
PREPARATION AND REACTIVITY OF SOME NEW DIAZAPHOSPHOLINE COMPOUNDS

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Abstract

A reaction of cyclohexanone phenylhydrazone with (het)aryldihalogenophosphines has been studied. Cyclohexanone phenylhydrazone reacts with phenyldichlorophosphine and 5-methyl-2-furyldichlorophosphine to provide the corresponding 1,2,3 diazaphospholines derivatives in high yields. These compounds (3-7) have been characterized by microanalytical, FT-IR, MS, ^1H , and ^{31}P -NMR, and UV spectra.

Keywords: cyclohexanone; phenylhydrazone; phenyldichlorophosphine; diazaphospholines

Introduction

1,2,3-Diazaphospholines having an exocyclic P-C bond are represented in the literature by fused heterocycles and by few examples of 3-alkyl diazaphospholines, which have been prepared by addition of dienes [1-3], 1,3-dipolar reagents [4, 5] as well as alkyl lithium reagents [6, 7] to the C=P bond of 1,2,3-diazaphospholes. In this work, we propose a method for synthesis of previously unknown 3-aryl and -hetaryl 1,2,3-diazaphospholines by the reaction of α -methyleneketones hydrazones with aryl- and hetaryl-dihalogenophosphines.

Results and Discussion

We have found that cyclohexanone phenylhydrazone **1** reacted with phenyldichlorophosphine in acetonitrile at room temperature to give diazaphospholine **3a**. The reaction comes to completion in 12 days and is accompanied by the formation of significant amounts of by-products and unidentified compounds. Phenyldichlorophosphine and 5-methyl-2-furyldichlorophosphine [8] react with cyclohexanone phenylhydrazone under the same conditions in 12 h affording 1,2,3-diazaphospholines **3b** in high yields. Starting from compounds **3a, b**, a set of pentavalent phosphorus derivatives such as sulfides **4a, b**, oxide **5**, imine **6**, and phosphonium salt **7** were prepared (see Scheme 1, Table 1 & 2).

Experimental

Phosphorus was determined gravimetrically as phosphoammonium molybdate using R. Voy method [9]. ^1H , and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz using TMS as an internal standard for ^1H and 85% H_3PO_4 as an external standard for ^{31}P at Microanalytical Center, Cairo University. All melting points recorded are uncorrected open capillary measurements. Elemental analyses were carried out at the "Microanalysis Department", National Research Center; their results were in agreement with the calculated values. IR spectra were determined with a Jasco FTIR 5300 spectrophotometer using the KBr technique at Microanalytical Center, Cairo University. Mass spectra were obtained by use of a Shimadzu-GC MS-QP 1000 EX instrument using the direct inlet system at Microanalytical Center, Cairo University. UV spectra were recorded on Shimadzu UV-2100 UV-Visible recording spectrophotometer using ethanol as solvent at Microanalytical Center, Cairo University.

2,3-Diphenyl/3-(5-Methyl-2-furyl)-2-phenyl-3,3a,4,5,6,7-hexahydro-2H-1,2,3-benzodiazaphosphole 3a, 3b

General procedure

To a solution of **1** (0.01 mol) in acetonitrile (30 mL) cooled to 0°C , **2a** or **2b** (0.01 mol) was added. The reaction mixture was leaving over night. The resulting precipitate was filtered off and the filtrate was evaporated under vacuum. The residue was treated with dry acetonitrile (20 mL) and the precipitate formed (in 78.74% yield) was filtered off and recrystallized from dry acetonitrile. The analytical data are listed in Table 1, 2.

2,3-Diphenyl/3-(5-Methyl-2-furyl)-2-phenyl-3,3a,4,5,6,7-hexahydro-2H-1,2,3-benzodiazaphosphole-3-sulfide 4a

General procedure

To a solution of **3a** or **3b** (0.01 mol) in anhydrous benzene (100 ml), elemental sulfur (0.015 mol) was added and the mixture was boiled to reflux for 1 h. Benzene was removed under vacuum and the product was extracted from the residue with diethyl ether. The analytical data are collected in Table (1, 2).

2,3-Diphenyl-3,3a,4,5,6,7-hexahydro-2H-1,2,3-benzodiazaphosphole-3-oxide 5

To an ice-cooled solution of **3a** (0.01 mol) in carbontetrachloride (25 mL), 30% hydrogen peroxide (2 mL) was added. The reaction mixture was allowed to stand at

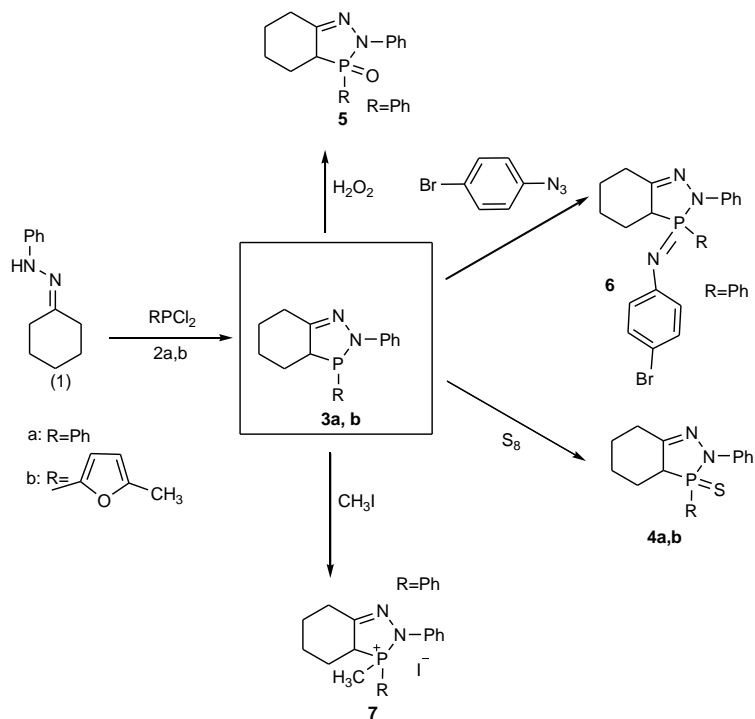
room temperature for 1 h. Then water (20 mL) was added and the organic layer was separated. The solvent was evaporated under vacuum and the residue was recrystallized from acetonitrile. The analytical data are listed in Table 1,2.

4-Bromo-N-(2,3-diphenyl-3,3,3a,4,5,6,7-octahydro-2H-1,2,3-benzodiazaphosphol-3-ylidene)aniline 6

To a solution of **3a** (0.01 mol) in dry benzene (20 mL), *p*-chlorophenylazide (0.01 mol) was added. The reaction mixture was heated under reflux for 2 h. After evaporating the solvent under vacuum, the product was extracted from the residue with diethyl ether (20 mL) and recrystallized from hexane (see Table 1, 2).

2,3-Diphenyl-3-methyl-3,3a,4,5,6,7-hexahydro-2H-1,2,3-benzodiazaphospholiumiodide 7

To **3a** (1.7 mmol), methyl iodide (0.02 mol) was added. The reaction mixture was allowed to stand at room temperature for 5 h. The resulting precipitate was filtered off and recrystallized from dry diethyl ether (see Table 1, 2).



SCHEME 1

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المخلص العربي

تحضير و دراسة بعض مركبات الدايازوفسفولين

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تم دراسة تفاعل مشتق الهكسانون الحلقي لمركب فينيل الهيدرازين مع مركب ثنائي الكلورو-فينيل الفوسفين وكذلك مركب ثنائي الكلورو-ميثيل-2-فورفورال-فوسفين لتكوين مشتقات بنسب انتاجيه عاليه. وتم دراسة خواص وتراكيب هذه المركبات بطرق التحليل العنصرى و الأشعه تحت الحمراء وطيف الكتله وطيف الرنين النووى المغناطيسى للبروتون و الرنين النووى المغناطيسى للفوسفور 31 و كذلك طيف الأشعه فوق البنفسجيه

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TABLE 1: Elemental analyses, yields, colours, melting points and mass spectra for compounds 3-7.

Compd. No. M.F. (M.Wt)	Reactants		m.p.°C (Yield%)	Color	Elemental analyses Found (Calc.), %					Mass spectra (mole peak, m/z)
					C	H	N	P	S	
3a C ₁₈ H ₁₉ N ₂ P (294)	1 (1.88 g, 0.001 mole)	2a (1.79 g, 0.01 mole)	192-194 (78.7)	Colorless	73.43 (73.46)	6.50 (6.51)	9.50 (9.52)	10.50 (10.52)	--	294
3b C ₁₇ H ₁₉ N ₂ OP (298)	1 (1.88 g, 0.001 mole)	2a (2.72 g, 0.01 mole)	101-103 (75.6)	Pale yellow	68.21 (68.45)	6.40 (6.37)	9.37 (9.39)	10.30 (10.40)	--	298
4a C ₁₈ H ₁₉ N ₂ OSP (326)	3a (2.94 g, 0.001 mole)	Elemental sulfur (0.48 g, 0.01 mole)	159-162 (97.4)	Yellow	66.20 (66.25)	5.83 (5.82)	8.56 (8.58)	9.48 (9.51)	9.80 (9.82)	326
4b C ₁₇ H ₁₉ N ₂ OSP (330)	3b (2.98 g, 0.001 mole)	Elemental sulfur (0.48 g, 0.01 mole)	157-159 (82.4)	Yellow	69.80 (61.82)	5.79 (5.75)	8.42 (8.48)	9.38 (9.39)	9.70 (9.71)	330
5 C ₁₈ H ₁₇ N ₂ OP (310)	3a (2.94 g, 0.001 mole)	H ₂ O ₂ (2ml (30%))	202-204 (83.4)	Yellowish white	69.62 (69.67)	5.78 (6.48)	9.00 (9.03)	9.96 (10.00)	--	310
6 C ₂₄ H ₂₃ N ₃ OCIP (464)	3a (0.50 g, 1.7 mmol)	p- bromophenylazide (0.35 g, 1.7 mmol)	208-210 (88.3)	Yellowish white	62.00 (62.08)	4.95 (4.99)	9.03 (9.05)	6.64 (6.67)	--	464
7 C ₁₉ H ₂₂ N ₃ IP (436)	3a (0.50 g, 1.7 mmol)	CH ₃ I (3 g, 0.02 mole)	138-141 (93.7)	Violet	52.30 (52.31)	5.02 (5.08)	6.40 (6.42)	7.00 (7.10)	--	436

TABLE 2: Spectroscopic data (.IR, UV& NMR) for compounds 3-7.

Comp d. No.	IR: $\bar{\nu}/\text{cm}^{-1}$	UV: λ/nm		NMR: δ/ppm			
		$\pi \rightarrow \pi^*$,	$n \rightarrow \pi^*$	$^1\text{H NMR}$			$^{31}\text{P NMR}$
				CH_3	CH_2	Ar-H	
3a	1415(P-aryl), 1223 (P-N), 1645 (C=N)	259, 266, 282	326		3.48	8.26	37.5
3b	1415(P-aryl), 1223 (P-N), 1646 (C=N)	259, 267, 283	328	2.28	3.58	7.85	14.9
4a	1415(P-aryl), 1223 (P-N), 635 (P=S), 1645 (C=N)	259, 266, 282	326		3.23	7..52	21.5
4b	1414(P-aryl), 1225 (P-N), 630 (P=S), 1247, 1311 (C-O), 1645 (C=N)	257, 268, 285	325	2.24	3.58	7.12	52.9
5	1420(P-aryl), 1227 (P-N), 1265 (P=N), 1645 (C=N)	257, 268, 287	326		4.08	7.64	36.7
6	1410(P-aryl), 1225 (P-N), 1118 (P=N), 1650 (C=N)	252, 264, 286	325		3.59	7.37	25.8
7	1425(P-aryl), 725 (P-methyl), 1223 (P-N), 1645 (C=N)	253, 264, 286	324	2.07	3.80	7.39	40.8