REACTION OF 1,3,2-OXAZAPHOSPHOLANES WITH ACID CHLORIDES OF TRIVALENT PHOSPHORUS

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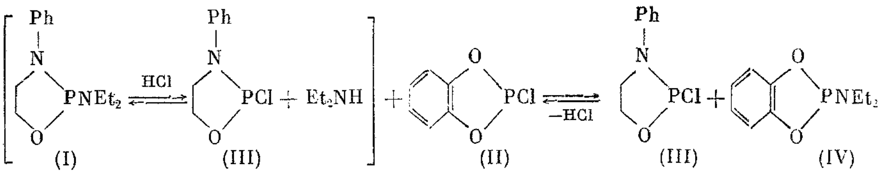
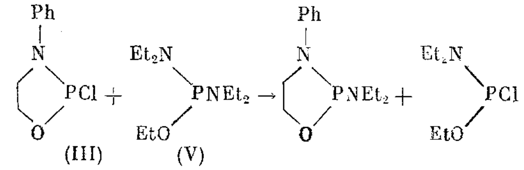
UDC 542.91:547.1'118

The reaction of acyl halides with oxaza- and diazaphospholanes can occur either at the P atom with the formation of acyl phosphonates [1] or at the exo- or endocyclic N atoms with the production of carbamoylation products [2], depending on their structure. The reactions of oxazaphospholanes with acid halides of phosphorus have not heretofore been studied.

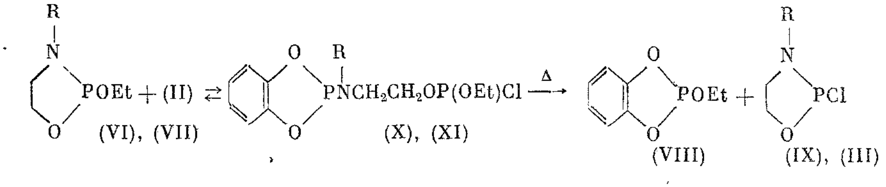
2-Diethylamino-3-phenyl-1,3,2-oxazaphospholane (I) readily interacts with pyrocatechol chlorophosphite (II) with exchange of the diethylamino group for a chlorine atom:



As in the case of acetyl and benzoyl halides, the exchange processes apparently take place with the participation of acidic admixtures (HCl, the hydrochloride of the amine), which are present in the reaction mixture [3]. The processes taking place in the system under consideration are reversible and should be subject to thermodynamic control. Dioxaphospholane IV, which has a very high stability, accumulates during the reaction. A similar phenomenon was observed in [4]. Exchange also takes place between oxazaphospholane III and ethyl tetraethyldiamidophosphite (V), since it is known that substituents which form a five-membered ring are more electronegative groupings than are the linear analogs:



The interaction of 2-alkoxy-3-methyl(phenyl)-1,3,2-oxazaphospholanes VI and VII with II also takes place with the exchange of the exocyclic substituents and the formation of 2-ethoxy-4,5-benzo-1,3,2-dioxaphospholane (VIII) and 2-chloro-1,3,2-oxazaphospholanes III and IX:



R = Me (VI, IX, X), Ph (III, VII, XI).

The study of the reaction of oxazaphospholane VI and II by ^{31}P NMR showed that the initial step involves cleavage of the endocyclic P−N bond and the formation of N,O-diphosphorylated methylaminoethanol X (δP 165, 147 ppm), which decomposes into the reaction products upon heating and distillation. It should be noted that the stability of N-methyl derivative X is somewhat higher than that of diphosphite XI, which forms during the reaction, decomposes rapidly, and only small amounts of it are detected spectroscopically in the reaction mixture.

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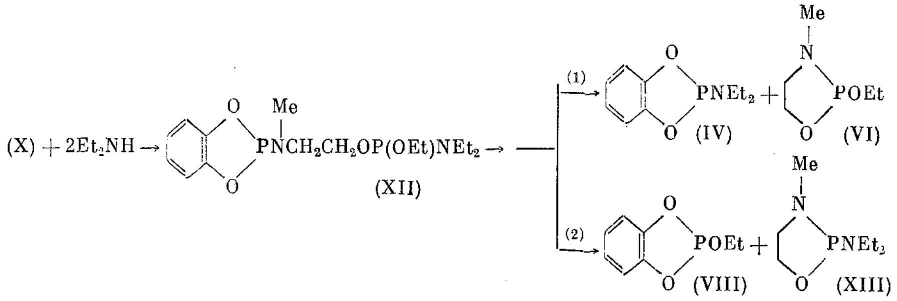
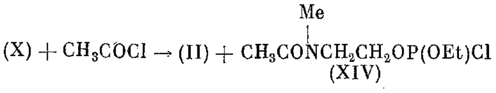
Diphosphite X undergoes aminolysis under mild conditions with the exchange of a chlorine atom for a diethylamino group to form amidophosphite XII (δP 148, 150 ppm).



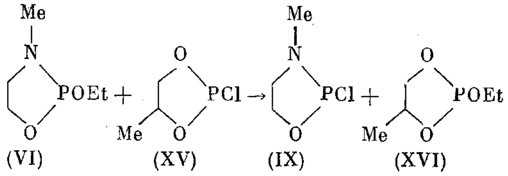
Its disproportionation can occur along two paths: with migration of the diethylamino group to the endocyclic P atom (path 1) or migration of the alkoxy group (path 2). The experimental data show that both paths are realized, but the first is slightly preferable. The ratio of the products IV and VI to VIII and XII is ~ 60: 40%.

According to the data from the ^{31}P NMR spectra, the interaction of diphosphite X with AcCl is accompanied by cleavage of the P–N bond and the formation of pyrocatechol chlorophosphite (δP 173 ppm) and chlorophosphite XIV (δP 165 ppm):



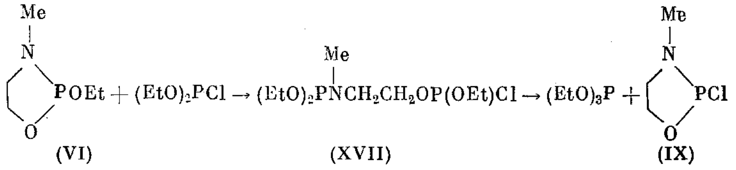
$$(X) + CH_3COCl \rightarrow (II) + CH_3CO\overset{Me}{\overset{|}{N}}CH_2CH_2OP(OEt)Cl \quad (XIV)$$

Exchange interactions also readily take place in the system consisting of oxazaphospholane VI and 2-chloro-4-methyl-1,3,2-dioxaphospholane (XV):

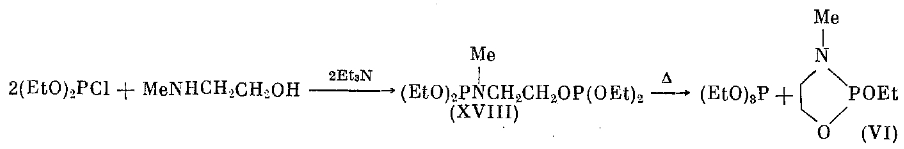


Such a course of the reaction is confirmed by the appearance in the ^{31}P NMR spectrum of a signal at δP 138 ppm for dioxaphospholane XVI. Acid chlorides IX and XV have similar values for the chemical shifts and are described in the form of a single broadened signal at 169-170 ppm. It has not been ruled out that the reason for this is intermolecular halogen exchange [5]. The isolation of the individual compounds in this reaction is complicated by the closeness of the boiling points.

The reaction between oxazaphospholane VI and diethyl chlorophosphite takes place according to the scheme



The ^{31}P NMR spectrum shows signals at δP 139 (triethyl phosphite) and 169 ppm (acid chloride IX). An increase in the intensity of the peaks corresponding to these products is observed upon heating. In this case, the reaction apparently takes place with initial opening of the ring at the P–N bond in oxazaphospholane VI to form diphosphite XVII. The latter cannot be detected because of its easy dissociation. We carried out a special study of the phosphorylation of methylaminoethanol under the action of diethyl chlorophosphite:



Diphosphite XVIII is characterized in the ^{31}P NMR spectrum by two singlets at 146 and 138 ppm. Upon heating it readily dissociates into triethyl phosphite and oxazaphospholane VI. A similar type of conversion was observed in the case of diphosphorylated glycols in [6].

EXPERIMENTAL

The ^{31}P NMR spectra were recorded on a KGU-4 spectrometer at a frequency of 10.2 MHz, the reference being 85% H_3PO_4.

Reaction of 2-Diethylamino-3-phenyl-1,3,2-oxazaphospholane (I) with Pyrocatechol Chlorophosphite (II). A mixture of 6.8 g of I and 5 g of II in 50 ml of dry benzene was held for 1 h at 20°C. Distillation resulted in the recovery of 4.1 g (68%) of oxazophospholane III with bp 99-101°C (0.01 mm Hg), n_D^{20} 1.6000, mp 57-58°C and 3.6 g (60%) of dioxaphospholane IV with bp 67°C (0.02 mm Hg), n_D^{20} 1.5400.

Reaction of 2-Chloro-3-phenyl-1,3,2-oxazaphospholane (III) with Ethyl Tetraethylamidophosphite. A mixture of 4.6 g of III and 5 g of ethyl tetraethylamidophosphite was heated at 150°C for 1 h. Distillation resulted in the isolation of 4.65 g (77.4%) of oxazaphospholane I, bp 96°C (0.02 mm Hg), n_D^{20} 1.5610 (compare [7]) and 2.9 g (53%) of ethyl diethylamidochlorophosphite, bp 34-38°C (0.02 mm Hg), n_D^{20} 1.4660 (compare [8]).

Reaction of 2-Ethoxy-3-methyl-1,3,2-oxazaphospholane (VI) with Pyrocatechol Chlorophosphite (II). a) A 3-g portion of VI was slowly given an addition of 4.34 g of II with cooling to −25°C. Distillation of the reaction mixture resulted in the isolation of 3.2 g (39%) of dioxaphospholane VIII with bp 92°C (12 mm Hg), n_D^{20} 1.5088, δ^{31}P 128 ppm (compare [9]) and 1.27 g (46%) of acid chloride IX, bp 75°C (12 mm Hg), n_D^{20} 1.5120, ^{31}P 169 ppm (compare [10]).

b) The reaction mixture obtained under the conditions of experiment a) was given an addition of 100 ml of benzene and then a dropwise addition of 1.32 g of diethylamine with cooling to 5°C. Distillation resulted in the isolation of 1.24 g (37.2%) of oxazaphospholane VI, bp 75°C (10 mm Hg), n_D^{20} 1.4520, 2.98 g (65.4%) of dioxaphospholane VIII, bp 86°C (10 mm Hg), n_D^{20} 1.5080 (compare [9]), and 3.57 g (64%) of dioxaphospholane IV, bp 122°C (10 mm Hg), n_D^{20} 1.5402.

Reaction of 2-Ethoxy-3-phenyl-1,3,2-oxazaphospholane (VII) with Pyrocatechol Chlorophosphite (II). A 3-g portion of VII was mixed with 2.48 g of II. Distillation of the reaction mixture resulted in the isolation of 2.15 g (85%) of dioxaphospholane VIII with bp 40°C (0.002 mm Hg), n_D^{20} 1.5080 [9] and 2.76 g (96.5) of acid chloride III, bp 96-98°C (0.001 mm Hg), n_D^{20} 1.6038, mp 57-58°C [7].

Reaction of 2-Ethoxy-3-methyl-1,3,2-oxazaphospholane (VI) with Diethyl Chlorophosphite. A mixture of 3 g of VI and 4 g of diethyl chlorophosphite was heated at 100°C for 1 h. Distillation resulted in the isolation of 2.4 g (57%) of triethyl phosphite, bp 55°C (10 mm Hg), n_D^{20} 1.4140 [11] and 2.3 g (83%) of oxazaphospholane (IX), bp 68-70°C (10 mm Hg), n_D^{20} 1.5100, δ^{31}P 169 ppm [10].

Phosphorylation of Methylaminoethanol. A mixture of 2 g of methylaminoethanol and 5.4 g of triethylamine in 100 ml of dry benzene was given a dropwise addition of 8 g of diethyl chlorophosphite with cooling to 10-15°C. Distillation of the reaction mixture resulted in the isolation of 7.87 g (92%) of triethyl phosphite, bp 59-60°C (12 mm Hg), n_D^{20} 1.4125 [11] and 2.16 g (67%) of oxazaphospholane VI, bp 81-84°C (12 mm Hg), n_D^{20} 1.4530.

CONCLUSIONS

The reaction of oxazaphospholanes with acid chlorides of trivalent phosphorus takes place with the cleavage of exo- or endocyclic P−N bonds. The opening of the ring produces diphosphorylated alkanolamines, which are converted as a result of disproportionation into 1,3,2-diheterophospholanes, the latter being products of the exchange of exocyclic substituents.

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CARBORANE DERIVATIVES WITH BORON – TIN BOND

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UDC 542.91:547.1'127:541.57:546.27:546.811

The B-mercuration reaction is a convenient method for the synthesis of B-mercurated carboranes [1, 2]. Symmetric carborane derivatives of mercury with the B–Hg bond were used in the reaction with halides of nontransition elements of groups III-V to obtain carboranyl derivatives of these elements with a boron–element bond [3]. With Hg [4] and Tl [5, 6] derivatives as examples, we compared the properties of B-metallated compounds synthesized with the properties of the previously known C-metallated derivatives of carboranes [7]. It was shown that C-metalcarboranes differ considerably in their properties from the organometallic compounds with alkyl and aryl substituents, while the B derivatives, although they have no C–M bond, are in many respects similar to the organometallic compounds.

To clarify the generality of this phenomenon, it was interesting to study the properties of the carborane compounds with a B–Sn bond, in comparison with the simplest organometallic compounds and carborane derivatives with the C–Sn bond.

We obtained the carboranyl derivatives of tin with a B–Sn bond by the reaction of boromercurated carboranes with tin dichloride in analogy with the known reaction of R_2Hg with $SnCl_2$ [8]. We were able to carry out this reaction for the corresponding boromercurated carboranes under severe conditions.* Thus, bis[o(m)-(9-carboranyl)]mercury reacts with an excess of $SnCl_2$ melt at 270-300°C to give bis[o(m)-(9-carboranyl)]tin dichlorides and metallic Hg:

$$(C_2R_2B_{10}H_9)_2Hg + SnCl_2 \xrightarrow[5\ \text{min}]{270-300^\circ} (C_2R_2B_{10}H_9)_2SnCl_2 + Hg$$

Under still more severe conditions, the o- and m-carboranylmercury chlorides also enter the reaction with the formation of carboranyltin trichlorides:

$$C_2R_2B_{10}H_9HgCl + SnCl_2 \xrightarrow[5\ \text{min}]{300-320^\circ} C_2R_2B_{10}H_9SnCl_3 + Hg$$

The preparation of carboranyltin trichlorides in a pure state indicates that these compounds are stable, in contrast to the usual organotin trichlorides, which are, in general, unstable and disproportionate into R_2SnCl_2 and $SnCl_4$.

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* For a preliminary communication, see [3].

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Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 4, pp. 907-912, April, 1983. Original article submitted June 24, 1982.