Azaphosphaullazines: 14π-Annulenes containing λ^3 σ^2-Phosphorus[1]

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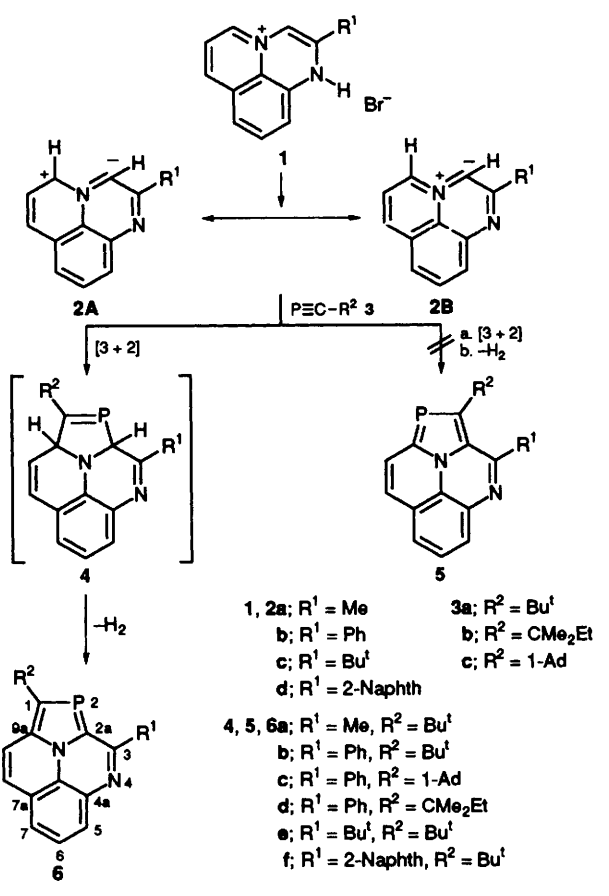
Reactions of the *in situ* generated peripheral azomethine ylide dipoles **2a–d** with the kinetically stabilised phosphaalkynes **3a–c** give rise to the title compounds **6a–f** which possess a 14π-perimeter including a phosphorus atom in a low coordination as shown by the limiting forms **6A** and **6B**.

In the course of our investigations on the synthesis of 1- and/or 2-phosphaindolizines[2] by 1,3-dipolar cycloadditions of phosphaalkynes to azomethine ylides, the possibility of preparing cyclazines containing low-coordinated phosphorus atoms became apparant. Cyclazines as such are defined as unsaturated, conjugated, polycyclic compounds with a planar structure resulting from the central nitrogen atom.[3,4] [3.2.2]-Cyclazines are, in principle, accessible by [3 + 2] cycloadditions of acetylenes[5] and arynes[6] to indolizines.

Unfortunately, our attempts to realise similar reactions of the synthesised phosphaindolizines with C–C multiple bonds were unsuccessful, even under drastic thermal conditions. We therefore turned our attention to a route involving the reaction of the peripheral azomethine ylides **2** with phosphaalkynes **3** to yield the corresponding phospha[3.3.2]-cyclazines.[7] Investigations on the reactivity of phosphorus-free representatives of this structural type prophesied an interesting chemical behaviour.[8]

Deprotonation of the salts **1a–d**† by triethylamine in toluene in a sealed Schlenk tube in the presence of the phosphaalkynes **3a–c**[9] under heating gave rise to the azaphosphaullazines **6a–f**[10] which were isolated in 30–43% yields as yellow crystalline powders (Scheme 1). The cycloaddition process is regiospecific: isomers originating from the reversed dipole orientation **5a–f** could not be detected by ^{31}P NMR spectroscopy on the crude reaction mixtures. The [3 + 2] cycloaddition is then followed by a dehydrogenation leading to the heteroaromatic system.



Scheme 1 *Reagents and conditions*: NEt$_3$–toluene (→ **2**), then 12–24 h in a sealed Schlenk tube at 130–140 °C

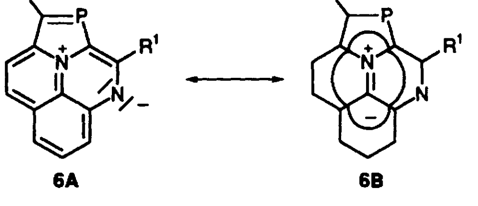
In agreement with our structural assignments, the ^{31}P NMR spectra of **6a–f** exhibit characteristic signals at δ 108.2–117.2 for the low coordinated phosphorus atom in the 1,3-azaphosphole system.[11] The ^{13}C NMR signals of the carbon atoms C-1 (δ 156.3–160.2) and C-2a (δ 140.0–143.4) are each split into doublets by $^{1}J_{C,P}$ couplings of 49.4–55.4 Hz. The carbon atoms C-9a (δ 131.3–133.6) and C-3 (δ 158.3–168.4) not surprisingly experience appreciably smaller splittings ($^{2}J_{C,P}$ 9.1–15.4 Hz).

The regiochemistry of the reaction can be deduced unequivocally from the magnitudes of the phosphorus couplings of the C atom of the organic group R^1 linked to the perimeter. Thus, the signal for the carbon atom of the methyl group at position 3 in **6a** appears as a doublet at δ 23.8 with a coupling constant of 7.5 Hz while the aromatic *ipso*-carbon atom at C-3 in **6b** (δ 139.4) exhibits a coupling of 20.2 Hz. The sizes of these splittings can only be reconciled with the 1,3-arrangement of the involved atoms as present in **6** and not with that in the isomeric structure **5**.[12]

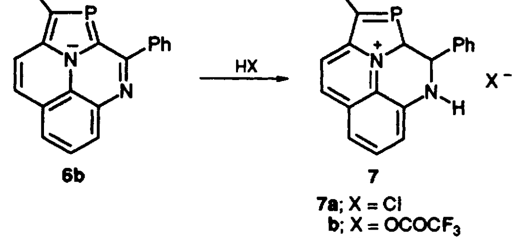
The chemical shifts of the hydrogen atoms H-5 to H-9 are in the range δ 7.0–7.9, *i.e.* in the same order of magnitude as for the phosphorus-free analogues.[7,8] The mass spectra (M$^{+\cdot}$: 35–100%) exhibit a paucity of lines, as is typical for aromatic systems.

As in the case of the parent ullazines,[10] the phosphaullazines **6** may also be considered as Hückel aromatic systems as represented by **6A** ⟷ **6B** (Scheme 2) in which the perimeters contain 14π-electrons. To the best of our knowledge, these compounds are the first annulenes with $\lambda^3\sigma^2$-phosphorus atoms to be reported.

These novel annulenes are protonated at N-4 by strong acids (Scheme 3), as has been demonstrated for the example of



Scheme 2



Scheme 3

reactions of **6b** with hydrogen chloride gas, trifluoroacetic acid, or trifluoromethanesulfonic acid in aprotic solvents.

The orange salts **7a–c** thus obtained in 91–96% yield were identified unambiguously by elemental and spectroscopic analyses. In comparison to that of **6b**, their ^{31}P NMR spectra reveal pronounced shifts of the signals to low field (δ 151.4–160.3) which, together with the paramagnetic shifts of the protons H-5 to H-9 (δ 7.8–8.2), is implicit. The protonation itself can be recognised, for example in the case of **7b**, by a broad NH signal at δ 14.8.

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Footnote

† The azomethine ylides **2c**, **d** and/or their precursors **1c**, **d** were not previously known; they were prepared in the same way as **1a**, **b** and **2a**, **b**, respectively.[7]

References

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