl carbons); (3)  ${}^{31}P$ ,  $\delta$  212 p.p.m.; <sup>1</sup>H,  $\delta$  5.80 (<sup>3</sup>J<sub>PH</sub> 6 Hz, CH<sub>2</sub>)]. The coupling constants  ${}^{3}J_{PH}$  and  ${}^{2}J_{PC}$  for (2a),  ${}^{2}J_{PC}$  and  ${}^{3}J_{PC}$  for (2b) show unambiguously the regiospecificity of the addition. So far, attempts to purify (3) have been unsuccessful; this product has been characterized in solution only (high resolution mass spectrometry measurements in agreement with proposed structure).

The reaction of (1) with diazocompounds (CH<sub>2</sub>Cl<sub>2</sub>, 1 equiv., -70 °C with methyl diazoacetate and -20 °C with diphenyldiazomethane) gives almost quantitatively the adducts (4) [two diastereoisomers for (4a)]. At -20 °C (4a) loses Me<sub>3</sub>SiCl leading to (5) (Scheme 1): isolated yield 26% after SiO<sub>2</sub> chromatography (CH<sub>2</sub>Cl<sub>2</sub>-diethyl ether, 1:2); m.p. 143—144 °C (mass spectrum and elemental analysis are in agreement with the proposed structure). The thermal behaviour of (4b) has not been studied. The structures of (4) and (5) were established by n.m.r. spectroscopy [(4a) <sup>31</sup>P,  $\delta$  73 (60%) and 72 p.p.m. (40%) (<sup>2</sup>J<sub>PH</sub> 0 and 39 Hz);<sup>7</sup> (4b) <sup>31</sup>P,  $\delta$  86 p.p.m.; <sup>13</sup>C,  $\delta$  96.7 and 116.7 (<sup>1</sup>J<sub>PC</sub> 83 and 60 Hz); (5) <sup>31</sup>P,  $\delta$ 134 p.p.m.; <sup>13</sup>C,  $\delta$  168.8 and 178.9 (<sup>1</sup>J<sub>PC</sub> 66 and 72 Hz)]. The large values of the coupling constants <sup>1</sup>J<sub>PC</sub> show that the P atom lies between the two cyclic carbon atoms.

The reaction of *p*-chlorobenzonitrile oxide (1 equiv.) with (1) (-20 °C, 1 h, CH<sub>2</sub>Cl<sub>2</sub>) gives the adduct (6). After 12 h at room temperature, the oxazaphosphole (7) is formed in 75% yield (Scheme 1). We have been unable to purify compound (7) (oil, n.m.r. spectra show no other major component, high resolution mass spectrum agrees with proposed structure) [n.m.r. data: (6) <sup>31</sup>P,  $\delta$  103 p.p.m.; <sup>13</sup>C,  $\delta$  95.1 and 159.7 (<sup>1</sup>J<sub>PC</sub> 81 and 53 Hz); (7) <sup>31</sup>P,  $\delta$  127 p.p.m.; <sup>13</sup>C,  $\delta$  223.7 and 177.7 (<sup>1</sup>J<sub>PC</sub> 77 and 68 Hz)]. The P atom is bound to two cyclic carbon atoms.

At room temperature, compound (1) reacts with 2,3dimethylbutadiene (7 equiv., without solvent) to give the cycloadduct (8),\$ isolated yield 60%; b.p. 130–135 °C/0.1

<sup>‡</sup> Solvent for <sup>31</sup>P n.m.r. spectra  $CH_2Cl_2$ ; downfield shift positive relative to  $H_3PO_4$  (85%).

§ Compound (8), treated with KF (7 equiv.) and 18-crown-6 (0.2 equiv.) for 7 h at 160 °C (*o*-dichlorobenzene as solvent) gives the phosphabenzene (9) in 30% yield (n.m.r. spectroscopy). The reaction is not optimized and the product has not been isolated. <sup>31</sup>P N.m.r. ( $\delta$  215 p.p.m.) and high resolution mass spectrometry are in agreement with the proposed structure.



Torr (<sup>31</sup>P n.m.r.,  $\delta$  129 p.p.m.; <sup>1</sup>H and <sup>13</sup>C n.m.r. and high resolution mass spectra in agreement with proposed structure).

The reaction of (1) with cyclopentadiene (2 equiv.,  $CH_2Cl_2$ ) is monitored by <sup>31</sup>P n.m.r. spectroscopy. After 1 h at -20 °C, the starting material ( $\delta$  340 p.p.m.) and adducts (10) and (10') ( $\delta$  144 and 148 p.p.m.) are in the ratio 1.2:1:2. After 6 h at room temperature, compound (1) has disappeared and the ratio (10): (10') is 9:1. The coupling constant <sup>2</sup>J<sub>PC</sub> between phosphorus and the methylene carbon (<sup>13</sup>C,  $\delta$  50.1) is zero and in agreement with the proposed structure for (10).<sup>8</sup> At room temperature, the Diels–Alder reaction is probably reversible<sup>9</sup> and the more stable adduct is mainly formed. The mass spectrum of the mixture of (10) and (10') shows cycloreversion and the molecular ion is not observed.

It would appear possible to extend this study to other trimethylsilylphospha-alkenes:  $R(Me_3Si)C=P-Cl$ . Starting from these compounds, it may be possible to obtain new phosphorus 'aromatic' heterocycles. Derivatives of type (1) appear to be phospha-alkyne equivalents. Märkl *et al.*, <sup>10</sup> in the

reaction of Ph(Me<sub>3</sub>Si)C=P-Cl with  $\alpha$ -pyrones and cyclopentadienones leading to phosphabenzene in rather low yield, postulated the formation of Ph-C=P as an intermediate and then a Diels-Alder reaction with this compound. Our procedure seems to be easier in that it is not necessary to generate the phospha-alkyne derivative prior to the cycloaddition.

Added in proof: for analogous 1,2,4-diazaphospholes, see G. Märkl *et al.* and A. Schmidpeter *et al.*, Angew. Chem., 1984, in the press (personal communications).

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