A Simple Synthesis of 3*H*-λ^5-Phosphole Derivatives from Alkyldiphenylphosphine Imines and Dimethyl Acetylenedicarboxylate

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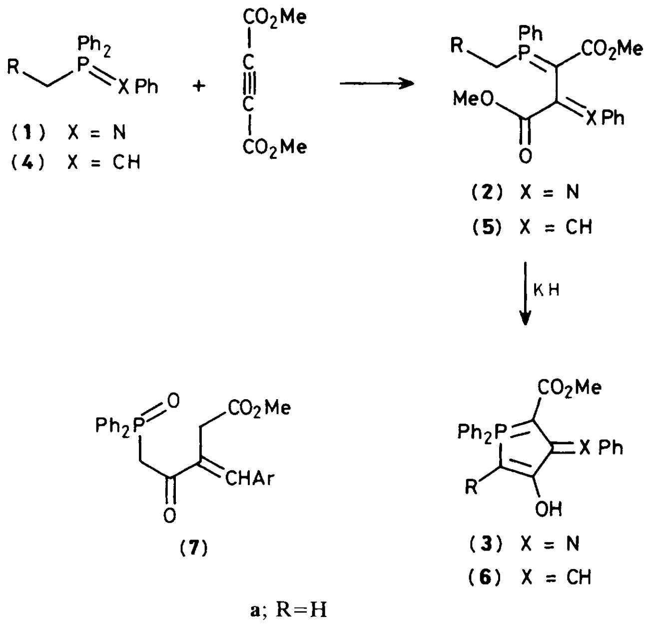
3*H*-λ^5-Phospholes were synthesized by reaction of alkyldiphenylphosphine imines (**1**) with dimethyl acetylenedicarboxylate and subsequent treatment of the adduct (**2**) with potassium hydride.

There has been much interest recently in the synthesis of five-membered phosphorus-containing heterocycles in order to compare their properties with those of the analogous pyrrole, furan, and thiophene. Whereas several procedures have been developed for synthesizing λ^3-phospholes and their oxides and sulphides,[1] access to 2*H*-λ^5-phospholes is limited to the reaction of phosphines[2] and phosphites[3] with dimethyl acetylenedicarboxylate (DMAD) under carefully controlled reaction conditions. It has also been reported that diphenyl(vinyl)phosphine reacts with DMAD to give unstable 3*H*-λ^5- and 2*H*-λ^5-phospholes, which were identified either by trapping with dienophiles or by hydrolysis.[4]

β-Enaminophosphine imine derivatives[5] are suitable starting materials for synthesis of 4-aza-λ^5-phosphinines.[6] We



a; R=H
b; R=Me
c; R=Ph
d; R=CH=CH$_2$

report here the first synthesis of stable 3*H*-λ^5-phospholes by reaction of simple alkyldiphenylphosphine *N*-phenylimines with dimethyl acetylenedicarboxylate.

The treatment of the imine (**1a**) with DMAD in tetrahydrofuran (THF) at room temperature for 4 h resulted in the formation of the 1:1 adduct (**2a**); the mechanistic pathway shown previously for the reaction of *Z*-1,5-diaza-2λ^5-phosphapenta-1,3-dienes with DMAD[6] also applies for the formation of (**2a**).

When a mixture of (**2a**) and KH in THF was heated at 50 °C for 6 h followed by methanolysis and aqueous work-up, cyclocondensation and formation of 3*H*-λ^5-phospholes (**3a**) took place. Yields and m.p.s of compounds (**2**) and (**3**) are given in Table 1.

Table 1. M.p.s and yields of compounds (**2**)—(**7**).

Compound	M.p., *t*/°C	Yield, %
(**2a**)	119—120	82
(**2b**)	100—101	87
(**2c**)	147—148	85
(**2d**)[a]	86—87	90
(**3a**)	199—200	91
(**3b**)	175—176	92
(**3c**)	119—120	95
(**3d**)	170—171	92
(**5a**)	135—136	86
(**7**)	134—135	65

[a] Isolated as a 40:60 mixture of (**2d**) and the *E* conjugated double bond isomer.

The enol structure (**3**) is supported by the n.m.r. data. Thus, the ^{1}H n.m.r. spectrum of (**3a**) shows 5-H at high field (δ 4.26, $^2J_{PH}$ 25.7 Hz) relative to the vinyl protons and OH at δ 9.35. Both 5-H and OH protons are exchangeable on shaking with D$_2$O. The ylidic nature of compounds (**3**) is clearly supported by variable temperature ^{1}H n.m.r. experiments[3] which reveals the presence of two rotamers. Thus, the spectrum of (**3a**) at −35 °C shows two OMe signals at δ 3.67 (minor) and 3.12 (major) for both rotamers. Furthermore, the ^{13}C chemical shifts and the P–C coupling constants for 2-C (δ 73.4, $^1J_{PC}$ 110.2 Hz) and 5-C (δ 60.7, $^1J_{PC}$ 114.1 Hz) observed in the ^{13}C n.m.r. spectrum of (**3a**) suggest the same hybridisation for both carbon atoms.

This type of reaction is not restricted to phosphine imines, but can be extended to phosphonium ylides. When compound (**5a**), formed by reaction of (**4a**) with DMAD, was treated with KH at 80 °C and then subjected to mild hydrolysis, compound (**7**) instead of its precursor (**6**) was isolated.

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