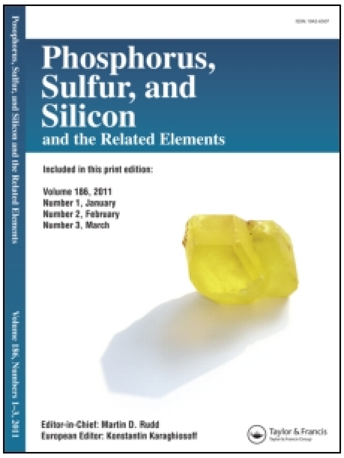

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Convenient Synthesis of [1,5-c]Quinazolo-2,3-dihydro-1,2,4,3-triazaphospholes and [1,5-C]Quinazolo-2,3-Dihydro-1,2,4,3-triazaphosphole-3-sulfides

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The condensation of the amino-iminoquinazolines **2***, with tris(dimethylamino) phosphine, leads to corresponding [1,5-*c*]quinazolo-2,3-dihydro-1,2,4,3-triazaphospholes* **3***. Oxidation of compounds* **3** *with sulfur gives the quinazolo-triazaphosphole-sulfides* **4***. The structure of these compounds is unambiguously confirmed by IR, ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy and by microanalysis of some of the products.*

Keywords [1,5-*c*]quinazolo-1,2,4,3-triazaphosphole; [1,5-*c*]quinazolo-1,2,4,3-triazaphosphole-3-sulfide; amino-iminoquinazoline, tris(dimethyl-amino) phosphine; hydrazine; imidate; methyl hydrazine

INTRODUCTION

An increasing interest has been paid for several years to the synthesis of triazaphospholes. These studies and syntheses are of particular interest due to the possible application of triazaphospholes in several domains.[1–11] Despite their wide applicability, there are only a few routes available for the synthesis of quinazolo-triazaphospholes.[12–15] The present article is a continuation of our previous investigations on the synthesis of fused heterocycles containing the triazaphosphole ring.[15] Here we report the synthesis of new quinazolo-triazaphospholes and triazaphosphole sulfides by cyclocondensation of amino-iminoquinazolines **2** with tris (dimetyhlamino) phosphine and subsequent oxidation of the products with sulfur.

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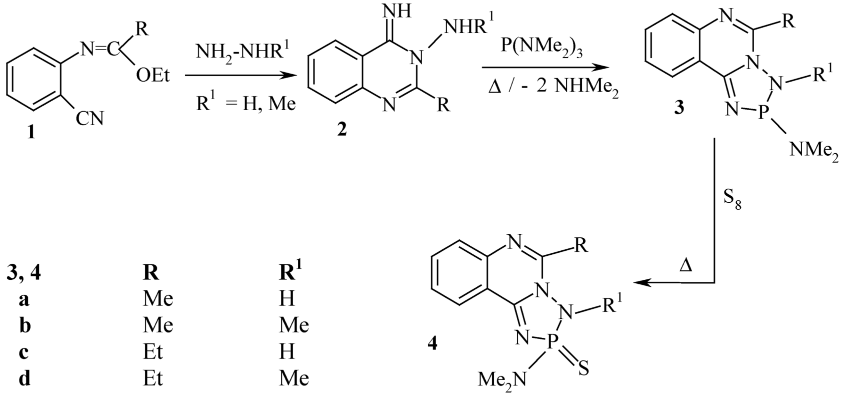
RESULTS AND DISCUSSION

We have obtained the annulated 2,3-dihydrotriazaphospholes **3** starting from the iminoesters **1** in two steps. First the iminoesters **1** were treated with one equivalent of hydrazine or methyl hydrazine to form amino-iminoquinazolines **2**.[12–14] In a second step a mixture of tris(dimethylamino) phosphine and compound **2** was heated under reflux for 24 h to yield the 2,3-dihydro triazaphospholes **3**. Triazaphosphole sulfides **4** are obtained by the oxidation of **3** with sulfur in refluxing toluene for 4 h in good yields.

Structural assignments of compounds **3** and **4** were made on the basis of their IR as well as ^{1}H, ^{13}C, and ^{31}P NMR spectra and are supported by the elemental analyses of some derivatives (see Experimental section).

The formation of the dihydrotriazaphospholes **3** was confirmed by the IR spectra showing the an NH band in the region around 3350 cm^{-1} and a strong band in the region 1090–1100 cm^{-1} indicating the presence of P-N fragments. Another band in the region around 1620 cm^{-1} was assigned to the C=N fragment.

^{1}H NMR spectra of **3** displayed in the case of **3a** and **3c** a signal characteristic for the NH proton at $\delta = 9.80–10.00$ and the expected signals for NMe$_2$ and the ring bonded methyl groups. ^{13}C NMR spectra displayed the characteristic signals of all carbons. The ^{31}P{^{1}H} NMR spectra of dihydro triazaphospholes **3** showed a signal at $\delta = 89.0–91.6$ ppm.



3, 4	R	R^1
a	Me	H
b	Me	Me
c	Et	H
d	Et	Me

SCHEME 1

The oxidation of **3** with sulfur gave sulfides **4** with a good yield. The structures of compounds **4** were established on the basis of their infrared spectra as well as ^{1}H, ^{13}C, and ^{31}P NMR spectra.

IR spectra of the sulfides **4** show a strong band in the region 1090–1100 cm^{-1} assigned to the P-N fragment, a band in the region 1620 cm^{-1}

assigned to the C=N moiety, and a band in the region 1159 cm^{-1} typical for the P=S fragment.

In the $^{31}P\{^{1}H\}$ NMR spectra of the triazaphosphole sulfides **4**, a singlet at $\delta = 63.0–64.6$ ppm is observed.

EXPERIMENTAL

Melting points were obtained using a Büchi melting point apparatus and are uncorrected. IR spectra were recorded in $CHCl_3$ solution with a Perkin Elmer Paragon 1,000 PC spectrometer. ^{1}H and ^{13}C NMR spectra were recorded with a Brucker AC 300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75.47 MHz,^{31}P: 121.49 MHz) in $CDCl_3$, or in a mixture of $CDCl_3$ and $(CD_3)_2SO$ as solvent containing TMS. The chemical shifts are reported in ppm relative to TMS (internal reference) for ^{1}H and ^{13}C and relative to 85% H_3PO_4 (external reference) for ^{31}P.

The iminoesters **1** and the amino-iminoquinazolines **2** were prepared according to reported procedures.[15]

Synthesis of the 2,3-Dihydro Triazaphospholes 3

A mixture of the respective amino-iminoquinazoline **2** (5 mmol) and tris(dimethylamino) phosphine (5 mmol) was heated (at 111°C) in toluene (30 mL) under reflux for 24 h. After completion of the reaction, the excess of solvent was removed under reduced pressure, and diethyl ether (20 mL) was added. The solid separated was filtered, washed with diethyl ether (20 mL) and recrystallised from hexane and toluene (1:1).

3a: Yield: 70%, m.p. = 266°C, IR ($CHCl_3$), ν(cm^{-1}): $\nu_{C=N} = 1620$, $\nu_{N-H} = 3360$, $\nu_{P-N} = 1090$. ^{1}H NMR ($CDCl_3$): 2.50 (d, $^{3}J_{PH} = 7.0$ Hz, 6H, $N(CH_3)_2$); 9.82 (s, 1H, NH); 2.28 (s, 3H, CH_3); 7.02–7.50 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$): 16.0 (CH_3); 36.7 (d, $^{2}J_{PC} = 6.0$ Hz, $N\underline{C}H_3$); 117.2; 126.4; 128.2 and 132.4 ($\underline{C}H_{arom}$); 144.3 ($HC_{arom} = \underline{C}—C_{arom}$); 149.7 ($N = \underline{C}—N$); 150.5 ($HC_{arom} = \underline{C}—N$); 162.0 ($-\underline{C}=N-P$). ^{31}P NMR ($CDCl_3$): 91.6. Anal. Calcd.: C, 53.40; H, 5.66; N, 28.31%; found: C, 53.00; H, 5.5; N, 8.60%.

3b: Yield: 69%, m.p. = 240°C, IR ($CHCl_3$), ν (cm^{-1}): $\nu_{C=N} = 1625$, $\nu_{P—N} = 1093$. ^{1}H NMR ($CDCl_3$+$(CD_3)_2SO$): 2.23 (s, 3H, CH_3); 2.50 (d, $^{3}J_{PH} = 6.9$ Hz, 6H, $N(CH_3)_2$); 3.15 (d, $^{3}J_{PH} = 6.9$ Hz, 3H, NCH_3); 7.02–7.80 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$+ $(CD_3)_2SO$): 15.1 ($\underline{C}H_3$); 35.9 (d, $^{2}J_{PC} = 6.0$ Hz $N\underline{C}H_3$); 36.7 (d, $^{2}J_{PC} = 5.5$ Hz, $N\underline{C}H_3$); 117.1; 122.3; 126.3 and 128.0 ($\underline{C}H_{arom}$); 132.4 ($HC_{arom} =\underline{C}-C_{arom}$); 144.4 ($HC_{arom}=\underline{C}—N$); 149.6 ($N=\underline{C}—N$); 158.6 ($—\underline{C}=N—P$). ^{31}P NMR ($CDCl_3$+$(CD_3)_2SO$): 91.3.

3c: Yield: 65%, m.p. = 166°C, IR ($CHCl_3$), ν(cm^{-1}): $\nu_{C=N} = 1625$, $\nu_{N-H} = 3358$; $\nu_{P-N} = 1091$. ^1H NMR ($CDCl_3$): 2.25 (q, $^3J_{HH} = 6.9$ Hz, 2H, CH_2); 2.70 (d, $^3J_{PH} = 7.5$ Hz, 6H, $N(CH_3)_2$); 9.95 (s, 1H, NH); 1.58 (t, $^3J_{HH} = 6.9$ Hz, 3H, CH_3); 7.02–7.90 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$): 12.1 ($-CH_2-\underline{C}H_3$); 27.1 ($-\underline{C}H_2-CH_3$); 36.7 (d, $^2J_{PC} = 5.0$ Hz, $N\underline{C}H_3$); 117.2; 123.9; 127.0 and 130.1 ($\underline{C}H_{arom}$); 131.4 ($HC_{arom}=\underline{C}-C_{arom}$); 143.0 ($N=\underline{C}-N$); 153.2 ($HC_{arom} = \underline{C}-N$); 162.3 ($-\underline{C}=N-P$). ^{31}P NMR ($CDCl_3$): 89.0. Anal. calcd.: C, 55.17; H, 6.10; N, 26.80%; found.: C, 55.00; H, 6.35; N, 26.60%.

3d: Yield: 65%, oil, IR ($CHCl_3$), ν (cm^{-1}): $\nu_{C=N} = 1625$, $\nu_{P-N} = 1099$. ^1H NMR ($CDCl_3$): 2.40 (q, $^3J_{HH} = 7.5$ Hz, 2H, CH_2); 2.70 (d, $^3J_{PH} = 7.5$ Hz, 6H, $N(CH_3)_2$); 1.42 (t, $^3J_{HH} = 7.5$ Hz, 3H, CH_3); 3.40 (d, $^3J_{PH} = 7.3$ Hz, 3H, NCH_3); 7.20–7.90 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$): 11.7 ($-CH_2-\underline{C}H_3$); 27.2 ($-\underline{C}H_2-CH_3$,); 36.4 (d, $^2J_{PC} = 4.5$ Hz, $N\underline{C}H_3$); 36.7 (d, $^2J_{PC} = 4.0$ Hz, $N\underline{C}H_3$); 117.3; 123.9; 127.0 and 128.1 ($\underline{C}H_{arom}$); 131.4 ($HC_{arom} = \underline{C}-C_{arom}$); 147.2 ($N=\underline{C}-NH$); 159.3 ($HC_{arom} = \underline{C}-N$); 167.4 ($-\underline{C}-N-P$). ^{31}P NMR ($CDCl_3$): 89.8.

Synthesis of 2,3-Dihydro Triazaphosphole Sulfides 4

An equimolar mixture of the triazaphosphole **3** and sulfur in toluene (30 mL) were heated at 111°C under reflux for 4 h. The solid product was filtered and washed with 25 mL of diethyl ether.

4a: Yield: 75%, m.p. = 162°C, IR ($CHCl_3$), ν(cm^{-1}): $\nu_{C=N} = 1620$, $\nu_{N-H} = 3360$; $\nu_{P=S} = 1150$. ^1H NMR ($CDCl_3$): 2.70 (d, $^3J_{PH} = 6.9$ Hz, 6H, $N(CH_3)_2$); 9.80 (s, 1H, NH); 2.21 (s, 3H, CH_3); 7.30–7.90 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$): 16.1 ($\underline{C}H_3$); 34.7 (d, $^2J_{PC} = 5.0$ Hz, $N\underline{C}H_3$); 120.2; 124.9; 129.5 and 132.4 ($\underline{C}H_{arom}$); 135.1 ($HC_{arom} = \underline{C}-C$); 149.3 ($HC_{arom} = \underline{C}-N$); 158.5 ($N= \underline{C}-N$); 170.2 ($\underline{C}=N-P$). ^{31}P NMR ($CDCl_3$): 63.6.

4b: Yield: 72%, m.p. = 172°C, IR ($CHCl_3$), ν (cm^{-1}): $\nu_{C=N} = 1625$; $\nu_{P=S} = 1155$. ^1H NMR ($CDCl_3$+ $(CD_3)_2SO$): 2.24 (s, 3H, CH_3); 2.70 (d, $^3J_{PH} = 7.0$ Hz, 6H, $N(CH_3)_2$); 3.45 (d, $^3J_{PH} = 7.0$ Hz, 3H, NCH_3); 7.01–7.80 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$+$(CD_3)_2SO$): 16.7 ($\underline{C}H_3$); 35.4 (d, $^2J_{PC} = 4.9$ Hz, $N\underline{C}H_3$); 37.4 (d, $^2J_{PC} = 5.0$ Hz, $N\underline{C}H_3$); 119.0; 123.1; 125.1 and 128.2 ($\underline{C}H_{arom}$); 138.4 ($HC_{arom}= \underline{C}-C_{arom}$); 149.1 ($HC_{arom}= \underline{C}-N$); 159.1 ($N=\underline{C}-N$); 170.8 ($\underline{C}=N-P$). ^{31}P NMR ($CDCl_3$+$(CD_3)_2SO$): 63.8. Anal. calcd.: C, 49.14; H, 5.46; N, 23.89%. Found: C, 49.20; H, 5.50; N, 23.60%.

4c: Yield: 69%, m.p. = 154°C, IR ($CHCl_3$), ν(cm^{-1}): $\nu_{C=N} = 1625$, $\nu_{N-H} = 3360$; $\nu_{P=S} = 1152$. ^1H NMR ($CDCl_3$): 2.30 (q, $^3J_{HH} = 6.9$ Hz, 2H, CH_2); 2.80 (d, $^3J_{PH} = 6.9$ Hz, 6H, $N(CH_3)_2$); 10.12 (s, 1H, NH);

1.30 (t, $^3J_{HH} = 6.9$ Hz, 3H, CH_3); 7.01–7.90 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$): 10.1 (—CH_2-$\underline{C}H_3$); 29.1 (—$\underline{C}H_2$-CH_3); 36.7 (d, $^2J_{PC} = 5.5$ Hz, N$\underline{C}H_3$); 117.2; 122.4; 128.3 and 131.4 ($\underline{C}H_{arom}$); 143 ($HC_{arom} = \underline{C}$—$C_{arom}$); 152.0 ($HC_{arom}$= $\underline{C}$—N); 162.1 (N=$\underline{C}$—N); 171.1 (-$\underline{C}$=N—P).^{31}P NMR ($CDCl_3$): 63.8.

4d: Yield: 65%, m.p. = 164°C, IR ($CHCl_3$), ν (cm^{-1}): $\nu_{C=N}$= 1625; $\nu_{P=S}$= 1153. ^1H NMR ($CDCl_3$): 2.40 (q, $^3J_{HH} = 7.0$ Hz, 2H, CH_2); 1.22 (t, $^3J_{HH} = 7.0$ Hz, 3H, CH_3); 2.72 (d, $^3J_{PH} = 7.0$ Hz, 6H, $N(CH_3)_2$); 3.30 (d, $^3J_{PH} = 7.0$ Hz, 3H, NCH_3); 7.20–7.55 (m, 4H, arom-H). ^{13}C NMR ($CDCl_3$): 11.7 (-CH_2-$\underline{C}H_3$); 24.8 (-$\underline{C}H_2$-CH_3,); 35.6 (d, $^2J_{PC} =$ 5.5 Hz, N$\underline{C}H_3$); 37.4 (d, $^2J_{PC} = 5.2$ Hz, N$\underline{C}H_3$); 120.2; 125.3; 128.2 and 131.4 ($\underline{C}H_{arom}$); 147.0 ($HC_{arom} = \underline{C}$—$C_{arom}$); 150.1 ($HC_{arom}$= $\underline{C}$—N); 166.2 (N=$\underline{C}$—N); 169.1 (-$\underline{C}$=N—P). ^{31}P NMR ($CDCl_3$): 64.2. Anal. calcd.: C, 50.80; H, 5.86; N, 22.80 %. Found: C, 50.42; H, 5.61; N, 22.60%.

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