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Synthesis of 3-Aryl(Hetaryl)-1,2,3-diazaphospholines

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ABSTRACT: *A reaction of cyclohexanone phenylhydrazone with (het)aryldihalogenophosphines has been studied. As shown, cyclohexanone phenylhydrazone reacts with phenyldibromophosphine and 5-methyl-2-furyldibromophosphine to provide the corresponding 1,2,3-diazaphospholines in high yields. The diazaphospholines thus obtained have been derivatized.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:81–83, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20074

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], 1,3-dipolar reagents [2] as well as alkyllithium reagents [3] 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-dihalogenphosphines.

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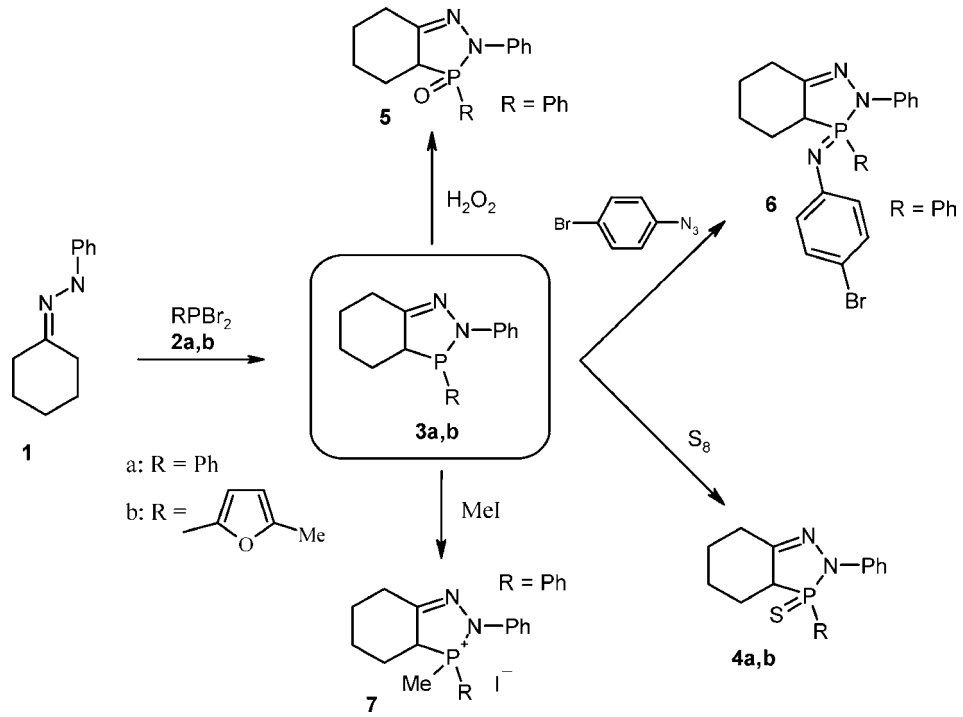
RESULTS AND DISCUSSION

We have found that cyclohexanone phenylhydrazone **1** reacted with phenyldichlorophosphine in pyridine at room temperature to give diazaphospholine **3a**. The reaction comes to completion in 14 days and is accompanied by the formation of significant amounts of by-products and unidentified compounds.

Use of dibromophosphine appeared to be more effective. Thus, phenyldibromophosphine and 5-methyl-2-furyldibromophosphine [4] react with cyclohexanone phenylhydrazone under the same conditions in 1 day affording 1,2,3-diazaphospholines **3a,b** 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).

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Varian VXR-300 spectrometer at 300 MHz using TMS as an internal standard for ^{1}H and ^{13}C, and 85% H_3PO_4 as an external standard for ^{31}P The assignement of the ^{13}C NMR signals is in part tentative. Mass spectra were measured on a MX-1321 instrument (EI, 70eV). Diazaphospholines **3a, b** were synthesized and manipulated under a dry argon atmosphere.



SCHEME 1

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

To a solution of **1** (1.88 g, 0.01 mol) in pyridine (25 mL) cooled to 0°C, **2a** (2.68 g, 0.01 mol) was added. The reaction mixture was held for 24 h. 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 was filtered off under dry argon and recrystallized from dry acetonitrile. *m/z* 294 $[M]^+$. ^{1}H NMR (C_6D_6): $\delta = 0.68$ (m, 3H, CH_2), 1.05 (m, 1H, CH_2), 1.35 (m, 2H, CH_2), 1.69 (m, 1H, CH—P), 1.91 (m, 2H, CH_2—C=N), 6.66 (t, $J = 5.9$ Hz, 1H, *p*-H(N-Ph)), 6.85 (m, 3H, Ph), 7.10 (m, 4H, Ph), 7.59 (d, $J = 7.2$ Hz, 2H, *o*-H(N-Ph)), ^{13}C NMR (C_6D_6) $\delta = 25.0$ (d, $^2J_{CP} = 7.4$, C_4), 25.4 (C_5), 25.7 (C_6), 28.8 (C_7), 48.7 (d, $^1J_{CP} = 13.6$, C-P), 115.6 (d, $^4J_{CP} = 10.6$, *p*-C(P-Ph)), 119.8 (*p*-C(N-Ph)), 129.6 (*o*-C(N-Ph)), 131.3(d, $J_{CP} = 21.9$, *o*-C(P-Ph)), 135.4 (d, $^1J_{CP} = 36.2$, C-P(Ph)), 146.8 (d, $^2J_{CP} = 10.6$, C=N), 152.9 (C-N(Ph)).

TABLE 1 Melting Points (°C) Isolated Yields (%) , ^{31}P NMR Data (δ ^{31}P, Multiplicity, $^2J_{PH}$ in HZ, Solvent) of Compounds **3–7**

	MP	*δ^{31}P Solvent*	*Yield*
3a	181–182	37.3 (d, 26.2) C_6H_6	83
3b	90–91	14.8 (d, 30.3) $CHCl_3$	57
4a	154–155	72.9 (d, 26.0) C_6H_6	60
4b	151–152	52.5; C_6H_6	45
5	184–185	36.9; C_6H_6	35
6	203–206	25.3; C_6H_6	36
7	135–137	40.9; C_6H_6	93

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

It was obtained similarly to compound **3a** starting from **1** (1.88 g, 0.01 mol) and **2b** (2.72 g, 0.01 mol). The product was recrystallized from dry hexane. *m/z* 298 $[M]^+$. ^{1}H NMR ($CDCl_3$): $\delta = 0.98$–2.18 (m, 6H, CH_2), 2.22 (c, 3H, CH_3), 2.38 (m, 2H, CH_2—C=N), 2.96 (m, 1H, CH-P), 5.88 (broad s, 1H, CH—C—CH_3), 6.65 (broad s, 1H, CH—C—P), 7.31 (m, 5H, Ph).

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

To a solution of **3a** (2.94 g, 0.01 mol) in anhydrous benzene (50 ml), elemental sulfur (0.48 g, 0.015 mol) was added and the mixture was boiled to reflux under a dry argon atmosphere for 0.5 h. Benzene was removed under vacuum and the product was extracted from the residue with diethyl ether (3 × 25 mL). ^{1}H NMR (C_6D_6): $\delta = 1.49$–2.06 (m, 6H, CH_2), 2.71 (m, 2H, CH_2—C=N), 3.62 (m, 1H, CH-P), 6.85 (m, 1H, Ph), 7.15 (m, 4H, Ph), 7.60 (m, 4H, Ph), 7.93 (m, 1H, Ph), ^{13}C NMR (DMSO-d_6): δ =23.5 (d, $^2J_{CP} = 13.5$ Hz,

C_4), 25.3 (C_5), 25.9 (d, $^4J_{CP} = 12.1$ Hz, C_6), 29.2 (d, $^3J_{CP} = 14.3$ Hz, C_7), 48.9 (d, $^1J_{CP} = 74.7$ Hz, CH-P), 115.6 (d, $^4J_{CP} = 21.9$ Hz, *p*-C(P-Ph)), 121.1 (*p*-C(N-Ph)), 128.2 (*m*-C(N-Ph)), 128.7 (d, $^2J_{CP} = 12.1$ Hz, *o*-C(P-Ph)), 131.1 (d, $^2J_{CP} = 11.3$ Hz, *o*-C(P-Ph)), 132.3 (*o*-C(N-Ph)), 140.8 (d, $^1J_{CP} = 6.0$ Hz, C-P(Ph)), 155.3 (d, $^2J_{CP} = 2.3$ Hz, C=N), 156.4 (C-N(Ph)).

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

It was obtained similarly to compound **4a** ^{1}H NMR (C_6D_6): $\delta = 1.25$–1.97 (m, 6H, CH_2), 2.68 (m, 2H, CH_2—C=N), 3.58 (m, 1H, CH—P), 6.29 (broad s, 1H, CH—C—CH_3), 6.90 (broad s, 1H, CH—C—P), 7.31 (m, 5H, Ph).

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** (2.94 g, 0.01 mol) in methylene chloride (10 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. ^{1}H NMR (DMSO-d_6): $\delta = 1.51$–2.09 (m, 6H, CH_2), 2.74 (m, 2H, CH_2—C=N), 3.17 (m, 1H, CH-P), 6.85 (m, 1H, Ph), 7.13 (m, 4H, Ph), 7.69 (m, 5H, Ph).

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

To a solution of **3a** (0.50 g, 1.7 mmol) in dry benzene (20 mL), *p*-bromophenyl azide (0.35g, 1.7 mmol) was added. The reaction mixture was boiled with a reflux condenser under a dry argon atmosphere for 1.5 h. After evaporating the solvent under vacuum, the product was extracted from the residue with diethyl ether (4 × 10 mL) and recrystallized from hexane. ^{1}H NMR (DMSO-d_6): $\delta = 1.43$–2.05 (m, 6H, CH_2), 2.68 (m, 2H, CH_2—C=N), 3.15 (m, 1H, CH-P), 6.67 (m, 1H, Ph), 6.97 (m, 4H, Ph), 7.14 (m, 4H, Ph), 7.52 (m, 5H, Ph).

2,3-Diphenyl-3-methyl-3,3a,4,5,6,7-hexahydro-2H-1,2,3-benzodiazaphospholium Iodide **7**

To **3a** (0.50 g, 1.7 mmol), methyl iodide (3 g, 0.02 mol) was added. The reaction mixture was allowed to stand at room temperature for 3 h. The resulting precipitate was filtered off and recrystallized from dry diethyl ether. The product is hygroscopic and decomposes on long storage. ^{1}H NMR (DMSO-d_6): $\delta = 1.35$–2.08 (m, 6H, CH_2), 2.79 (d, $^2J_{HP} = 13.9$ Hz, 3H P-CH_3), 2.86 (2H, CH_2—C=N), 3.77 (m, 1H, CH-P), 7.21 (m, 5H, Ph), 7.68 (m, 5H, Ph).

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