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A SIMPLE SYNTHESIS OF THE FIRST 1-2λ^5-BENZAZAPHOSPHININE RING.

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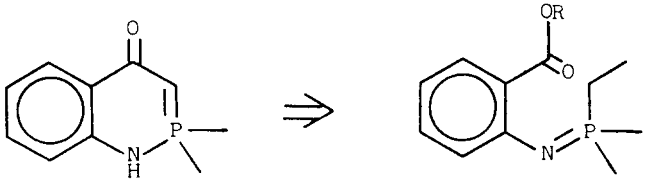
Summary. Benz-azaphosphininones (1) are synthesized by intramolecular cyclocondensation of phosphine imides (2) in the presence of base.

Synthesis and reactions of pyridines and their benz-derivatives have been well studied in the last years[1]. A few examples of 1,2-[2] and 1,4-λ^5-azaphosphinines[3], heterocyclic analoges of pyridine containing phosphorus, are known, but no examples of the corresponding benz-derivatives have been described, to the best of our knowledge[4].

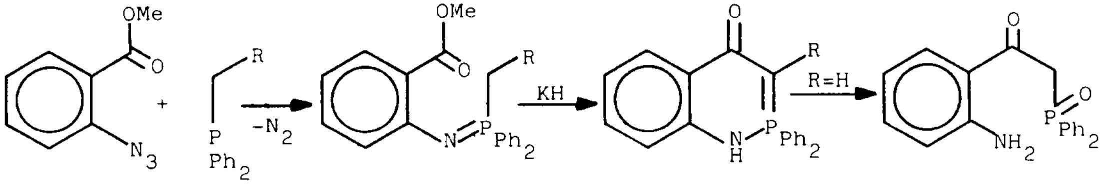
Recently Snieckus *et al.* reported[5] an elegant synthesis of 4-quinolones through a modified Niementowski reaction. We have previously reported on the ability of α-metallated phosphine imides to react with electrophiles[6]. Continuing our interest in the synthesis of phosphorus-containing heterocycles[7] we describe here the first synthesis of 1*H*-1,2-benzazaphosphinin-4-ones (1) by intramolecular condensation of phosphine imides (2).

(1)



(2)

The preparation of the desired phosphine imides[8] (2) was accomplished very easily through the classical Staudirger reaction[6] of methyl o-azidobenzoate (3) with alkyldiphenylphosphines (4) in ether.



(3) (4) (2) (1) (5)

When a mixture of (2) and KH in THF was heated at 60°C for 3 hours followed by methanolysis and aqueous work-up, cyclocondensation took place to give 4-oxo-1*H*-1,2λ^5-benzazaphosphinines[9] (1) in excellent yields (Table); in the case of

R= H the corresponding compound (1) could not be isolated and the o-amino derivative[10] (5), resulting from its hydrolysis was formed instead.

This methodology appears to offer a simple and useful procedure for benzazaphosphinine ring construction.

Table of physical data for the compounds obtained.

Compound	R	M.p.(°C)	Yield (%)
(2a)	H	oil	97
(2b)	CH_3	101-102	98
(2c)	CH_2=CH	100-101	97
(2d)	C_6H_5	193-194	95
(1a)	CH_3	277-278	86
(1b)	CH_2=CH	218-219	92
(1c)	C_6H_5	281-282	87
(5)	-	162-163	82

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8.- All new compounds reported here gave satisfactory elemental analysis. Spectral data for (2a): δ_H(80MHz,$CDCl_3$)= 2.0(d,3H,$^2J_{PH}$=12.6Hz,CH_3); 3.83(s, 3H,CH_3); 6.83-7.91(m,14Harom.);δ_C(20MHz,$CDCl_3$)=15.2(d,$^1J_{PC}$=73.4Hz);50.2; 108.9-150.3 (18Carom.); 167.4; δ_P(30MHz,$CDCl_3$)= +30.2 ppm.

9.- Spectral data for (1a): ν(cm^{-1},KBr): 3080(NH), 1620(C=O), 1120(P=C);δ_H(80MHz, $CDCl_3$)=1.71(d,3H,$^2J_{PH}$=14.2Hz,CH_3); 6.71-8.16(14Harom.+NH);δ_C(20MHz,$CDCl_3$= 10.4 (d,$^2J_{PC}$=14.2Hz); 66.0(d,$^1J_{PC}$=159.2Hz), 121.5-147.8(18Carom.); 194.4;δ_P(30MHz, $CDCl_3$)=+32.1 ppm; M^+(m/z)= 331.

10.- Spectral data for (5):δ_H(80MHz,$CDCl_3$)=4.04(d,2H,$^2J_{PH}$=14.2Hz,CH_2); 6.08(s, 2H,NH_2); 6.31-8.0(m,14Harom.);δ_C(20MHz,$CDCl_3$)=43.0(d,$^1J_{PC}$=60.6Hz); 114.2-150.8(18Carom.); 193.6(d,$^2J_{PC}$=3.1Hz);δ_P(30MHz,$CDCl_3$)=+27.5 ppm. M^+(m/z)= 335.

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