A Simple Synthesis of 4-Aza-λ^5-phosphinines from *Z*-1,5-Diaza-2λ^5-phosphapenta-1,3-dienes and Dimethyl Acetylenedicarboxylate

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4-Aza-λ^5-phosphinines were synthesized by reaction of *Z*-1,5-diaza-2λ^5-phosphapenta-1,3-dienes (**1**) with dimethyl acetylenedicarboxylate in acetonitrile.

λ^5-Phosphinine heterocycles, most of them symmetrical, are generally prepared from cyclic precursors.[1] Unlike the corresponding λ^3-derivatives these compounds do not show 'aromatic' behaviour.[2] However, azaphosphinine derivatives have received little attention. Access to aza-λ^5-phosphinines has been limited to one synthetic route, which starts with 4-pyran phosphonium salts and leads to symmetrical 1,1,3,5-tetraphenyl-4-aza-λ^5-phosphinines;[3] the authors suggest that such heterocycles exhibit aromatic character.

Primary enamines having electron-withdrawing substituents at the β-position are versatile reagents in heterocyclic synthesis.[4] Likewise, we have shown that β-imino enamines are important key intermediates in the synthesis of acyclic[5] and heterocyclic[6] derivatives. Recently, we have synthesized analogous phosphine imines[7] and we describe here preliminary results on their use as precursors of phosphorus containing heterocycles.

The reaction of the phosphine *N*-phenylimine (**1a**) with dimethyl acetylenedicarboxylate (DMAD) in acetonitrile† at room temperature gave after stirring for 6 h the 1 : 1 adduct (**2a**) [δ_H(80 MHz, $CDCl_3$) 2.26(s, 3H, Me), 3.16(s, 3H, OMe), 3.39(s, 3H, OMe), 4.57(d, 1H, =CH, $^2J_{PH}$ 14.2 Hz), and 6.16—7.93(m, 19H, ArH, NH_2); δ_C(80 MHz, $CDCl_3$) 21.0(Me), 49.6(OMe), 51.2(OMe), 60.8(d, ylide C=P, $^1J_{PC}$ 109.7 Hz), 67.7(d, C_α, $^1J_{PC}$ 102.8 Hz), 120.4—149.9(24 ArC), 161.1(d, C_β, $^2J_{PC}$ 1.9 Hz), 161.7(d, C=N, $^2J_{PC}$ 3.0 Hz), 166.9(d, CO, $^2J_{PC}$ 12.6 Hz), and 168.6(d, CO, $^3J_{PC}$ 12.6 Hz); δ_P(80 MHz, $CDCl_3$, 85% H_3PO_4 standard) 3.9 p.p.m.; *m/z* 550(*M*)]. Compound (**2**), by analogy with simple phosphine-imines,[8] is formed through 2 + 2 cycloaddition of the P=N linkage of (**1**) to the carbon–carbon triple bond of DMAD, to give the non-isolable 1-aza-2-phosphete followed by an electrocyclic ring opening. The process is favoured by the use of a polar solvent[9] such as acetonitrile.

Heating (**2a**) at 80 °C allows the cyclocondensation with loss of aniline giving the 4-aza-λ^5-phosphinine (**3a**) [δ_H(80 MHz, $CDCl_3$) 2.31(s, 3H, Me), 3.49(s, 3H, OMe), 3.87(s, 3H, OMe), 5.33(d, 1H, =C*H*,$^2J_{PH}$ 11.0 Hz), and 6.63—7.95(m, 14H Ar); δ_C(80 MHz, $CDCl_3$) 20.8(Me), 50.6(OMe), 52.1 (OMe), 67.0(C-2, $^1J_{PC}$ 107.1 Hz), 76.5(C-6, $^1J_{PC}$ 90.6 Hz), 126.5—139.4(18 ArC), 160.5(C-3, $^2J_{PC}$ 3.6 Hz), 161.8(C-5), 166.7(CO, $^2J_{PC}$ 10.7 Hz), and 168.7(CO, $^3J_{PC}$ 14.5 Hz); δ_P(80 MHz, $CDCl_3$) 1.2 p.p.m.; *m/z* 457(*M*)] in excellent yield (90%). Similarly, (**2b**) and (**3b**) were obtained from (**1b**). Heterocycles (**3a,b**) were also synthesized in one step when (**1a,b**) were treated with DMAD in acetonitrile at reflux. Table 1 summarises the yields and m.p.s for the new compounds. However, when (**1c**—**e**) $R^1 \neq H$ were used as starting material at room temperature, the reaction underwent direct cyclocondensation to 4-aza-λ^5-phosphinines (**3c**—**e**), without isolation of the intermediate (**2**).

The n.m.r. spectral data of compounds (**3**) indicate that they have no aromatic character. Thus, the H_α signal in (**3a**) is shifted to a higher field (δ_H 5.33, $^1J_{PH}$ 11.0 Hz) compared to that of H_α in 3,5-diphenyl-4-aza-λ^3-phosphine[10] (δ_H 8.66, $^1J_{PH}$ 18 Hz), a result in accord with that observed in other λ^3- and λ^5-phosphinines.[2] Likewise, the large $^1J_{PC}$ coupling constant of C-2 (107.1 Hz) and C-6 (90.6 Hz) as well as the

Table 1. M.p.s and yields of derivatives (**2**) and (**3**).

Compound[a]	m.p./°C	Yield/%
(**2a**)	166—167	86
(**2b**)	179—180	82
(**3a**)	228—229	80(90)[b]
(**3b**)	186—187	77(88)[b]
(**3c**)	209—210	76
(**3d**)	210—211	79
(**3e**)	215—216	78

[a] All new compounds reported here gave satisfactory elemental analyses. [b] Yield from (**2**).

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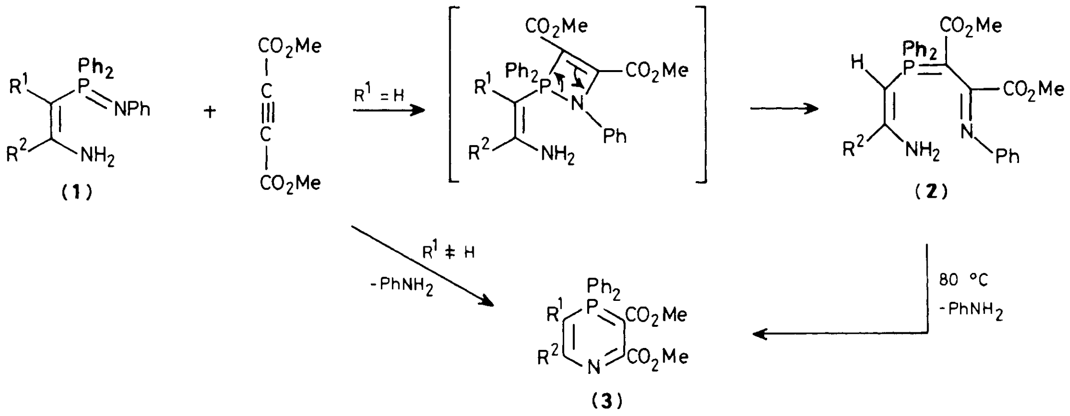
† When benzene was used as solvent the starting material was recovered.



a; R^1 = H, R^2 = p-MeC_6H_4
b; R^1 = H, R^2 = cyclohexyl
c; R^1 = Me, R^2 = p-MeC_6H_4
d; R^1 = CH_2=$CHCH_2$, R^2 = p-MeC_6H_4
e; R^1 = CH_2Ph, R^2 = cyclohexyl

high field chemical shifts (δ 66.5 for C-2, 76.5 for C-6) observed in ^{13}C n.m.r. spectrum appear to be an approximate measure of the degree of positive character at the phosphorus atom.[2]

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