Synthesis of Alkylidenephosphiranes by Extrusion of Nitrogen from 3-Alkylidene-4,5-dihydro-3H-1,2,4-diazaphospholes

Berthold Manz and Gerhard Maas*†

Fachbereich Chemie, Universität Kaiserslautern, D-67663 Kaiserslautern, Germany

The 3-alkylidene-4,5-dihydro-3H-1,2,4-diazaphospholes 4, obtained from diphenylmethylene(mesityl)phosphine 3 and silyl diazo ketones 1, undergo thermal extrusion of nitrogen to form alkenyl phosphines 7 and alkylidenephosphiranes 8; the structures of these products have been established by single crystal X-ray structure analyses.

Three-membered rings containing a phosphorus atom have been investigated in some detail only in the last few years:[1] in particular, phosphiranes[1,2] and 1H-phosphirenes.[3] Phosphacyclopropanes bearing an exocyclic double bond, such as alkylidenephosphiranes,[4] 2,3-bisalkylidenephosphiranes[5,6] and alkylidenediphosphiranes[6,7] are known, but their properties and chemistry have been less well studied. Structure, ring strain and inversion barriers at phosphorus of the first two systems mentioned have been determined by *ab initio* calculations for the parent compounds.[8] The only alkylidenephosphirane so far known was obtained by addition of dichlorocarbene to a 1-phosphaallene.[4] Herein, we describe a new synthetic route to this ring system, providing the first derivatives functionalised at the exocyclic C=C bond, and report the experimentally determined geometry.

Silyl diazo ketones maintain an equilibrium with minor (< 1%) amounts of 2-siloxy-1-diazoalkenes 2, which can be trapped by [3 + 2] cycloaddition with suitable alkenes.[9] Similarly, 1a,b react readily, even at 20 °C, with phosphaalkene 3 to form the 3-alkylidene-4,5-dihydro-3H-1,2,4-diazaphospholes 4 (4a, 30 min, 78% yield; 4b, 16 h, 77%).‡ The regioselectivity of the cycloaddition step is the same as for the cycloaddition of diazoalkanes to several other phosphaalkenes.[10,11] The E-configuration at the exocyclic double bond is indicated by the magnitude of the coupling constant $^4J_{P,CH_3}$ (9.3–9.4 Hz) and is confirmed by a single crystal X-ray structure determination of 4a which will be reported elsewhere.

Thermal extrusion of nitrogen from 4a,b occurs in boiling toluene in 16 h, yielding a mixture of the (2-siloxy-1-alkenyl)phosphines 7a,b and of the alkylidenephosphiranes 8a,b (yields: 7a, 32%; 8a, 47%; 7b, 33%; 8b, 48%.§ These major products can be isolated simply by fractionating crystallisation. The solids are neither oxygen- nor moisture-sensitive. The phosphirane structure is indicated by the ^{31}P NMR signal at high

field ($\delta \approx -135$); as expected, the P nucleus is more strongly shielded than in 2,2-dichloro-3-diphenylmethylene-1-(2,4,6-tri-*tert*-butylphenyl)phosphirane (δ −93.4).[4] The *cis*-relationship between the phosphorus atom and the siloxy group with respect to the exocyclic double bond (Z-configuration) is suggested by a $^5J_{P,CH}$ coupling constant of 4.0 Hz.

Single crystal X-ray structure determinations of 7a and 8a (Figs. 1 and 2) establish that the double bond configuration is E

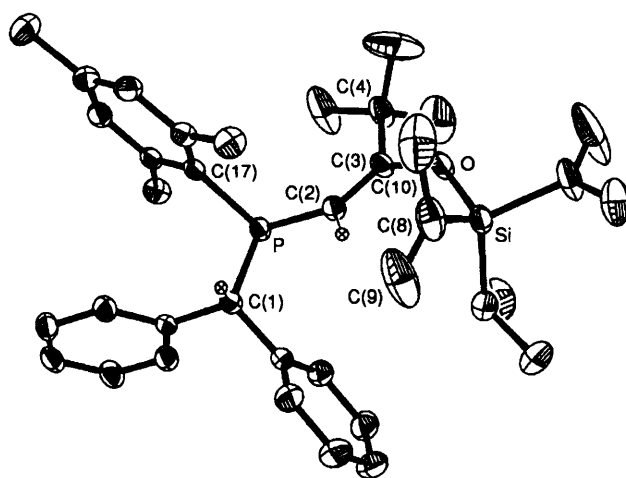
Fig. 1 Crystal structure of 7a with 30% thermal ellipsoids. Selected bond distances (Å) and angles (°): P–C(1) 1.886(4), P–C(2) 1.805(4), P–C(17) 1.853(4), C(2)–C(3) 1.342(5), C(3)–O 1.378(4), O–Si 1.647(3), C(8)–C(9) 1.314(9), C(8)–C(10) 1.500(9); C(1)–P–C(2) 99.3(2), C(1)–P–C(17) 98.7(2), C(2)–P–C(17) 109.1(2), P–C(2)–C(3) 132.6(3), C(2)–C(3)–C(4) 130.2(4), C(2)–C(3)–O 120.1(3), C(3)–O–Si 133.8(2). Selected torsion angles (°) : P–C(2)–C(3)–C(4) 13.1(8), P–C(2)–C(3)–O −169.8(3), C(2)–C(3)–O–Si 10.2(6). See footnote¶ for disorder of the isopropyl group [C(14), C(15), C(16)].
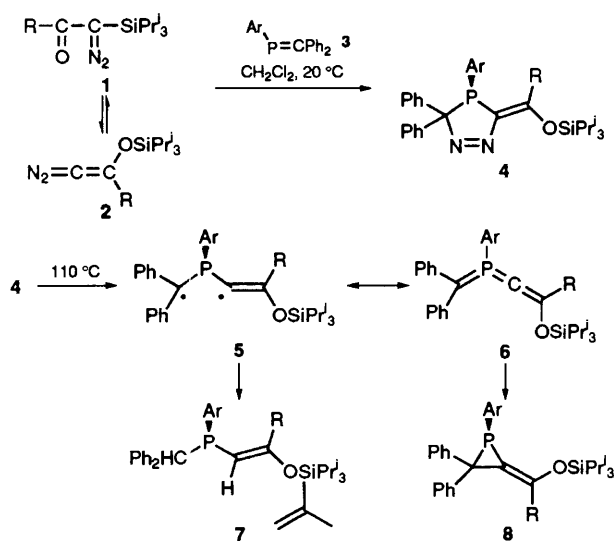
4–8: Ar = 2,4,6-Me₃-C₆H₂; a: R = Buᵗ; b: R = 1-adamantyl
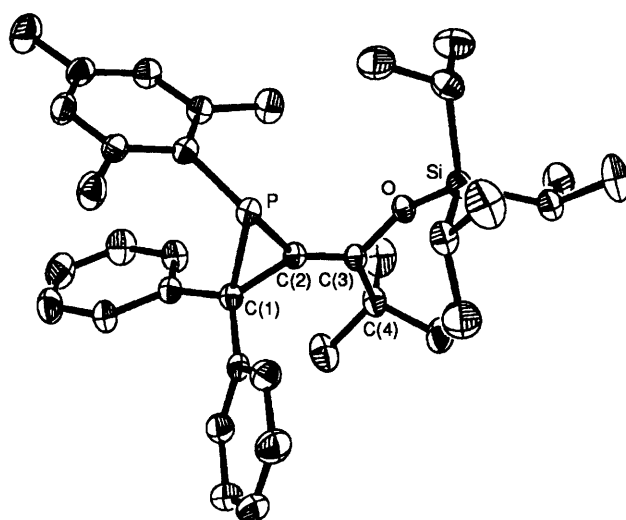
Scheme 1

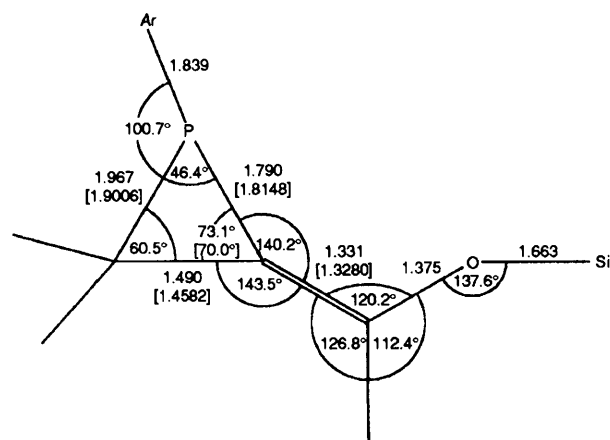Fig. 2 Crystal structure of 8a. For selected bond lengths and angles, see Fig. 3.

Fig. 3 Bond lengths (Å) and angles (°) in **8a**. Estimated standard deviations are 0.003–0.004 Å for bond lengths, 0.1° for bond angles at P, and 0.2–0.3° for the other angles. Values obtained for the geometry-optimised MP2/6-31G* structure of the parent compound[8] are given in brackets. The angle between the plane of the three-membered ring and the P–C-aryl bond vector (or P–H bond vector) is 82.5° (83.9°).

in **7a**, but Z in **8a**.¶ Thus, formation of phosphine derivatives **7** from **4** occurs with retention, whereas formation of alkylidene-phosphiranes **8** occurs with inversion of the configuration at the siloxy-substituted C=C bond. These observations suggest that thermolysis of **4** initially generates the diradical **5**, which can either abstract hydrogen atoms from a silicon-attached iso-propyl group or undergo isomerisation to the 2-phosphabuta-triene **6**. By analogy to the 2-phosphaallene → phosphirane isomerisation,[12] a (conrotatory) 4π-cyclisation[13] leads to **8**, whereby the obviously thermodynamically more favourable Z-diastereoisomer is formed exclusively.

Fig. 3 shows the experimentally determined values for the geometry of the alkylidenephosphirane skeleton of **8a** together with those obtained for the parent 2-methylenephosphirane[8] from *ab initio* calculations. Remarkably, the two ring-bonds involving the diphenyl-substituted ring atom in **8a** are distinctly longer than in the parent system. Presumably, this is mainly due to the steric repulsion between the two phenyl rings and the P-attached mesityl ring as well as the Bu^t group. The steric overcrowding at the three-membered ring of **8a** is also evident from the torsion angles around the exocyclic double bond [*e.g.* P–C(2)–C(3)–O 13.7(5)° and C(1)–C(2)–C(3)–C(4) 26.9(6)°] and is likely to be responsible for the slight pyramidalisation of the ring atom C(2) (sum of valence angles 356.8°); thus, the bond vector C(2)=C(3) forms an angle of 11.8° with the ring plane and points in the direction opposite to the P–C(17) vector which forms an angle of 82.5° with the ring.

Footnotes

‡ All new compounds gave satisfactory elemental analyses, and were characterised by ^{1}H, ^{13}C (CDCl$_3$, 100.61 MHz), and ^{31}P NMR (CDCl$_3$, 161.98 MHz) spectra. *Selected data* for **4a**: yellow, decomp. temp. 112 °C; ^{13}C NMR (J/Hz) δ 29.0 (d, $^4J_{P,C}$ 9.4, C*Me*$_3$), 105.0 (d, $^1J_{P,C}$ 27.3, CPh$_2$), 139.6 (d, $^1J_{P,C}$ 36.1, P–C=), 176.9 (d, $^2J_{P,C}$ 25.4, =C–O); ^{31}P NMR δ −55.0.

4b: yellow, decomp. temp. 111 °C; ^{31}P NMR δ −55.0.

§ *Selected data* **7a**: colourless, mp 111 °C; ^{13}C NMR (T = 333 K, J/Hz)

δ 29.1 (d, $^4J_{P,C}$ 9.3, C*Me*$_3$), 38.8 (d, $^3J_{P,C}$ 2.6, C*Me*$_3$), 52.2 (d, $^1J_{P,C}$ 11.1, CHPh$_2$), 99.0 (d, $^1J_{P,C}$ 21.6, P–CH=), 166.9 (d, $^2J_{P,C}$ 24.9, =C–O); ^{31}P NMR δ −25.3.

7b: colourless, mp 115 °C; ^{31}P NMR δ −25.8.

8a: colourless, mp 135 °C; ^{13}C NMR (J/Hz) δ 14.2 (d, $^5J_{P,C}$ 4.0, SiCH), 28.7 (s, C*Me*$_3$), 39.8 (s, C*Me*$_3$), 52.1 (d, $^1J_{P,C}$ 21.3, CPh$_2$), 114.8 (d, $^1J_{P,C}$ 47.6, P–C=), 164.5 (d, $^2J_{P,C}$ 7.2, =C–O); ^{31}P NMR δ −134.5.

8b: colourless, mp 168 °C; ^{31}P NMR δ −135.4.

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