SOME REACTIONS OF DICHLOROMETHYLENEAMIDES OF DIALKYLPHOSPHORIC ACIDS

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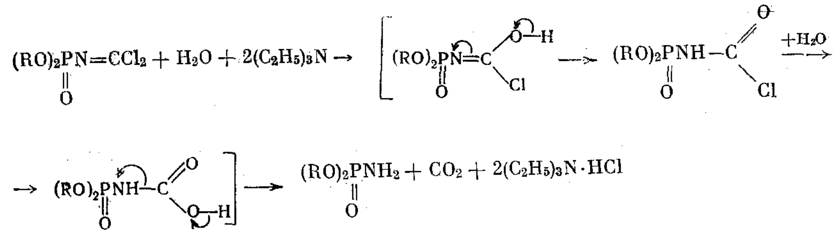
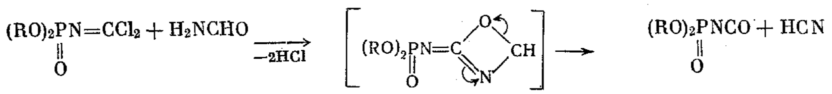
The synthesis and study of the properties of the dichloromethyleneamides of dialkylphosphoric acids had been done previously [1]. These compounds serve as the starting materials for the preparation of the derivatives of the N-phosphorylated iminocarbonic acids [2], and the N-phosphorylated cyclic urethans and imidohydantoins [3, 4]. A study of the reactions of the dichloromethyleneamides of dialkylphosphoric acids with compounds that contain a labile hydrogen atom, and specifically with water, formamides and amines, is continued in the present paper.

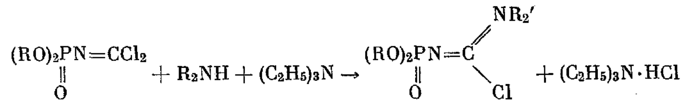
The corresponding amides of dialkylphosphoric acids are formed when the dichloromethyleneamidophosphates are reacted with water in the presence of triethylamine in a 2 : 1 : 2 ratio. Apparently, the reaction proceeds via the formation of the acid chlorides of the N-phosphorylated iminocarbonic and carbamic acids and N-phosphorylated carbamic acid. The latter decomposes into the amide of the dialkylphosphoric acid and CO_2



The reaction of the dichloromethyleneamides of dialkylphosphoric acids with formamide proceeds in an interesting manner. The reaction was run both in the presence of a base and without it. In both cases the sole reaction product was the isocyanatophosphoric acid ester. The reaction proceeds best when the reactants are mixed without a solvent and a base. The formamide apparently reacts with the dichloride in the iso form; the cyclic ester-amide of the N-phosphorylated iminocarbonic acid is formed initially, and then decomposes to the isocyanatophosphoric acid ester and HCN



If one chlorine atom in the dichloromethyleneamide of the dialkylphosphoric acid is replaced by a dialkylamino group, then the acid chloride of the N-phosphorylated iminocarbamic acid is formed



The disubstituted N-phosphorylated urea derivative was isolated as the main reaction product when the acid chloride was reacted with formamide in the presence of triethylamine. Its formation can be depicted in the following manner. The carbon atom, attached to the chlorine atom in the acid chloride, attacks either the oxygen of the carbonyl group of the formamide or the oxygen of the hydroxyl group of the iso form of the amide, in which connection the corresponding iminocarbamic acid ester is formed. HCN is liberated when

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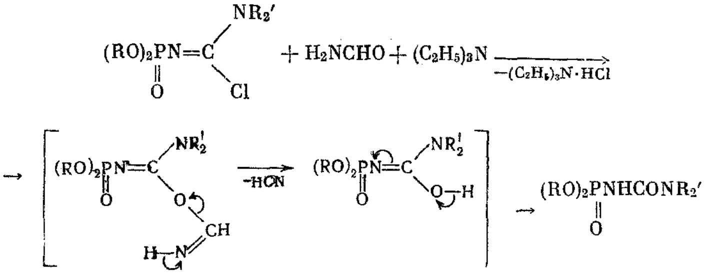
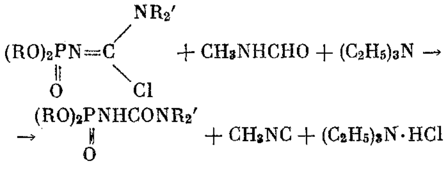
this ester is cleaved and the N-phosphorylated iminocarbamic acid is formed, which is then converted to the N-phosphorylated urea



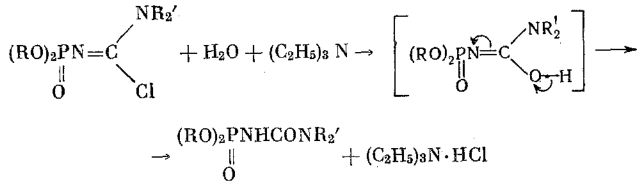
$$(RO)_2\overset{\displaystyle O}{\overset{\|}{P}}N{=}C(NR_2')Cl + H_2NCHO + (C_2H_5)_3N \xrightarrow[-(C_2H_5)_3N\cdot HCl]{} \left[(RO)_2P(O)N{=}C(NR_2')OCH{=}NH \xrightarrow{-HCN} (RO)_2P(O)N{=}C(NR_2')O{-}H\right] \rightarrow (RO)_2P(O)NHCONR_2'$$

The reaction of the acid chloride of the iminocarbamic acid with methylformamide also proceeds in a similar manner



$$(RO)_2P(O)N{=}C(NR_2')Cl + CH_3NHCHO + (C_2H_5)_3N \rightarrow (RO)_2P(O)NHCONR_2' + CH_3NC + (C_2H_5)_3N\cdot HCl$$

In order to confirm one of the steps in the reaction of the acid chloride of the iminocarbamic acid with formamides, namely the formation of the iminocarbamic acid and its rearrangement to the urea, we attempted to prepare the N-phosphorylated iminocarbamic acid by the reaction of the calculated amount of water with the acid chloride of the iminocarbamic acid, but the N-phosphorylated urea was isolated also in this case. Undoubtedly it was formed from the corresponding iminocarbamic acid



$$(RO)_2P(O)N{=}C(NR_2')Cl + H_2O + (C_2H_5)_3N \rightarrow \left[(RO)_2P(O)N{=}C(NR_2')O{-}H\right] \rightarrow (RO)_2P(O)NHCONR_2' + (C_2H_5)_3N\cdot HCl$$

The structure of the N-phosphorylated ureas was confirmed by counter synthesis form HNR_2' and $(RO)_2P(O)\cdot NCO$, by a comparison of their physical constants and IR spectra. The bands of the stretching vibrations of a bound NH group (3190-3220 cm^{-1}) are present in the IR spectra of the phosphorylated ureas. The band of "amide I" is located in the 1670-1675 cm^{-1} region, while the band of "amide II" is located in the 1480-1490 cm^{-1} region. The $P{=}O$ group appears as a doublet with a frequency of 1250 and 1280 cm^{-1}. The peaks in the vicinity of 990 and 1055 cm^{-1} belong to the stretching vibrations of the $P{-}O{-}C$ group.

EXPERIMENTAL METHOD

Reaction of Dichloromethyleneamide of Diethylphosphoric Acid with Water. With cooling, to an acetone solution of 9.36 g of $(C_2H_5O)_2P(O)N{=}CCl_2$ was added an acetone solution of 1.4 g of water and 8.08 g of triethylamine. The reaction began at ~0°C, a gas was evolved. The mixture was stirred at ~20° for 1 h. After removing the triethylamine hydrochloride precipitate and the solvent, the residue was distilled twice in vacuo. We isolated 4.2 g (82%) of diethylphosphoric acid amide with bp 125-128° (0.5 mm); the material crystallized on standing, mp 50-51°. The mixed melting point with an authentic specimen was not depressed.

Reaction of Dichloromethyleneamide of Diethylphosphoric Acid with Formamide. To 7.31 g of $(C_2H_5O)_2\cdot P(O)N{=}CCl_2$ at $-10°$ was added 1.4 g of formamide and the mixture was stirred at 20° for 2 h. After two distillations we isolated 3.32 g (62%) of the ethyl ester of isocyanatophosphoric acid with bp 85-86° (11 mm); n_D^{20} 1.4184; d_4^{20} 1.1760 [5]. Found: N 8.03; P 17.1%; MR 38.12. $C_5H_{10}NO_4P$. Calculated: N 7.82; P 17.32%; MR 38.65.

The IR spectrum contains an intense band at 2285 cm^{-1}, which belongs to the stretching vibrations of the NCO group, and also the absorption bands of the $P{=}O$ (1290 cm^{-1}) and $P{-}OC_2H_5$ (990, 1050 cm^{-1}) groups.

The reaction of $(C_2H_5O)_2P(O)N{=}CCl_2$ with formamide in the presence of triethylamine proceeds in a similar manner. The reaction was run in acetone. However, marked tarring of the reaction mixture was observed in the given case, and the yield of the isocyanatophosphoric acid ester was less than 18%.

Reaction of Acid Chloride of N-Diethoxyphosphorylimino-N'-diethylcarbamic Acid with Formamide. To an ether solution of 9.36 g of $(C_2H_5O)_2P(O)N=CCl_2$, cooled to −80°, was added an ether solution of 2.92 g of diethylamine and 4.04 g of triethylamine, and the temperature was gradually raised to room temperature. Then the $(C_2H_5)_3N \cdot HCl$ and solvent were removed, and 10.66 g of $(C_2H_5O)_2P(O)N=CN(C_2H_5)_2Cl$ was obtained from the residue.

The crude chloride (9.47 g) was added at ~20° to an acetone solution of 1.58 g of formamide and 3.54 g of triethylamine, and the mixture was stirred at 40-45° for 1 h. Then the $(C_2H_5)_3N \cdot HCl$ and solvent were removed, and the residue was vacuum-distilled twice. We isolated 4.5 g (51%) of $(C_2H_5O)_2P(O)NHCO-N(C_2H_5)_2$ with bp 98-99° (0.5 mm); n_D^{20} 1.4564; d_4^{20} 1.1295. Found: N 11.25; P 11.99%; MR 60.72. $C_9H_{21}N_2O_4P$. Calculated: N 11.11; P 12.30; MR 61.57. The IR spectrum was identical with the spectrum of the disubstituted phosphorylated urea, obtained by counter synthesis.

The reaction of $(C_2H_5O)_2P(O)N=CN(C_2H_5)_2Cl$ with $CH_3NH-CHO$ proceeds in a similar manner. The yield of $(C_2H_5O)_2P(O)NHCON(C_2H_5)_2$ was 42%, bp 105-107° (2 mm); n_D^{20} 1.4570; d_4^{20} 1.1260. Found: N 10.97; P 12.65%; MR 60.95. $C_9H_{21}N_2O_4P$. Calculated: N 11.11; P 12.30%; MR 61.57.

Reaction of Acid Chloride of N-Diethoxyphosphorylimino-N'-dibutylcarbamic Acid with Water. To 9.5 g of $(C_2H_5O)_2P(O)N=CN(C_4H_9)_2Cl$ was added an acetone solution of 2.93 g of triethylamine and 0.52 g of water, and the mixture was stirred at 50-55° for 3 h. After removal of the $(C_2H_5)_3N \cdot HCl$ and solvent the residue was distilled to give 36% of product with bp 109-110° (0.5 mm); n_D^{20} 1.4558; d_4^{20} 1.0552. Found: N 9.32; P 9.72%; MR 79.26. $C_{13}H_{29}N_2O_4P$. Calculated: N 9.09; P 10.06%; MR 80.04.

$(C_2H_5O)_2P(O)N=CN(C_2H_5)_2Cl$ reacts in a similar manner with water. From 10.81 g of the acid chloride, 0.72 g of water and 4.04 g of triethylamine was obtained 4.3 g (34%) of substance with bp 93-94° (0.02 mm); n_D^{20} 1.4540; d_4^{20} 1.1248. Found: N 11.25; P 12.67%; MR 60.66. $C_9H_{21}N_2O_4P$. Calculated: N 11.11; P 12.30%; MR 61.57.

Preparation of N-Diethoxyphosphoryl-N'-dibutylurea. To an ether solution of 7.16 g of $(C_2H_5O)_2P(O) \cdot NCO$ was added in drops an ether solution of 5.16 g of $(C_4H_9)_2NH$ at ~5°. The next day the substance was distilled. The yield of product was 7.88 g (64%), bp 113-114° (1 mm). In order to remove the $(C_2H_5O)_2P(O) \cdot NCO$ impurity the product was treated with 0.52 g of dibutylamine and the mixture was allowed to stand overnight. The excess dibutylamine was removed in vacuo. The substance has the constants: n_D^{20} 1.4550; d_4^{20} 1.0554. Found: N 9.67; P 10.12%; MR 79.21. $C_{13}H_{29}N_2O_4P$. Calculated: N 9.09; P 10.07%; MR 80.04.

Preparation of N-Diethoxyphosphoryl-N'-diethylurea. The compound was obtained as described in the preceding experiment; yield 54%, bp 91-93° (0.02 mm); n_D^{20} 1.4582; d_4^{20} 1.1285. Found: N 11.1; P 12.66%. MR 60.78. $C_9H_{21}N_2O_4P$. Calculated: N 11.11; P 12.30%; MR 61.57.

CONCLUSIONS

1. The amides of dialkylphosphoric acids are formed when the dichloromethyleneamidophosphates are treated with water in the presence of triethylamine; isocyanatophosphoric acid esters are formed when the same dichlorides are treated with formamide.

2. The corresponding N-phosphorylated iminocarbamic acids are apparently formed as intermediate products when formamide, methylformamide or water is reacted with the acid chlorides of the N-phosphorylated iminocarbamic acids, which then rearrange to the N-phosphorylated ureas.

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