Preparation of Derivatives of 2,3-Dihydro[1,3]benzothiazole[3,2-*d*][1,2,4,3]triazaphosphole

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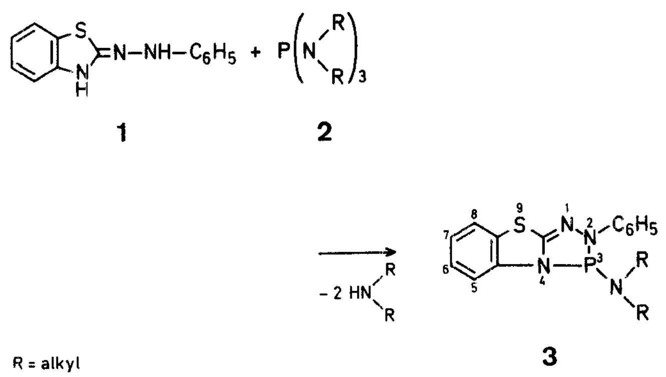
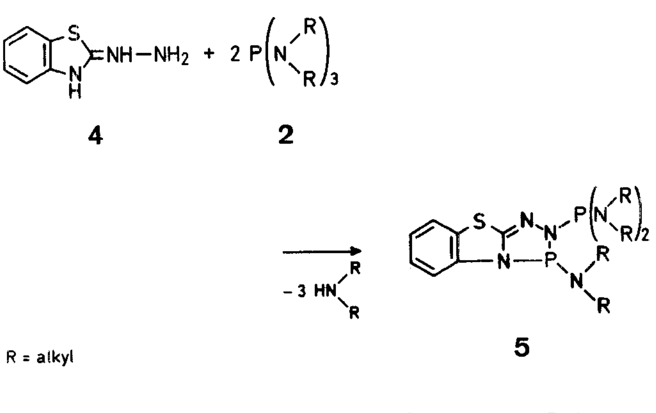
The first tricyclic fused triazaphosphole derivatives, namely, 2,3-disubstituted 2,3-dihydro[1,3]benzothiazolo[3,2-*d*][1,2,4,3]triazaphospholes, were obtained by cyclocondensation of 2-phenylhydryzono- or 2-hydrazono-2,3-dihydro-1,3-benzothiazoles with tris[dialkylamino]-phosphines.

Within the rapid development of the chemistry of phosphorus heterocycles[1], triazaphospholes have received considerable attention[2-5]. However, fused tricyclic triazaphospholes have so far not been described, except for the dimers of a few monocyclic triazaphospholes with pentacoordinated phosphorus[3,4].

We report here the synthesis of the first representatives of fused tricyclic triazaphospholes, namely of 2,3-disubstituted 2,3-dihydro[1,3]benzothiazolo[3,2-*d*][1,2,4,3]triazaphospholes (**3, 5**) by intermolecular cyclocondensation reactions. Thus, the reaction of 2-phenylhydrazono-2,3-dihydro-1,3-benzothiazole[6] (**1**) with tris[dialkylamino]-phosphines (**2**) in xylene or without solvent at 100 °C under nitrogen at a pressure of ~ 100 torr (to remove the dialkylamine formed) affords the 3-dialkylamino-2-phenyl derivatives **3** in reasonable purity and good yield. Products **3** can be isolated by preparative T.L.C.



Unsubstituted 2-hydrazono-1,3-benzothiazole (**4**) reacts with tris[dialkylamino]-phosphines (**2**) under similar conditions (85 °C/80 torr) to afford the 3-dialkylamino-2-(bis[dialkylamino]-phosphino) derivatives **5**. These compounds are very sensitive to moisture and to acidic conditions; they cannot be satisfactorily purified by T.L.C. but they are sufficiently resistant to basic conditions and to certain solvents such as dichloromethane and can be stored under nitrogen.



3-Dimethylamino-2-phenyl-2,3-dihydro[1,3]benzothiazolo[3,2-*d*][1,2,4,3]triazaphosphole (3a); Typical Procedure:

Xylene (10 ml) tris[dimethylamino]-phosphine (**2a**; 1.5 g, 11.8 mmol), and 2-phenylhydrazono-2,3-dihydro-1,3-benzothiazole (**1**; 1.0 g, 4 mmol) are placed in a 60 ml round-bottom flask. This mixture is heated at 100 °C under a nitrogen atmosphere of 100 torr for 4.5 h. The solvent is then evaporated in vacuo and the residual crude product **3a** (1.24 g) is purified by preparative T.L.C. on silica gel using ether petroleum ether (1/9) as eluent; yield of pure **3a**: 0.85 (68 %); white crystals, m.p. 60–61 °C.

Table 1. 2,3-Disubstituted 2,3-Dihydro[1,3]benzothiazolo[3,2-**d**][1,2,4,3]triazaphospholes (**3,5**) prepared

Product	R	Yield[a] [%]	Physical Properties	Molecular Formula[b]
3a	CH_3	68	m.p. 60–61 °C, white crystals	$C_{15}H_{15}N_4PS$ (314.4)
3b	C_2H_5	89[c]	m.p. 89–90 °C, yellow crystals	$C_{17}H_{19}N_4PS$ (342.3)
3c	n-C_3H_7	82	yellow sticky liquid	$C_{19}H_{23}N_4PS$ (370.4)
3d	n-C_4H_9	86	yellow sticky liquid	$C_{21}H_{27}N_4PS$ (398.45)
5a	CH_3	75	yellow sticky liquid	$C_{13}H_{22}N_6P_2S$ (356.3)
5b	C_2H_5	75	yellow sticky liquid	$C_{19}H_{34}N_6P_2S$ (440.5)
5c	n-C_3H_7	69	yellow sticky liquid	$C_{25}H_{46}N_6P_2S$ (524.6)
5d	n-C_4H_9	82	yellow sticky liquid	$C_{31}H_{58}N_6P_2S$ (608.8)

[a] Yield of isolated product.

[b] The microanalyses showed the following maximum deviations from the calculated values: C ± 0.20, H ± 0.08, P ± 0.22 (for **3a, b**) and P ± 0.16 (for **3c, d** and **5a–d**).

[c] M.S.: $m/e = 342$ (M^+, 34%), 270 (74, base peak).

Table 2. Spectral Data of Compounds **3** and **5**

Compound	I.R. (KBr or film)[a] ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3/TMS_{int}$)[b] δ [ppm]	^{13}C-N.M.R. ($CDCl_3/TMS_{int}$)[b] δ [ppm]	^{31}P-N.M.R. ($CDCl_3$/85% H_3PO_{4ext})[b] δ [ppm]
3a	1315s, 1291s (C—N); 1214s, 968s (P—N)	2.5 (d, 6H, $^3J_{HP}$ = 8.5 Hz, 2CH_3); 6.9–7.3 (m, 9H_{arom})	$\underline{C}H_3$: 36.5 (d, $^2J_{CP}$ = 17.6 Hz) $\underline{C}_{cycl}$: 111.8 (d, $^3J_{CP}$ = 5.8 Hz); 114.5, 115.2 (2s); 120.3 (d, $^3J_{CP}$ = 1.7 Hz); 126.2, 128.9 (2s)	74.14
3b	1315s, 1291s (C—N); 1214m, 968m (P—N)	0.84 (t, 6H, 2CH_3); ~2.9 (4d, 4H, $^3J_{HP}$ = 7.8 Hz, 2CH_2); 6.9–7.4 (m, 9H_{arom})	$\underline{C}H_2$—CH_3: 40.1 (d, $^2J_{CP}$ = 17.6 Hz) CH_2—$\underline{C}H_3$: 14.22 (d, $^3J_{CP}$ = 2.7 Hz) $\underline{C}_{cycl}$: 111.9 (d, $^3J_{CP}$ = 5.8 Hz); 114.6, 115.3 (2s); 120.9 (d, $^3J_{CP}$ = 1.6 Hz); 122.9 (d, $^3J_{CP}$ = 1.9 Hz); 126.5, 128.9 (2s)	71.13
3c	1314s, 1290s (C—N); 1211s, 1002s (P—N)	~1.0 (m, 10H, CH_2, CH_3); 2.7 (3d, 4H, $^3J_{HP}$ = 8.6 Hz, CH_2); 7.0–7.3 (m, 9H_{arom})	$\underline{C}H_2$—CH_2—CH_3: 48.4 (d, $^2J_{CP}$ = 17.6 Hz) CH_2—$\underline{C}H_2$—CH_3: 22.5 (d, $^3J_{CP}$ = 4.9 Hz) CH_2—CH_2—$\underline{C}H_3$: 11.2 (s) $\underline{C}_{cycl}$: 112.3 (d, $^3J_{CP}$ = 5.8 Hz); 115.2, 116.0, 120.5, 122.9, 126.2, 128.9 (6s)	72.4
3d	1314s, 1290s (C—N); 1211s, 922s (P—N)	~1.0 (m, 14H, CH_2, CH_3); 2.7 (3d, $^3J_{HP}$ = 8.2 Hz, CH_2); 6.9–7.4 (m, 9H_{arom})	$\underline{C}H_2$—CH_2—CH_2—CH_3: 46.3 (d, $^2J_{CP}$ = 17.6 Hz) CH_2—$\underline{C}H_2$—CH_2—CH_3: 31.0 (d, $^3J_{CP}$ = 3.8 Hz) CH_2—CH_2—$\underline{C}H_2$—CH_3: 20.0 (s) CH_2—CH_2—CH_2—$\underline{C}H_3$: 11.2 (s) $\underline{C}_{cycl}$: 111.8 $^3J_{CP}$ = 5.8 Hz); 114.8, 115.3, 120.0, 122.6, 126.1, 128.9 (6s)	72.4
5a	1200s, 1020s, 960s, 930s (P—N)	1.9 (d, 6H, $^3J_{HP}$ = 8.4 Hz, CH_3); 2.0 (d, 6H, $^3J_{HP}$ = 10.3 H, CH_3); 2.1 (d, 6H, $^3J_{HP}$ = 9.8 Hz, CH_3)	$\underline{C}H_3$: 35.9 (d, $^2J_{CP(cycl)}$ = 17.0 Hz); 37.3 (d, $^2J_{CP(acycl)}$ = 19.0 Hz); 37.6 (d, $^2J_{CP(acycl)}$ = 18.0 Hz)	39.12 (d, $^2J_{PNP}$ = 165 Hz, P_{cycl}; 71.95 (d, $^2J_{PNP}$ = 165 Hz, P_{acycl})
5b	1195s, 1020s, 960s, 930s (P—N)	0.9 (t, 6H, CH_3); 1.0 (t, 6H, CH_3); 1.1 (t, 6H, CH_3); 2.8–3.3 (m, 12H, CH_2)	$\underline{C}H_2$—CH_3: 39.7 (d, $^2J_{CP(cycl)}$ = 9.8 Hz); 39.9 (d, $^2J_{CP(acycl)}$ = 9.8 Hz); 40.1 (d, $^2J_{CP(acycl)}$ = 9.7 Hz) CH_2—$\underline{C}H_3$): 13.8, 14.0, 14.3 (3s)	76.98 (d, $^2J_{PNP}$ = 188 Hz, P_{cycl}); 106.63 (d, $^2J_{PNP}$ = 188 Hz, P_{acycl})
5c	1200s, 1020s, 960s, 930s (P—N)	0.6–1.0 (m, 16H, CH_3); 1.1–2.9 (m, 12H, CH_2); 2.5–3.0 (m, 12H, CH_2)	$\underline{C}H_2$—CH_2—CH_3: 47.9 (d, $^2J_{CP(cycl)}$ = 15 Hz); 48.4 (d, $^2J_{CP(acycl)}$ = 19.0 Hz); 48.9 (d, $^2J_{CP(acycl)}$ = 18.0 Hz CH_2—$\underline{C}H_2$—CH_3: 21.5, 21.7, 21.8 (3s) CH_2—CH_2—$\underline{C}H_3$: 10.8, 11.1, 11.3 (3s)	77.3 (d, $^2J_{PNP}$ = 195 Hz, P_{cycl}); 111 (d, $^2J_{PNP}$ = 195 Hz, P_{acycl})
5d	1201s, 1018s, 968s, 930s (P—N)	0.8–1.0 (m, 16H, CH_3); 1.05–1.7 (m, 24H, CH_2); 2.6–3.2 (m, 12H, CH_2)	$\underline{C}H_2$—CH_2—CH_2—CH_3: 45.7 (d, $^2J_{CP(cycl)}$ = 10.0 Hz); 46.1 (d, $^2J_{CP(acycl)}$ = 18.0 Hz); 46.6 (d, $^2J_{CP(acycl)}$ = 18.0 Hz) CH_2—$\underline{C}H_2$—CH_2—CH_3: 30.7, 30.8 (2s) CH_2—CH_2—$\underline{C}H_2$—CH_3: 19.9, 20.1, 20.3 (3s) CH_2—CH_2—CH_2—$\underline{C}H_3$: 13.6, 13.3 (2s)	77.17 (d, $^2J_{PNP}$ = 204 Hz, P_{cycl}); 108.75 (d, $^2J_{PNP}$ = 204 Hz, P_{acycl})

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[a] Recorded with a Perkin-Elmer 983 spectrometer.

[b] Recorded with Varian XL-200 and Bruker WP-80 spectrometers.

[c] For compounds **5**, ^{1}H- and ^{13}C-N.M.R. data are only given for the alkyl groups R.

3-Dimethylamino-2-(bis[dimethylamino]-phosphino)-2,3-dihydro[1,3]benzothiazolo[3,2-*d*][1,2,4,3]triazaphosphole (5a); Typical Procedure:

In a 50 ml round-bottom flask, 2-hydrazono-2,3-dihydro-1,3-benzothiazole (**4**; 0.5 g, 3 mmol) is added to tris[dimethylamino]-phosphine (**2a**; 1.5 g, 11.8 mmol) and this mixture is heated at 85 °C with stirring under a nitrogen atmosphere of 80 torr for 1 h. The mixture is then allowed to cool and product **5a** is isolated by preparative T.L.C. on silica gel using petroleum ether/triethylamine (13/7) as eluent; yield: 0.8 g (75%) of liquid with a strong odor.

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