THIYLATING EFFECT OF 2-CHLORO-2-THIONO-5-METHYL-1,2-OXAPHOSPHOLANE

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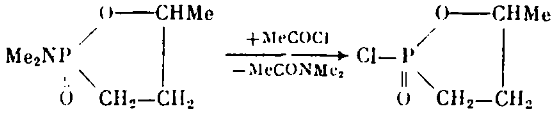
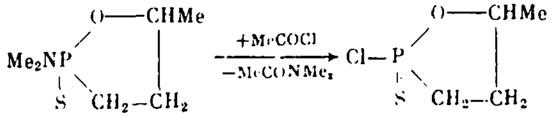
It was found that 2-chloro-2-thiono-5-methyl-1,2-oxaphospholane has a thiylating effect toward some compounds with carbonyl and phosphoryl groups.

Earlier we showed that the reaction of 2-dimethylamino-2-oxo-5-methyl-1,2-oxaphospholane (I) with acetyl chloride results in 2-chloro-2-oxo-5-methyl-1,2-oxaphospholane (II), which can be purified by distillation, although a significant portion of it is lost during distillation because of resinification [1].


(I) (II)

(1)

The reaction of 2-dimethylamino-2-thiono-5-methyl-1,2-oxaphospholane (III) with acetyl chloride also produces the corresponding acid chloride (IV). However, the ^{31}P NMR spectrum of the distilled reaction mixture always contained two signals corresponding to compounds (IV) and (II).


(III) (IV)

(2)

The substances obtained after distillation of the products of reaction (2) and that did not contain phosphorus contained sulfur.

Proceeding from the hypothesis that the phosphorus sulfides (III) or (IV) can possess thiylating action, initially we heated dimethylacetamide with thiophosphonate (III) at 100-120°C. The starting compounds were recovered upon distillation. A second thiylating agent could be 2-chloro-2-thiono-5-methyl-1,2-oxaphospholane (IV). It was obtained as a result of the reaction of (II) with P_2S_5.

$$\text{(II)} \xrightarrow{P_2S_5} \text{(IV)} \qquad (3)$$

It turned out that (IV) exhibits thiylating action toward dimethylacetamide and dimethylbenzamide. Heating of (IV) with these substances resulted in (V) and (VI), respectively.

$$\text{(IV)} + RCONMe_2 \longrightarrow \text{(II)} + RC(S)NMe_2 \qquad (4)$$

R = Me (V), Ph (VI).

The constants of (V) and (VI) are identical to those of compounds obtained by reaction mechanism (5).

$$RCONMe_2 \xrightarrow{P_2S_5} RC(S)NMe_2 \qquad (5)$$

R = Me (V), Ph (VI).

It is probable that in the course of reactions that follow mechanism (4) there is a redistribution of the substituents on the phosphorus and carbon that leads to energetically

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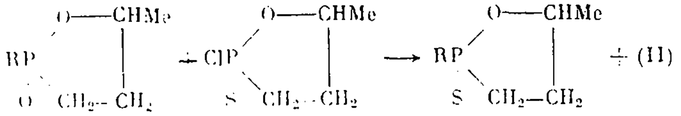
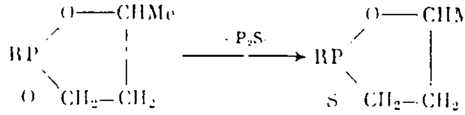
more advantageous compounds (HSAB principle). Based on this principle, we assumed that the phosphoryl oxygen would be replaced by sulfur in those phosphoryl compounds that already have a "soft" R substituent on the phosphorus.



(6)

Indeed, if R = Me_2N and p-PrS these reactions proceed with quantitative formation of the proposed compounds (VII) and (VIII).

The constants and IR spectra of (VII) and (VIII) are identical to the compounds obtained from the corresponding phosphoryl compounds of P_2S_5:



(7)

R = Me_2N (VII), n-PrS (VIII).

EXPERIMENTAL

Synthesis of 2-Chloro-2-thiono-5-methyl-1,2-oxaphospholane (IV). Phosphorus pentasulfide (0.91 g) was heated in boiling C_6H_6 for 30-40 min with 3.2 g (II) (reactant ratio 1:5). The benzene solution containing precipitate was poured off, the benzene was driven off, and the residue was distilled. (IV), bp 67°C (0.09 mm Hg), d_4^{20} 1.2900, n_D^{20} 1.5342, δ ^{31}P 109 ppm. Found, %: C 28.60; H 4.91; S 18.03; Cl 20.0; P 18.02. C_4H_8ClOPS. Calculated, %: C 28.15; H 4.69; S 18.77; Cl 20.82; P 18.18. Yield 2.51 g (71%).

Reactions of 2-Chloro-2-thiono-5-methyl-1,2-oxaphospholane (IV) with Compounds Containing Carbonyl or Phosphoryl Groups. Equimolar amounts of (IV) and a compound with a C=O or P=O group were heated without solvent at 110-140°C, monitoring the reaction from the ^{31}P NMR spectrum [disappearance of the signal of (IV)]. Then $CHCl_3$ was added to the reaction mixture, the solution was passed through a short column containing silica gel, the $CHCl_3$ was driven off, and the residue was analyzed.

(V), mp 71°C. Found, %: N 13.47; S 30.39. C_4H_9NS. Calculated, %: N 13.59; S 31.06.

(VI), mp 65°C. Found, %: N 8.47; S 19.39. $C_9H_{11}NS$. Calculated, %: N 3.48; S 19.39.

The PMR spectra of (V) and (VI) are identical to those given in [2].

(VII), bp 60-64°C (0.07 mm Hg), d_4^{20} 1.1364, n_D^{20} 1.5250. Found, %: S 18.54. $C_6H_{14}NOPS$. Calculated, %: S 17.87. δ ^{31}P 105 ppm (cf. [3]: d_4^{20} 1.1371, n_D^{20} 1.5230. δ ^{31}P 107 ppm).

(VIII), d_4^{20} 1.1425, n_D^{20} 1.5507. Found, %: S 30.00. $C_7H_{14}OPS_2$. Calculated, %: S 30.47. δ ^{31}P 115 ppm.

The constants of compounds (V), (VI), and (VIII) [mechanisms (5) and (7)] are identical to those obtained from the reaction with (IV) by mechanisms (4) and (6).

LITERATURE CITED

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2. J. Perregaard, I. Thomsen, and S.-O. Lawesson, Bull. Soc. Chim. Belg., 86, 321 (1977).
3. O. N. Nuretdinova and F. F. Guseva, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2416 (1988).