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REACTION OF SULFONYL CHLORIDES AND CHLOROPHOSPHATES WITH 1,3,2-DIHETEROPHOSPHOLANES

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Depending on the conditions and structure of the reagents, the reactions of carboxylic acid halides with cyclic amidophosphites proceed either at the P atom with the formation of phosphonium halides [1] or products of the Arbuzov rearrangement [2], or at the endo- or exocyclic N atoms with splitting of the P-N bond [3]. We have shown recently that the reactions of oxazaphospholanes with trivalent phosphorus acid chlorides proceed with splitting of the exo- or endocyclic P-N bonds and the formation of exchange products [4]. In the development of this path, we studied the reaction of certain trivalent phosphorus derivatives with benzenesulfonyl chloride (BSC) and dialkyl chlorophosphates. Examples are known of the oxidation of overall phosphites by the action of alkyl and arylsulfonyl chlorides [5]. We attempted to find reactions which would proceed with splitting of the P-N bond and the formation of P-S derivatives.

Hexamethyl- and hexaethyltriaminophosphines react with BSC exothermally to form the corresponding triamidophosphates as oxidation products:

R = Me, Et.

The reactions proceed not unequivocally, as indicated by the ³¹P NMR spectrum of the reaction mixture containing not only the main signals, but also several low-intensity signals. When hexaethyltriaminophosphine is used, immediately after the reagents are mixed, a signal with δ ³¹P 48 ppm appears in the PMR spectrum, which disappears in the course of the reaction. It is possible that, as in the case of benzoyl halides, phosphonium chloride is formed as an intermediate product [1]. The reaction of 2-diethylamino-3-phenyl-1,3,2-oxazaphospholane (I) with BSC is also accompanied by the oxidation of the phosphorus atom



To create the most favorable conditions for the exchange reaction in the reaction with BSC, we used 2-diethylamino-4,5-benzo-1,3,2-dioxaphospholane (II), in which the nucleophilic properties of the phosphorus atom are strongly decreased. However, in this case also, even when acid catalysts are used (carboxylic acids, amine hydrochlorides), only 2-diethylamino-2-oxo-4,5-benzo-1,3,2-dioxaphospholane (III) was isolated.



A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, pp. 1859-1863, August, 1983. Original article submitted November 22, 1982. Thus, in contrast to carboxylic acid halides, in the reactions with amide derivatives of trivalent phosphorus, sulfonic acid chlorides appear in the role of oxidizing agents.

In contrast to BSC, the reaction of phospholane (I) with diethyl- and diisopropyl chlorophosphates is accompanied by an exchange of the diethylamino group for chlorine and the formation of 2-chloro-3-phenyl-1,3,2-oxazaphospholane and dialkylphosphoric acid diethylamide.



Exchange processes of this type probably take place with the participation of acidic impurities, in particular traces of HCl present in the reaction mixture. If the exocyclic P-Nbond is not present in the oxazaphospholane molecule, the reaction proceeds with an initial ring opening at the endocyclic P-N bond and the formation of diphosphorylated alkanolamine (IV)



In the ³¹P NMR spectrum of compound (IV), there are two singlet signals with δ ³¹P 165 and 17 ppm, indicating the presence of tri- and tetracoordinated phosphorus atoms. As shown in [4], diphosphorylated alkanolamines with two trivalent phosphorus atoms smoothly disproportionate into cyclic and linear phosphites

 $(EtO)_{2} PNCH_{2}CH_{2}OP(OEt)_{2} \xrightarrow{\Delta} (V) POEt + P(OEt)_{3}$

On distillation, compound (IV) also disproportionates, but this process is more complex, and only 2-chloro-3-methyl-1,3,2-oxazaphospholane (V) was isolated in the individual state. The alcoholysis of acid chloride (IV) leads to diphosphorylated methylaminoethanol (VII) (δ ³¹P 138 and 16 ppm) which, on heating, gives a complex mixture of compounds. Product (VII) obtained by another method, i.e., by phosphorylation of β -methylaminoethyl diethyl phosphite by diethyl chlorophosphate behaves in a similar way



In view of the data obtained, it was interesting to study the thermal stability of the diphosphorylated derivatives of methylaminoethanol having two tetracoordinated phosphorus atoms. For this purpose, compound (VII) was treated by methyl iodide to yield phosphonate (VIII) (δ ³¹P 30 and 16 ppm).



On fractional distillation of (VIII), only the product of its decomposition, 0,0-diethyl methylphosphonate, can be isolated. Addition of sulfur to compound (VII) gives diphosphate (IX), from which triethyl thiophosphate separated out on heat treatment. From diphosphite (VI), under mild conditions, compounds (X) and (XI) were obtained, containing two phosphonate and thiophosphate centers, respectively.



Similarly to phosphonate (VIII), diphosphonate (X) is thermally slightly stable and gives a complex mixture of compounds, from which 0,0-diethyl methylphosphonate can be only distilled. In contrast to (X), dithiophosphate (XI) is completely stable and is obtained in a high yield. In the ³P NMR spectrum of (XI) there are two singlets at 70 and 16 ppm. Thus, the stability of the diphosphorylated alkanolamines is determined by the coordination number and environment of the two phosphorus atoms. In contrast to the trivalent derivatives, the decomposition of compounds with tetracoordinated phosphorus atoms proceeds in general in a complex way with the formation of poorly distillable products.

EXPERIMENTAL

The ^{31}P NMR spectra were run on the NMR KGU-4 apparatus (10.2 MHz), with 85% $\rm H_3PO_4$ as standard.

Reaction of Hexamethyltriaminophosphine with Benzenesulfonyl Chloride. Benzenesulfonyl chloride, 1.1 g, was added with stirring and cooling to 3.25 g of hexamethyltriaminophosphine in 30 ml of dry ether. Fractional distillation gave 2.17 g (92%) of hexamethyltriamidophosphate, bp 46-47°C (0.009 mm), n_D^{20} 1.4585, δ^{31} P 23 ppm (cf. [6]).

Reaction of Hexaethyltriaminophosphine with Benzenesulfonyl Chloride. Benzenesulfonyl chloride, 1.42 g, was added with stirring and cooling to 8 g of hexaethyltriaminophosphine in 50 ml of dry ether. The reaction mixture stratified. According to the data of ³¹P NMR spectrum, the upper ether layer consists of unreacted triaminophosphine, and the lower viscous layer is probably phosphonium chloride (δ ³¹P 48 ppm). Fractional distillation gave 4 g (57%) of hexaethyltriamidophosphate, bp 86-87°C (0.04 mm), n_D^{20} 1.4708, δ ³¹P 24 ppm (cf. [7]).

Reaction of 2-Diethylamino-3-phenyl-1,3,2-oxazaphospholane (I) with Benzenesulfonyl Chloride. Benzenesulfonyl chloride, 1.47 g, was added with stirring and cooling to 6 g of oxazaphospholane (I) in 60 ml dry benzene. Fractional distillation gave 2.5 g (60%) of 2diethylamino-2-oxo-3-phenyl-1,3,2-oxazaphospholane, bp 129-132°C (0.001 mm), mp 85°C, 6³¹P 19 ppm (cf. [8]).

Reaction of 2-Diethylamino-4,5-benzo-1,3,2-dioxaphospholane (II) with Benzenesulfonyl Chloride. A mixture of 5.4 g of dioxaphospholane (II) and 1.5 g of BSC was heated for 5 h at 100°C. Fractional distillation gave 2.4 g (62%) of dioxaphospholane (III), bp 102°C (0.001 mm), $n_D^{2^\circ}$ 1.5125, $\delta^{3^\circ}P$ 22 ppm (cf. [8]).

Reaction of 2-Diethylamino-3-phenyl-1,3,2-oxazaphospholane (I) with Diethyl Chlorophosphate. A mixture of 6.9 oxazaphospholane (I) and 5 g of diethyl chlorophosphate was heated for 1 h at 100°C. Fractional distillation gave 1) 4.2 g (83%) of 2-chloro-3-phenyl-1,3,2-oxazaphospholane, bp 98°C (0.02 mm), mp 56-58°C, δ^{31} P 158 ppm (cf. [9]); 2) 5.5 g (91%) of diethylamide of diethylphosphoric acid, bp 44°C (0.02 mm), n_D^{20} 1.4410. δ^{31} P 11 ppm (cf. [6]).

<u>Reaction of 2-Ethoxy-3-methyl-1,3,2-oxazaphospholane with Diethyl Chlorophosphate.</u> Diethyl chlorophosphate, 5.1 g, was added with stirring and cooling to 4.3 g of 2-ethoxy-3methyl-1,3,2-oxazaphospholane in 40 ml of dry benzene. Fractional distillation gave 1.9 g (45%) of 2-chloro-3-methyl-1,3,2-oxazaphospholane, bp 78°C (12 mm), n_D^{20} 1.5012 (cf. [10]).

Reaction of Diphosphorylated Methylaminoethanol (VII) with Methyl Iodide. A mixture of 2 g of compound (VII) and 1.2 g of methyl iodide was heated in an ampul for 30 min at 70°C. Fractional distillation gave 0.33 g (36%) of 0,0-diethyl methylphosphonate, bp 44-45°C (0.02 mm), $n_D^{2^\circ}1.4165$. $\delta^{31}P$ 28 ppm (cf. [6]).

Addition of Sulfur to Diphosphorylated Methylaminoethanol (VII). A mixture of 4 g of compound (VII) and 0.3 g of sulfur powder was left to stand for 24 h at 20°C. Fractional distillation gave 0.68 g (29%) of triethyl thiophosphate, bp 44°C (0.04 mm), $n^{2^{\circ}}D$ 1.4472, $\delta^{3^{1}}P$ 68 ppm (cf. [6]).

<u>Preparation of N,O-Bis(diethoxythiophosphinyl)-N-methylaminoethanol (XI).</u> Diethyl chlorophosphite, 8 g, was added with stirring and cooling to a solution of 1.92 g of methyl-aminoethanol and 5.15 g of triethylamine in 100 ml of benzene. After the separation of triethylamine hydrochloride precipitate (5 g, 72%), and evaporation of benzene, 0.85 g of powdered sulfur was added to 2 g of crude product (VI), and the reaction mixture was left to stand for 12 h. Fractional distillation gave 2.28 g (93%) of compound (XI), bp 137°C (0.04 mm), $n_D^{2°}$ 1.4845. δ ³¹P 76 and 68 ppm. Found: N 3.52, P 16.51%. C₁₁H₂₇NO₅P₂S₂. Calculated: N 3.69, P 16.34%.

CONCLUSIONS

1. The reactions of benzenesulfonyl chloride with linear and cyclic amide derivatives of trivalent phosphorus are accompanied by oxidation at the phosphorus atom.

2. The reactions of trivalent phosphorus amides with diethyl chlorophosphate proceed with splitting of the P-N bond and lead to exchange products of the amine group at P atom for Cl. Several diphosphorylated derivatives of methylaminoethanol were synthesized, and their thermal stability was studied.

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