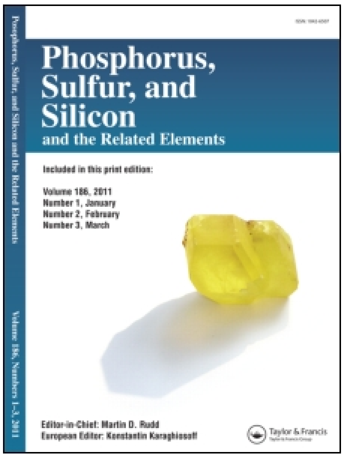

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NEW DERIVATIVES OF 4,5-BENZO-1,3,2-OXAZA (OR D1AZA)-PHOSPHOLANE FROM CONVENIENT CONDENSATION OF SUBSTITUTED UREA WITH TRIS(DIALKYLAMINO)PHOSPHINE

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NEW DERIVATIVES OF 4,5-BENZO-1,3,2-OXAZA (OR DIAZA)-PHOSPHOLANE FROM CONVENIENT CONDENSATION OF SUBSTITUTED UREA WITH TRIS(DIALKYLAMINO)PHOSPHINE

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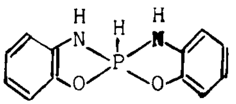
The condensation of *N*-phenyl-*N'*-(2-hydroxylphenyl)urea or *N*-phenyl-*N'*-(2-aminophenyl)urea with tris(dialkylamino)phosphine afforded derivatives of 4,5-benzo-1,3,2-oxaza (or diaza)-phospholane which formed intramolecular hydrogen bond. The cleavage of the amide bond to give *N,N*-dialkyl-*N'*-phenylurea together with polymers of 1,3,2-benzodiazaphosphole was observed in the latter reaction.

Key words: Condensation reaction; 1,3,2-benzoxazaphospholane; 1,3,2-benzodiazaphospholane; intramolecular hydrogen bond; urea derivatives; 4-bond P–H coupling constants.

INTRODUCTION

Earlier studies have shown that the reactions of *o*-aminophenol with trivalent phosphorus reagents such as *i*-$PrOP(NEt_2)_2$,[1] $EtP(NEt_2)_2$,[2] $P(OPh)_3$[3] give rise to dioxadiazadibenzophosphaspirononane **1** or 1,3,2-benzoxazaphospholane **2**. Further reaction of **2** (R' = H) with *o*-aminophenol gave the spiro compounds **1**, and heating **1** with two moles of $P(NR_2)_3$ at 120–140°C afforded **2**.[4] Recently, we have developed a convenient method to synthesize a new class of fused tricyclic triazaphosphole,[5] which can be applied to other similar systems. Now we wish to report the synthesis and characterization of the new derivatives of 1,3,2-benzoxaza (or benzodiaza)phospholane from the condensation reaction of *N*-phenyl-*N'*-[2-hydroxyl (or amino)phenyl] urea with tris(dialkylamino)phosphine.



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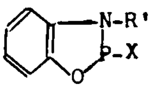
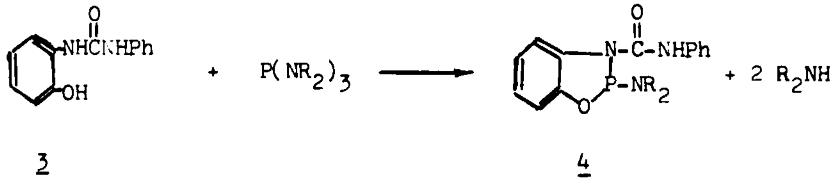


2 X = OR, R' = H;
X = NR_2, R' = $P(NR_2)_2$

RESULTS AND DISCUSSION

One and a half equivalents of compounds **3** were heated with neat tris(dialkylamino)phosphine under a nitrogen atmosphere of reduced pressure, compounds **4** were afforded in 91–95% yields as depicted in Scheme I.

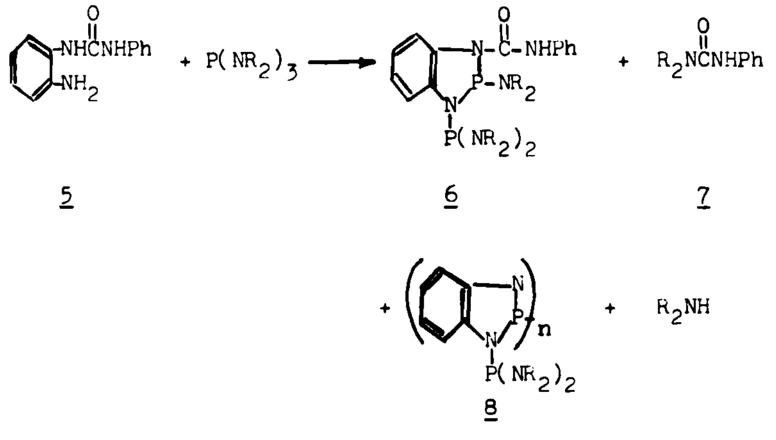


SCHEME I

There were no spirophosphoranes formed in this reaction, even when the molar ratio of **3** to $P(NR_2)_3$ was increased.

When *N*-phenyl-*N'*-(2-aminophenyl)urea **5** was treated under the same conditions, products **6** were formed, which were further fragmented to *N,N*-dialkyl-*N'*-phenylurea **7** as the main product together with other side products (Scheme II). A small amount of compound **6** could be isolated if *R* = *n*-butyl, but when *R* was methyl, ethyl or *n*-propyl, only trace amount could be detected. Compounds **6** were very unstable, even in the absence of light and under the protection of nitrogen at −5° ~ −40°C. In the case of *R* = methyl, after isolation of **6** and **7** by preparative T.L.C., the EIMS of the residue showed that there were dimer, m/z 525($C_{20}H_{33}N_8P_4^+$, 36%), and trimer, m/z 787($C_{30}H_{49}N_{12}P_6^+$, 27%) and other polymers formed. ^{31}P NMR analysis of the residue gave two series of signals, ones at 99 ppm ($^2J_{PNP} = 52$ Hz), 105 ppm ($^2J_{PNP} = 59$ Hz) etc., the others at 131 ppm ($^2J_{PNP} = 52$ Hz), 135 ppm ($^2J_{PNP} = 59$ Hz) etc. It seems that the former NMR signals could come from the resonance of the cyclic phosphorus atom and the latter from that of acyclic phosphorus atom of products **8** ($n = 2$, 3 etc.),[5] but no signals were found in a range from +180 ~ +300 ppm, typical for dicoordinated phosphorus compounds.

It is worth while to note that the ^1H NMR spectra of compounds **4** and **6** displayed extremely large 4-bond P—H coupling constants (PNCNH) of *ca.* 9.5 Hz, and in compound **6d**, α-hydrogens of dialkylamino group attached to cyclic phosphorus are more strongly coupled to phosphorus than those attached to acyclic phosphorus. A similar phenomenon was observed in the ^{13}C NMR



SCHEME II

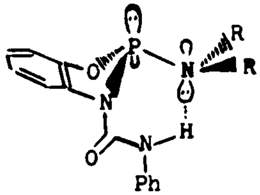


FIGURE 1

spectra in which ${}^2J_{C_\alpha P} = 21 \sim 22$ Hz, whereas ${}^2J_{C_{c=0}P} = 9.6 \sim 11.7$ Hz. It seems reasonable to assume that an intramolecular hydrogen bond is formed in compounds **4** and **6**. For example, in the case of compounds **4** (Figure 1), the hydrogen atom of the anilino group approaches the nitrogen along the symmetric axis of its lone pair,[7] which leads to the trans orientation of the lone pairs of phosphorus and nitrogen, rather than their usual orthogonal situation.[8] Therefore, the two alkyl groups of dialkylamino are cis to the lone pair of phosphorus, and the α-carbon and α-hydrogen are strongly coupled to phosphorus. The IR spectra of compounds **4** and **6** also confirmed the existence of the hydrogen bond. The formation of a hydrogen bond leads to the shift of N—H absorption to lower frequency and the depression of their melting points (Table I and II).

EXPERIMENTAL

Melting points were taken on a Thomas–Hoover capillary melting point apparatus and are not corrected. ^1H and ^{13}C NMR were recorded on Varian XL-300 and are reported in parts per million downfield from internal tetramethylsilane. ^{31}P NMR spectra were measured using 85% H_3PO_4 as external reference. Infrared spectra were measured as KBr plates or film on NaCl cell on a Simadzu 430 spectrometer. Electron-impact mass spectra (EIMS) were determined with a JMS M-80A, GC-MS mass spectrometer (JEOL Ltd. Tokyo, Japan). The rotary T.L.C. apparatus used to purify the products is LBG-1 Model from Qingying Instrument Factory, China.

Reaction of N-phenyl-N′-(2-hydroxylphenyl)urea **3** *with Tris(dialkylamino)phosphine.* General procedure. To a 10 ml round-bottom flask with 1.6 g (6.6 mmol) of tris(diethylamino)phosphine, 1.0 g

TABLE I

Reactions of **3** or **5** with tris(dialkylamino)phosphine

Entry	*R*	Molar ratio 3 or 5: P(III)[a]	Temp. °C	N_2 press. torr	Time h	Yield[b] %	mp[c] °C
4a	Me	1:1.5	90	20	1	90.0	Colorless sticky liquid
4b	Et		105	10		94.0	
4c	*n*-Pr		110	15		98.8	
4d	*n*-Bu		115	15		93.5	
7a	Me	1:2.5	90	45	1	77.0	134–136 (135)
7b	Et		90	40		79.5	85–86 (86–87)
7c	*n*-Pr		95	45		83.0	71–72 (71–72)
7d	*n*-Bu	1:2.5	90	40	1	82.5	81–83 (82–84)
6d						17.0	Sticky Liquid

[a] P(III) represents $P(NR_2)_3$.
[b] Isolated yield.
[c] The data in parentheses are the literature values reported in Reference 6.

TABLE II

^1H, ^{31}P NMR and IR spectra of compounds **4** and **6d**

Compd	^1H NMR δ (ppm)	IR $\nu(cm^{-1})$				^{31}P NMR[a] δ (ppm)
		N—H	C=O	P—H	P—O	
4a	2.82(d, 6H, $^3J_{HP} = 11.8$ Hz) 6.70–7.51(m, 9H); 7.93(d, 1H, $^4J_{HP} = 9.6$ Hz)	3350	1688	1176 996	1020 867	121.4
4b	0.90(t, 6H); 3.15(dq, 4H, $^2J_{HP} = 11.7$ Hz); 6.71–7.52 (m, 9H); 7.92(d, 1H, $^4J_{HP} = 9.5$ Hz)	3350	1686	1176 935	1018 867	121.7
4c	0.62–1.18(m, 6H); 1.20–1.53(m, 4H); 2.85(dq, 4H, $^3J_{HP} = 11.9$ Hz); 6.73–7.49 (m, 9h); 7.95(d, 1H, $^4J_{HP} = 9.9$ Hz)	3354	1688	1180 996	1020 868	120.9
4d	0.61–0.93(m, 6H); 1.00–1.63(m, 8H); 2.60–3.15(m, 4H, $^3J_{HP} = 11.6$ Hz); 6.73–7.50(m, 9H); 7.93(d, 1H, $^4J_{HP} = 9.7$ Hz)	3348	1688	1178 996	1026 869	120.8
6d	0.75–1.10(m, 18H); 1.10–1.90(m, 24H); 2.62–2.90 (m, 4H, $^3J_{HP} = 12.3$ Hz); 2.90–3.25(m, 8H, $^3J_{HP} = 7.4$ Hz); 6.70–7.62(m, 9H); 8.00(d, 1H, $^4J_{HP} = 9.1$ Hz)	3361	1689	1167 987		131(68) 94.5(68)

[a] Figures in parentheses are coupling constants ($^2J_{PNP}$) in hertz.

TABLE III

^{13}C NMR spectra of compounds **4** and **6d**[a]

Compd	C_{alkyl}				C_{arom}	$C_{C=O}$
	α-C	β-C	ν-C	δ-C		
4a	37.5 (20.4)				150.4 (11.9); 137.6; 130.0; 127.3; 123.6; 118.9; 116.0	152.1 (9.8)
4b	39.5 (21.9)	15.6			149.3 (11.7); 137.4; 129.6; 127.7; 122.9; 118.6; 114.3	151.3 (11.7)
4c	47.5 (20.7)	22.0	11.4		150.2 (12.2); 138.2; 130.5; 129.2; 123.0; 120.0; 116.0	152.3 (9.7)
4d	45.5 (20.6)	31.1	20.6	14.1	150.1 (12.1); 138.1; 130.4; 129.1; 122.6; 120.5; 116.0	152.0 (9.6)
6d	46.5 (20.5) 47.6 (21.8) 48.5 (21.0)	31.6	21.3	14.5	149.6 (10.6); 137.5; 131.4; 129.5; 123.5; 118.9; 114.5	154.5 (9.9)

[a] The coupling constants of the carbon as split by the phosphorus atom are given in hertz in parentheses.

(4.4 mmol) of **3** was added. The mixture was heated at 105°C with stirring for 1 h under a nitrogen atmosphere of 10 torr. After the mixture was cooled to the ambient temperature, the reaction system was opened to the air carefully. The obtained colorless sticky mixture was dissolved in 5.0 ml of dichloromethane and purified by column chromatography on silica gel using diethyl ether/petroleum ether (1:10) as a gradient eluent to afford **4b** (1.34 g, 94.0%) as a colorless sticky liquid. MS, *m/e* (rel. intensity): For **4a**, 301($C_{15}H_{16}N_3O_2P^+$, 83.4), 182($C_8H_{11}N_2OP^+$, 61.3), 137($C_6H_4NOP^+$, 100), 119($C_7H_5NO^+$, 44.5). For **4b**, 329($C_{17}H_{20}N_3O_2P^+$, 98.4), 258($C_{13}H_{11}N_2O_2P^+$, 6.8), 210($C_{10}H_{15}N_2OP^+$, 53.3), 137($C_6H_4NOP^+$, 100), 119($C_7H_5NO^+$, 39.5). For **4c**, 357($C_{19}H_{24}N_3O_2P^+$, 90.7), 119($C_7H_5NO^+$, 45.8), 238($C_{12}H_{19}N_2OP^+$, 70.5), 137($C_6H_4NOP^+$, 100). For **4d**, 385($C_{21}H_{28}N_3O_2P^+$, 100), 266($C_{14}H_{23}N_2OP^+$, 77.8), 137($C_6H_4NOP^+$, 95.4), 119($C_7H_5NO^+$, 52.5). Anal. Calcd for **4a**, $C_{15}H_{16}N_3O_2P$: C, 59.80; H, 5.32; P, 10.30. Found: C, 59.75; H, 5.28; P, 10.21. Anal. Calcd for **4b**, $C_{17}H_{20}N_3O_2P$: C, 62.01; H, 6.08; P, 9.42. Found: C, 62.10; H, 6.14; P, 9.49. Anal. Calad for **4c**, $C_{19}H_{24}N_3O_2P$: C, 63.87; H, 6.72; P, 8.68. Found: C, 63.92; H, 6.83; P, 8.74. Anal. Calcd for **4d**, $C_{21}H_{28}N_3O_2P$: C, 65.45; H, 7.27; P, 8.05. Found: C, 65.51; H, 7.35; P, 8.12.

Reaction of N-phenyl-N'-(2-aminophenyl)urea **5** *with Tris(dialkylamino)phosphine.* General procedure. To a 10 ml round-bottom flask containing tris(dibutylamino)phosphine (4.6 g, 11 mmol) was added 1.0 g (4.4 mmol) of **5**. The mixture was stirred at 90°C under a nitrogen atmosphere of 40 torr for 1 h. The residue was purified by rotary T.L.C. apparatus on silica gel using diethyl ether/petroleum ether (1:10) as eluent firstly to afford **6d**, and then using diethyl ether/petroleum ether (1:3) as eluent to afford **7d**. After further purification by preparative T.L.C. on silica gel employing the eluent described above, **6d** (0.5 g, 17.0%) and **7d** (0.91 g, 82.5%) were obtained respectively. For **6d**, MS. *m/e* (rel. intensity): 671($M^+ + 1$, 4.5), 295($C_{14}H_{23}N_3P_2^+$, 3.5), 136($C_6H_5N_2P^+$, 91.7), 128($C_8H_{18}N^+$, 99.5), 119($C_7H_5NO^+$, 100). Anal Calcd for **6d**, $C_{37}H_{64}N_6OP_2$: C, 66.27; H, 9.55; P, 9.25. Found: C, 66.31; H, 9.58; P, 9.34.

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