A Stereoselective Route from a Dihydro-1,2,4λ^3-diazaphosphole to a λ^3-Phosphirane *via* a Bismethylenephosphorane Intermediate

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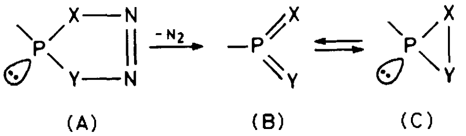
The dihydro-1,2,4λ^3-diazaphosphole (**3**) decomposes stereoselectively to the bismethylenephosphorane (**4**), which then undergoes conrotatory ring closure to the λ^3-phosphirane (**6**), by a route controlled entirely by orbital symmetry.

Although the reactions (A) to (C) and (C) to (B) have been investigated for a number of phosphorus–nitrogen compounds ($X = NR$, $Y = NR$,[1] CR_2[2]) their stereochemical courses are not known. Here we report the first experimental evidence for the concerted nature of the coupled reaction sequence (A) → (B) → (C) for the case $X = Y = CHR$.

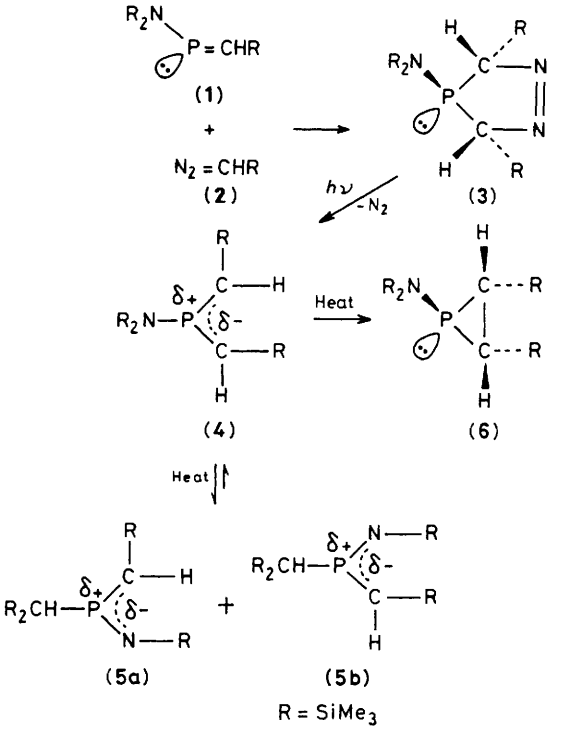
Dihydro-1,2,4λ^3-diazaphosphole (**3**) was synthesized as described previously[3] by the reaction of bis(trimethylsilyl)-aminotrimethylsilylmethylenephosphine (**1**) with trimethylsilyldiazomethane (**2**) in n-hexane at 0 °C. A crystalline solid was obtained quantitatively after removal of solvent and recrystallizing once from a small portion of n-hexane. The crystals are thermolabile at 60 °C. Photochemically induced elimination of N_2 from (**3**) in n-hexane yields the pure bismethylenephosphorane (**4**). On attempting to separate (**4**) by vacuum distillation (b.p. 72—76 °C, 0.1 Torr), it is partially equilibrated with the isomeric iminomethylenephosphoranes (**5a,b**). The equilibration is almost complete after 1 h at 120 °C. Further heating to 190 °C results in the gradual formation of a λ^3-phosphirane (**6**), which is complete after 3 days. Compound (**6**) can be purified by distillation at 96—98 °C/0.3 Torr.

The structures of (**3**) and (**6**) were confirmed by elemental analyses, molecular weight determinations, and n.m.r. data [those of the intermediates (**4**) and (**5a,b**) were confirmed only by n.m.r. spectroscopy].[†] The ^{31}P n.m.r. spectrum of (**3**) shows a resonance signal at δ −0.7 p.p.m. as expected for dihydro-1,2,4λ^3-diazaphospholes. The *cis* configuration of the ring bonded trimethylsilyl groups in (**3**) follows from the appearance of one set of signal groups for both CHSi≡ fragments in the $\{^1H\}^{13}C$ n.m.r. spectrum (δ 91.4 p.p.m.; $^1J_{CP}$ 58.7 Hz). The loss of N_2 from (**3**) drastically deshields the phosphorus nucleus (δ 161.3 p.p.m.) in (**4**) which is typical of the bismethylenephosphoranes reported recently.[4] Noticeable is the formation of only one isomeric form of (**4**). The *E,Z* configuration of the H–C–P–C–H fragment is evident from two separate doublets and from the different absolute values for the ^{13}C–^{31}P-coupling constants in the ^{13}C n.m.r. spectrum (δ 38.5, 51.7 p.p.m.; $^1J_{CP}$ 112.0, 88.4 Hz). The coalescing of these signals at 45 (±3) °C is reversible and independent of the concentration of (**4**). This indicates that the exchange of magnetic sites proceeds *via* an intramolecular process; a coupled rotation of the two methylene groups. Evidence for the formation of the isomeric iminomethylenephosphoranes (**5a,b**) is provided by a novel pair of two sets of doublets for



(A) (B) (C)

[†] N.m.r. data: $\{^1H\}^{13}C$ n.m.r. ($CDCl_3$) (**3**) δ 0.8 ($^3J_{CP}$ 5.2 Hz, $PCSiC_3$), 4.4 (J 7.9 Hz, $PNSiC_3$); (**4**) (−30 °C) 0.7, 2.1 (J 5.8, 5.0 Hz, $PCSiC_3$), 2.2 (J 2.1 Hz, $PNSiC_3$); (60 °C) 1.6 (J 5.5 Hz, $PCSiC_3$), 2.4 (J 2.2 Hz, $PNSiC_3$); (**5a**) 1.1 (6C, J 3.6 Hz), 2.1 (3C, J 5.5 Hz, $PCSiC_3$), 3.1 (J 2.9 Hz, $PNSiC_3$); (**5b**) 0.9 (6C, J 4.5 Hz), 1.2 (3C, J 7.0 Hz, $PCSiC_3$), 2.3 (J 4.3 Hz, $PNSiC_3$); (**6**) 1.6 (J 4.2 Hz, $PCSiC_3$), 4.8 p.p.m. (J 5.1 Hz); ^1H n.m.r. ($CDCl_3$) δ 0.1, 0.2 (J 0.7, 0.9 Hz, $PCSiCH$, $PNSiCH$), 0.8 ($^2J_{HP}$ 0.6 Hz, PCH); $\{^1H\}^{29}Si$ n.m.r. ($CDCl_3$) δ 0.5 ($^2J_{SiP}$ 17.5 Hz, $PCSi$), 6.5 p.p.m. (J 1.5 Hz, PNSi). Data measured at 28 °C with Me_4Si as internal standard (^1H, ^{13}C).



the carbon atoms directly bonded to phosphorus, one at higher field, δ 29.9 ($^1J_{CP}$ 22.2 Hz) (**5a**), 24.4 p.p.m. ($^1J_{CP}$ 50.9 Hz) (**5b**) and the other one at lower field, δ 70.4 ($^1J_{CP}$ 107.1 Hz) (**5a**), 67.8 p.p.m. ($^1J_{CP}$ 72.5 Hz) (**5b**). The shift of the phosphorus nucleus, δ 145.3 (**5a**); 129.0 p.p.m. (**5b**), establishes co-ordination number three for this atom. The structural assignment of (**6**) as a λ^3-phosphirane and not as an λ^3-azaphosphiridine [by ring closure of (**5a,b**)] was ascertained by its $\{^1H\}^{13}C$ n.m.r. spectrum. Both carbon atoms directly bonded to phosphorus as well as the phosphorus atom itself show the expected strong deshielding [^{13}C n.m.r. δ 20.7 p.p.m. ($^1J_{CP}$ 63 Hz); ^{31}P n.m.r. δ −110.9 p.p.m.]. Furthermore, the stereochemistry of (**6**) corresponds to the sterically least hindered *trans*-arrangement of the phosphorus group and the trimethylsilyl groups at the ring carbon atoms. This is supported by the low value of $^2J_{HP}$ (0.6 Hz) for the hydrogen atomic *trans* to the lone pair at the phosphorus atom[5] and by the high value of $^2J_{SiP}$ (17.5 Hz) for the *cis* silicon atom.[6]

From the viewpoint of MO theory, the parent compound (**4**) is isovalent with the anion of trimethylenemethane.[7] However, in the electrocyclic[8] ring closure (**4**) → (**6**), only four electrons are involved, two from the lone pair (at P) and two from the carbon atoms. Consequently, the interconversion of (**4**) into (**6**) corresponds to a conrotatory ring closure, analogous with the electrocyclic cleavage of aziridines.[9] Similarly, all the other events on the hypersurface between (A) and (C) are controlled by orbital symmetry. The double rotation process in (**4**) proceeds in a conrotatory manner without loss of stereochemistry at the carbon atoms, while the silyl migration is a suprafacial 1,3-sigmatropic shift. The stereochemistry of (**4**) is therefore maintained before conrotatory ring closure to (**6**) takes place. These results are one example of a reaction sequence strictly controlled by orbital symmetry where each step of the route is accessible to direct experimental investigation.

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