N-PHOSPHORYLATED 1,3,2-DIHETEROPHOSPHOLANES

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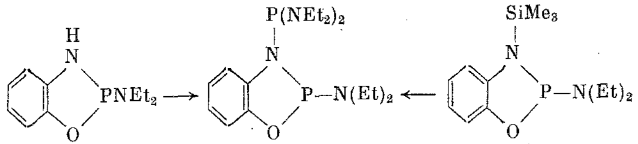
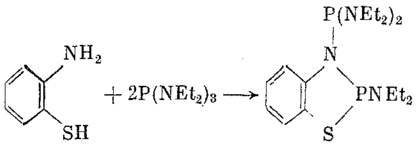
Previously we described the preparation of the first N-phosphorylated oxazaphospholanes from o-aminophenol [1]. In the present paper, we propose new methods for synthesis of derivatives of N-phosphorylated 1,3,2-oxaza- and 1,3,2-thiazaphospholanes. An approach for the preparation of heterocycles containing the P–N–P system is phosphorylation of oxazaphospholanes with NH or NSi groups. Thus, the reaction of 2-(diethylamino)-4,5-benzo-1,3,2-oxazaphospholane (I) with tetraethyldiaminochlorophosphine in the presence of a base gives 2-(diethylamino)-3-bis(diethylamino)phosphino-4,5-benzo-1,3,2-oxazaphospholane (II).



(I) (II) (III)

The same product (II), but in a higher yield, is formed in the reaction with 2-(diethylamino)-3-(trimethylsilyl)-4,5-benzo-1,3,2-oxazaphospholane (III).

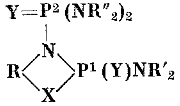
The first representative of N-phosphorylated 1,3,2-thiazaphospholanes could be obtained by the reaction of o-aminothiophenol with hexaethyltriaminophosphine



(IV)

In the ^{31}P NMR spectrum of 2-(diethylamino)-3-bis(diethylamino)phosphino-4,5-benzo-1,3,2-thiazaphospholane (IV), the phosphorus nuclei are characterized by two doublets of $\delta\ ^{31}P$ of 105 and 114 ppm, $^2J_{PNP}=20$ Hz. Previously, for compound (II) [2], it was established that the signal in the strong field belongs to the P atom located outside the ring, and the signal in the weak field belongs to the P atom contained in the ring. Using these data and comparing the numerical values of the chemical shifts of compounds (II) and (IV), we can state that the signal at 105 ppm in the spectrum of phospholane (IV) belongs to the exocyclic P atom, and the signal at

TABLE 1. Chemical Shifts and Spin–Spin Coupling Constants of N-Phosphorylated 1,3,2-Diheterophospholanes



Compound	R	R′	R″	X	Y	$\delta^{31}P^1$, ppm	$\delta^{31}P^2$, ppm	J_{PNP}, Hz
(II)	C_6H_4	Et	Et	O	–	133	106	–
(IV)	C_6H_4	Et	Et	S	–	114	105	20
(V)	C_6H_4	Me	Me	S	–	113	105	20
(VI)	C_6H_4	Me	Me	S	S	87	70	–
(VII)	$(CH_2)_2$	Me	Me	O	–	134	107	140
(VIII)	$(CH_2)_2$	Et	Et	O	–	136	106	120
(IX)	$(CH_2)_2$	Me	Me	O	S	85	69	40
(X)	$(CH_2)_2$	Et	Et	O	S	81	69	40

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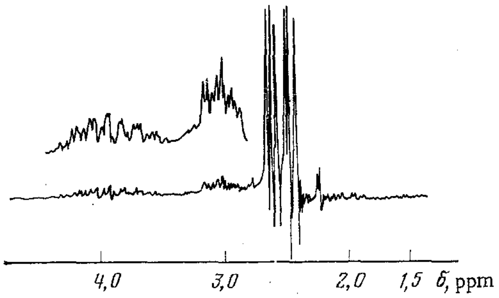
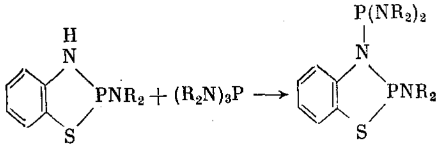


Fig. 1. PMR Spectrum of 2-(dimethylamino)-3-bis-(dimethylamino)phosphino-1,3,2-oxazaphospholane (VII).

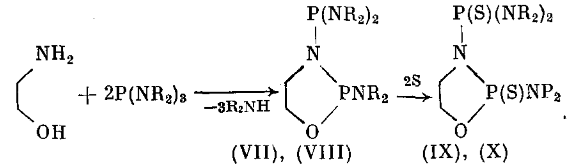
114 ppm belongs to the endocyclic P atom. The methyl analog of compound (IV), 2-(dimethylamino)-3-bis(dimethylamino)phosphino-4,5-benzo-1,3,2-thiazaphospholane (V), is unstable, because of which it was identified spectrally (Table 1) and also by conversion to 2-(dimethylamino)-2-thioxo-3-bis(dimethylamino)thiophosphinyl-4,5-benzo-1,3,2-thiazaphospholane (VI) after addition of two equivalents of sulfur. The addition of sulfur does not proceed selectively, and it is not possible to obtain the product of monoaddition.

N-Phosphorylated derivatives (IV) and (V) are also formed in the transamidation of triaminophosphines in the presence of 2-(dialkylamino)-4,5-benzo-1,3,2-thiazaphospholanes



However, because of the low thermal stability of these thiazaphospholanes and their partial decomposition, it is difficult to isolate the reaction products in this case.

Previously unknown N-phosphorylated 1,3,2-oxazaphospholanes (VII) and (VIII) were obtained by cyclophosphorylation of ethanolamine in the presence of hexaalkyltriaminophosphines



R = Me (VII), (IX); Et (VIII), (X).

Phospholanes (VII) and (VIII) easily add two equivalents of sulfur, becoming four-coordinate derivatives. The proton NMR spectrum of oxazaphospholane (VII) shows the presence of three doublets of δ CH_3 of 2.54, 2.61, and 2.65 ppm, $J_{CH_3P} = 8.8$ Hz, belonging to three dimethylamino groups (Fig. 1). This fact indicates anisochronicity of the NMe_2 groups because of asymmetricity of the endocyclic P or N atoms. The data of the ^{31}P NMR spectra of the obtained compounds are given in Table 1. In considering Table 1, we note the anomalously large spin–spin coupling constants of the phosphorus nuclei in phospholanes (VII) and (VIII). For example, in N-phosphorylated thiazaphospholanes (IV) and (V), the spin–spin coupling constants have values of ~20 Hz, and in analog (II), differing from (VIII) in the presence of a phenylene group, splitting is altogether absent. In phosphorylated 1,3,2-oxazaphospholanes obtained from ethanolamine where the P atoms have different coordinations [3], the spin–spin coupling constant does not exceed 50 Hz. It is also known that the value of the spin–spin coupling constant of the P nuclei in the geminal system is affected by the angular parameters of the geminal system, the electronegativity of the substituents [4], and the presence of unshared electron pairs or π-electron systems at atoms adjacent to phosphorus [5]. Since compounds (II), (VII), and (VIII) have close chemical structures, such difference in the values of the spin–spin coupling constant should apparently be attributed to different steric factors.

EXPERIMENTAL

The ^{31}P NMR spectra were recorded with a KGU-4 NMR instrument at a frequency of 10.2 MHz, and the standard was 85% H_3PO_4. The PMR spectra were recorded with a Varian T-60 instrument, and the internal standard was tetramethylsilane.

2-(Diethylamino)-3-bis(diethylamino)phosphino-4,5-benzo-1,3,2-oxazaphospholane (II). 1) To a mixture of 9 g of (I) and 4.3 g of triethylamine in 200 ml of benzene, 9 g of tetraethyldiaminochlorophosphine was added dropwise at 5-10°C, and the whole was stirred for 1 h at ~20°C. After separation of triethylamine hydrochloride (71% yield), removal of the solvent, and distillation, 6.8 g (42%) of (II) was obtained, bp 152-154°C (0.001 torr), n_D^{20} 1.5412; cf. [1].

2) A mixture of 8.1 g of (III) and 6.3 g of tetraethyldiaminochlorophosphine was heated for 1.5 h at 120°C until trimethylchlorosilane was no longer evolved. By distillation, 8.05 g (70%) of (II) was obtained, bp 152°C (0.008 torr), n_D^{20} 1.5468.

2-(Diethylamino)-3-bis(diethylamino)phosphino-4,5-benzo-1,3,2-thiazaphospholane (IV). A mixture of 8.4 g of o-aminothiophenol and 33 g of hexaethyltriaminophosphine was heated for 1 h at 130-140°C until diethylamine was no longer evolved. By distillation we obtained 11.3 g (42%) of (IV), bp 164°C (0.003 torr), n_D^{20} 1.5750. Found: C 53.55; H 8.65; N 14.12%. $C_{18}H_{34}N_4P_2$. Calculated: C 54.00; H 8.50; N 14.00%..

2-(Dimethylamino)-2-thioxo-3-bis(dimethylamino)thiophosphinyl-4,5-benzo-1,3,2-thiazaphospholane (VI). A mixture of 4.3 g of o-aminothiophenol and 11.4 g of hexamethyltriaminophosphine was boiled in a solution of benzene for 3 h, 2.1 g of powdered sulfur was added, and the whole was heated for 1 h more. By distillation we obtained 8.5 g (70.8%) of (VI), mp 142-144°C (from benzene). Found: C 37.65; H 5.87; N 14.53%. $C_{12}H_{24}N_4P_2S_3$. Calculated: C 37.89; H 5.79; N 14.80%.

2-(Dimethylamino)-3-bis(dimethylamino)phosphino-1,3,2-oxazaphospholane (VII). A mixture of 32.6 of hexamethyltriaminophosphine and 6.3 g of ethanolamine in the presence of a catalytic amount of triethylamine hydrochloride or ammonium sulfate was heated for 1 h at 130-150°C. By distillation we obtained 10 g (31%) of (VII), bp 110°C (0.08 torr), n_D^{20} 1.5130, d_4^{20} 1.1041. Found: C 37.98; H 8.55; N 22.00%. $C_8H_{22}N_4OP_2$. Calculated: C 38.09; H 8.73; N 22.22%.

2-(Diethylamino)-3-bis(diethylamino)phosphino-1,3,2-oxazaphospholane (VIII). Compound (VIII) was obtained similarly to the preceding one in 22% yield, bp 125°C (0.08 torr), n_D^{20} 1.5000, d_4^{20} 1.0153. Found: C 49.86; H 10.20; N 16.40%. $C_{14}H_{34}N_4OP_2$. Calculated: C 50.00; H 10.11; N 16.66%.

2-(Dimethylamino)-2-thioxo-3-bis(dimethylamino)thiophosphinyl-1,3,2-oxazaphospholane (IX). A mixture of 5.57 g of (VII) and 1.41 g of powdered sulfur was heated for 1 h at 130°C. By distillation we obtained 2 g (60%) of (IX), bp 120°C (0.001 torr), mp 73°C. Found: C 30.30; H 6.80; N 17.72; P 19.60%. $C_8H_{22}ON_4P_2S_2$. Calculated: C 30.30; H 6.96; N 17.72; P 19.62%.

2-(Diethylamino)-2-thioxo-3-bis(diethylamino)thiophosphinyl-1,3,2-oxazaphospholane (X). Compound (X) was obtained similarly in 58% yield, mp 91°C (from cyclohexane). Found: C 41.79; H 8.46; N 14.60; S 15.42%. $C_{14}H_{34}N_4OP_2S_2$. Calculated: C 42.00; H 8.50; N 14.00; S 15.40%.

CONCLUSIONS

Methods have been proposed for phosphorylation of 4,5-benzo-1,3,2-oxazaphospholanes. Novel N-phosphorylated 1,3,2-oxaza- and -thiazaphospholanes have been synthesized.

LITERATURE CITED

1. A. N. Pudovik, M. A. Pudovik, and S. A. Terent'eva, Inventor's Certificate No. 395,396, 1973, Byull. Izobret., No. 35 (1973).
2. M. A. Pudovik, S. A. Terent'eva, Yu. Yu. Samitov, and A. N. Pudovik, Zh. Obshch. Khim., 45, 266 (1975).
3. M. A. Pudovik and A. N. Pudovik, Zh. Obshch. Khim., 46, 222 (1976).
4. E. Y. Finer, J. Mol. Spectrosc., 23, 104 (1967).
5. Y. E. Nixon, J. Chem. Soc., A, 1083 (1969).