

A Simple Synthesis of $3H-\lambda^5$ -Phosphole Derivatives from Alkyldiphenylphosphine Imines and Dimethyl Acetylenedicarboxylate

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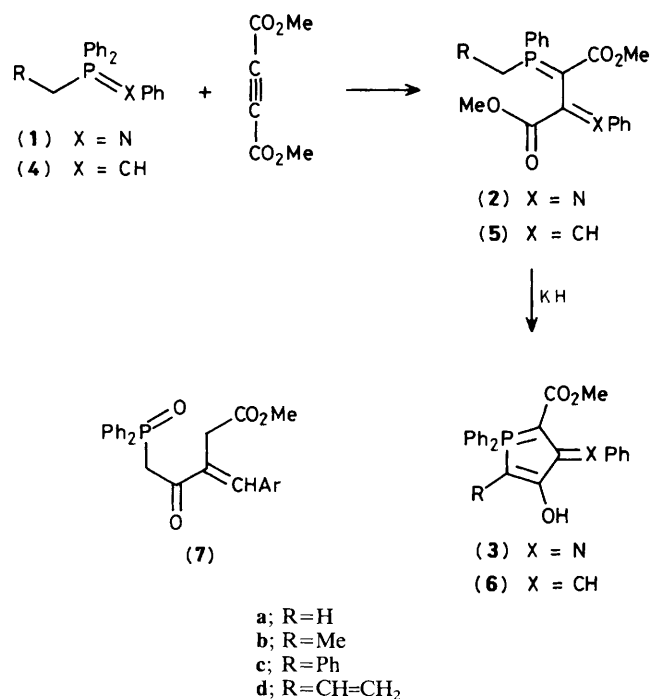
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$3H-\lambda^5$ -Phospholes were synthesized by reaction of alkyldiphenylphosphine imines (**1**) with dimethyl acetylenedicarboxylate and subsequent treatment of the adduct (**2**) with potassium hydride.

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 $2H-\lambda^5$ -phospholes is limited to the reaction of phosphines² and phosphites³ with dimethyl

acetylenedicarboxylate (DMAD) under carefully controlled reaction conditions. It has also been reported that diphenyl-(vinyl)phosphine reacts with DMAD to give unstable $3H-\lambda^5$ - and $2H-\lambda^5$ -phospholes, which were identified either by trapping with dienophiles or by hydrolysis.⁴

β -Enaminophosphine imine derivatives⁵ are suitable starting materials for synthesis of 4-aza- λ^5 -phosphinines.⁶ We



report here the first synthesis of stable $3H$ - λ^5 -phospholes by reaction of simple alkyl-diphenylphosphine 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- $2\lambda^5$ -phosphapenta-1,3-dienes with DMAD⁶ 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 $3H$ - λ^5 -phospholes (3a) took place. Yields and m.p.s of compounds (2) and (3) are given in Table 1.

The enol structure (3) is supported by the n.m.r. data. Thus, the ¹H n.m.r. spectrum of (3a) shows 5-H at high field (δ 4.26, ² J_{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 D₂O. The ylidic nature of compounds (3) is clearly supported by variable temperature ¹H n.m.r. experiments³ 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 ¹³C chemical

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.

shifts and the P–C coupling constants for 2-C (δ 73.4, ¹ J_{PC} 110.2 Hz) and 5-C (δ 60.7, ¹ J_{PC} 114.1 Hz) observed in the ¹³C 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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