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2-AMINO 1-PHENYLPHOSPHOLES FROM DICHLOROPHENYLPHOSPHINE AND ENAMINES.

Wai Hé-Line Wai Tan, André Foucaud *

Groupe de Chimie Structurale, Associé au C.N.R.S., Université de Rennes,
Campus de Beaulieu, 35042 Rennes, France.

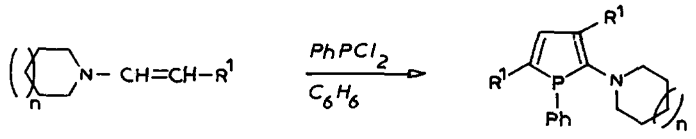
Abstract - The reaction of dichlorophenylphosphine with two equivalents of enamines at room temperature gives 2-amino 1-phenylphospholes.

We have shown that dichlorophenylphosphine reacts with imines to give 2-oxo 1,2-azaphospholenes and 1,2-dihydro 1,2-λ^3-azaphosphinines[1]. In some cases, only azaphospholenes are produced[2]. In continuation to our efforts to further explore methods for constructing heterocycles with a phosphorus atom, we have investigated the reaction of dichlorophenylphosphine with enamines and we report here our results.

The reaction of dichlorophenylphosphine with two equivalents of enamines **1a-c**, in benzene, at room temperature, gives 1-phenyl 2-aminophospholes **2**, as oils which are purified by silica gel column chromatography (30-35 % yield of purified phospholes). Structural assignments are based on spectral data (table). The ^{31}P NMR data are in agreement with the literature[3] ; the intracyclic $^1J_{C-P}$ coupling constant in low[3,4,5]. The position of the amino group at C-2 is established by ^{13}C NMR spectroscopy.

The coupling constant $^3J_{PCNC}$ of the CH_2 bound to nitrogen is 8-9 Hz. When R^1 = Et, the coupling constant of the carbon of the methyl group is $^3J_{PCCC}$ = 6 Hz (R^1 at C_{-5}) and $^4J_{PCCCC}$ = 0 (R^1 at C_{-3}).

	n	R¹
1a	1	Me
b	1	Et
c	0	Et



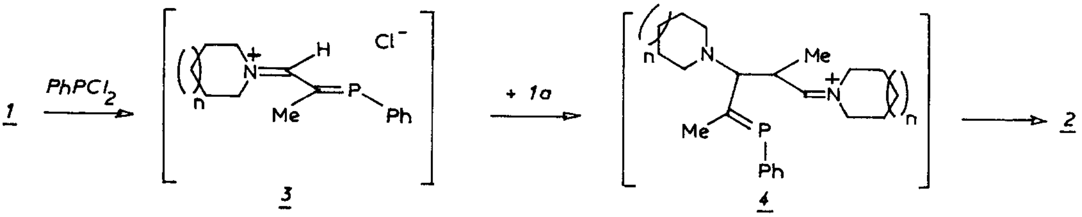
2a-c

The formation of **2** can be visualized as represented in scheme I. In a first step, the nucleophilic attack of **1** on $PhPCl_2$ gives an intermediate **3** which can react with a second mole of enamine to yield **4**. Piperidine or pyrrolidine elimination from **4** and cyclization yield **2**.

Table - Selected NMR spectral data[a] (δ_{ppm}, J Hertz, $CDCl_3$) and mass spectra of phospholes **2.**

2	$\delta^{31}P$	δH-4 $^3J_{PH}$	δC-2 $^1J_{PC}$	δC-3 $^2J_{PC}$	δC-4 $^2J_{PC}$; $^1J_{CH}$	δC-5 $^1J_{PC}$	δC-1'[b] $^1J_{PC}$	MS (70 eV) m/z
a	-6.3	6.32	156.5	132.0	136.3	141.0	133.0	Calcd M$^+$ 271.1490
		11	7.5	16	9 ; 161	0	11	Obsd 271.1491
b	-9.6	6.47	156.0	138.5	132.2	148.0	133.0	Calcd M$^+$ 299.1803
		12	8	15	8 ; 158	1	12	Obsd 299.1795
c	-1.7	6.37	153.0	132.9	134.8	141.4	127.9	Calcd M$^+$ 285.1646
		12	1	12	9 ; 155	0	13	Obsd 285.1646

a ^{1}H NMR (80 MHz) ; ^{13}C NMR (75.5 MHz) ; ^{31}P (32.38 MHz). b Quaternary carbon of the phenyl group.



A typical procedure is as follows : a solution of $PhPCl_2$ (30 mmol) in dry benzene (20 ml) was added to a solution of enamine (60 mmol) in benzene (40 ml). The mixture was stirred for 3 h 30 at 20°C, under nitrogen. Triethylamine (60 mmol) and MeOH (60 mmol) were added. The mixture was stirred for 1 h, then filtered. The solvent and the dimethyl phenylphosphonite were removed in vacuo. The residue was chromatographed on silica gel (30 g) using ether-petroleum ether (1:5) as an eluant.

This method offers an useful way for 2-amino phospholes which are not yet known.

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