REACTION OF ACID CHLORIDES WITH AMIDES OF DIALKYLPHOSPHORIC AND CARBOXYLIC ACIDS

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Previously in [1] it was shown that the acid chlorides of dialkylphosphorus acids, when reacted with substituted and unsubstituted formamides, form either formylamido phosphites or, depending on the nature of the substituent, the esters of pyrophosphorus acid and the corresponding isonitrile. The acid chloride of diethylphosphoric acid with either formamide or N-ethylformamide forms the ethyl ester of pyrophosphoric acid and respectively either hydrogen cyanide or ethyl isocyanide. The reaction of SO_2Cl_2 with the amides of dialkylphosphoric acids in the presence of triethylamine yields N,N'-bis (dialkylphophono-sulfamides [2]. In connection with the discussed data it was interesting to study the reaction of the acid chlorides of carboxylic and dialkylphosphoric acids with the amides of these acids, and on the basis of the obtained products determine the reaction schemes in the various cases. In the present paper we studied the reaction of the acid chlorides of carboxylic acids with the amide of diethylphosphoric acid and of the acid chloride of diethylphosphoric acid with the amides of carboxylic acids.

Acylamidophosphates are formed when the acid chlorides of carboxylic acids are reacted with the amide of diethylphosphoric acid in the presence of diethylaniline.

$$(C_2H_5O)_2P(O)NH_2 + ClCOR + C_6H_5N(C_2H_5)_2 \rightarrow (C_2H_5O)_2P(O)NHCOR + 2C_6H_5N(C_2H_5)_2 \cdot HCl$$

R=CH_3 (I); C_3H_7 (II); $(CH_3)_2CH$ (III)

In the given case the reaction apparently proceeds by the scheme of simple substitution, with attack of the nitrogen atom by the carbon of the carbonyl group. The yields of acylamidophosphates (I)-(III), formed as a result of this reaction, are respectively 72, 67 and 64% of theory.

The reaction of the acid chlorides of dialkylphosphoric acids with the amides of carboxylic acids proceeds in a different manner; here the esters of pyrophosphoric acid and the corresponding nitriles are formed, for example:

$$2(C_2H_5O)_2P(O)Cl + RCONH_2 + 2(C_2H_5)_3N \rightarrow (C_2H_5O)_2P(O)-O-P(O)(OC_2H_5)_2 + RCN + 2(C_2H_5)_3N \cdot HCl$$

R=CH_3; C_3H_7; C_6H_5

The reaction scheme can apparently be depicted in the following manner. The phosphorus atom of the acid chloride attacks either the oxygen atom of the carbonyl group of the amide or the oxygen atom of the hydroxyl group of the isoform of the amide, in which connection an unstable mixed phosphoric acid ester is formed, which then decomposes into the dialkylphosphoric acid and the corresponding alkyl or aryl cyanide. The dialkylphosphoric acid reacts with the second half of the acid chloride taken for reaction to give the pyrophosphoric acid ester.

$$(C_2H_5O)_2P(O)Cl + H_2NCOR + (C_2H_5)_3N \xrightarrow[-(C_2H_5)_3N \cdot HCl]{}$$

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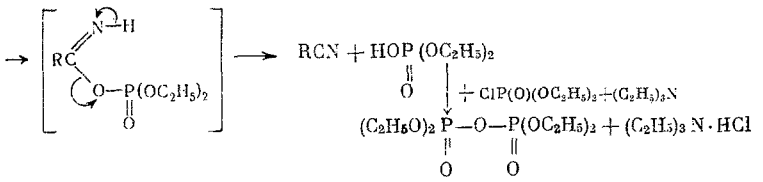
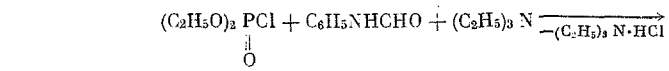
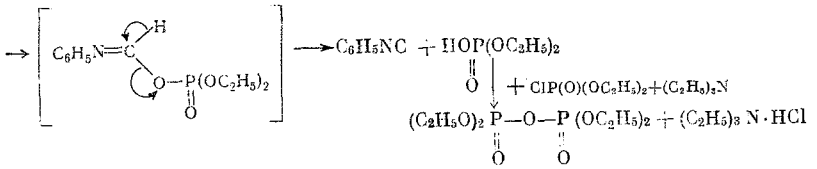


The acid chlorides of dialkylphosphoric acids react with formanilide in a similar manner to give the pyrophosphoric acid ester and phenyl isocyanide.





As a result, from the performed experiments it follows that the reaction of the acid chlorides of carboxylic acids with the amides of dialkylphosphoric acids leads to the formation of acylamidophosphates; in the case of the reaction of the acid chlorides of dialkylphosphoric acids with the amides of carboxylic acids the reaction products are the pyrophosphoric acid esters and the corresponding nitrile or isonitrile in the case of a substituted formamide.

EXPERIMENTAL METHOD

Reaction of Acetyl Chloride with the Amide of Diethylphosphoric Acid. A mixture of 7.65 g of diethylphosphoric acid amide, 3.92 g of CH_3COCl and 7.45 g of diethylaniline was stirred at 30°C for 3 h. Then the reaction mixture was diluted with 50 ml of ether and the precipitate of diethylaniline hydrochloride was filtered. Distillation of the crude product gave diethyl acetamidophosphate (I) with bp 122-123° (1 mm); n_D^{20} 1.4420; d_4^{20} 1.1766; yield 7.02 g (72% of theory). Found: P 15.6; N 6.64%; MR 44.12. $C_6H_{14}NO_4P$. Calculated: P 15.89; N 7.17%; MR 43.83.

Diethyl Ester of N-Butyrylamidophosphoric Acid. A mixture of 7.65 g of diethylphosphoric acid amide, 5.32 g of butyryl chloride and 7.45 g of diethylaniline was stirred at 60° for 4.5 h. The yield of diethyl butyrylamidophosphate (II) was 7.5 g (67.2%), bp 128-129° (2.5 mm); n_D^{20} 1.4418; d_4^{20} 1.1231. Found: P 14.10; N 6.26%; MR 52.52. $C_8H_{18}NO_4P$. Calculated: P 13.9; N 6.27%; MR 53.35.

Diethyl Ester of N-isobutyrylamidophosphoric Acid. From 7.65 g of diethylphosphoric acid amide, 5.32 g of isobutyryl chloride and 7.45 g of diethylaniline, under the conditions of the preceding experiments, was obtained 7. 15 g (64%) of diethylisobutyrylamidophosphate (III), bp 124-125° (1.5 mm); n_D^{20} 1.4380; d_D^{20} 1.1156. Found: P 14.31; N. 5.95%; MR 52.45. $C_8H_{18}NO_4P$. Calculated: P 13.90; N 6.27%; MR 53.35.

Reaction of Acid Chloride of Diethylphosphoric Acid with Acetamide. To a mixture of 5.9 g of acetamide and 20.2 g of triethylamine was added 34.5 g of diethylphosphoryl chloride at 60°, in which connection the temperature of the mixture rose 6°. The mixture was stirred at 65-67° for 3.5 h. The precipitate of $(C_2H_5)_3N \cdot HCl$ was washed with 15 ml of ether. The yield of the amine salt $(C_2H_5)_3N \cdot HCl$ was 24.5 g (89%). Distillation of the crude product gave two main fractions: I) bp 81°; n_D^{20} 1.3440 (literature data for acetonitrile [3], n_D^{20} 1.3442); yield 1.2 g (30%). Found: C 58.91; H 7.29; N 34.35%. C_2H_3N. Calculated: C 58.53; H 7.31; N 34.14%. II) bp 122-123° (1 mm); n_D^{20} 1.4198; d_4^{20} 1.1904; yield 10 g (34.4%). Found: C 33.52; H 6.96; P 21.09%; MR 61.65. $C_8H_{20}O_7P_2$. Calculated: C 33.11; H 6.89; P 21.37%; MR 61.48.

As a result, fraction I is acetonitrile, and fraction II is tetraethyl pyrophosphate.

Reaction of Acid Chloride in Diethylphosphoric Acid with Amide of Butyric Acid. To a mixture of 4.35 g of butyramide and 10.1 g of triethylamine at 60° was added 17.24 g of $(C_2H_5O)_2P(O)Cl$ in drops, and then the mixture was stirred at 65° for 3.5 h. We obtained 12.3 g (90%) of triethylamine hydrochloride. Distillation of the crude product gave two fractions. I) bp 114-115°; n_D^{20} 1.3842; n_D^{20} 1.3820; [literature data for butyronitrile [4], n_D^{20} 1.3816; bp 115.4-115.6° (739 mm)], yield 2.5 g (72%). Found: C 69.42; H 10.52; N 19.92%. C_4H_7N. Calculated: C 69.56; H 10.14; N 20.29%. II) bp 127-129° (2.5 mm); n_D^{20} 1.4196; d_4^{20} 1.1911; yield 5 g (34.5%). Found: C 33.39; H 6.87; P 21.39%; MR 61.60. $C_8H_{20}O_7P_2$. Calculated: C 33.11; H 6.89; P 21.37%; MR 61.48.

As a result, fraction I is butyronitrile, and fraction II is tetraethyl pyrophosphate.

Reaction of Acid Chloride of Diethylphosphoric Acid with Benzamide. To a mixture of 12.1 g of benzamide, 20.2 g of triethylamine and 15 ml of absolute acetone at room temperature was added 34.5 g of $(C_2H_5O)_2P(O)Cl$. The temperature of the mixture rose from room temperature to 42° in 1 h. The dark brown reaction mass was stirred at 36-40° for 3 h. The precipitate was filtered and washed with ether. We obtained 23.2 g (84.4%) of $(C_2H_5)_3N \cdot HCl$; the crude product weighed 39.1 g (~ 100%). Distillation of the crude product gave two main fractions: I) bp 65-66° (10 mm); n_D^{20} 1.5271; d_4^{20} 1.0074; yield 5.5 g (53.4%). Found: C 81.88; H 4.83; N 13.86%; MR 31.45. C_7H_5N. Calculated: C 81.55; H 4.85; N 13.59%; MR 30.62. II) bp 124-126° (2 mm); n_D^{20} 1.4211; d_4^{20} 1.1935; yield 10.3 g (36%). Found: C 33.5; H 6.84; P 21.39%; MR 61.61. $C_8H_{20}O_7P_2$. Calculated: C 33.11; H 6.89; P 21.37%; MR 61.48.

As a result, fraction I is benzonitrile, and fraction II is the ethyl ester of pyrophosphoric acid.

Reaction of Acid Chloride of Diethylphosphoric Acid with Formanilide. To a solution of 12.1 g of formanilide and 20.2 g of triethylamine in 20 ml of absolute ether at room temperature was added 34.5 g of $(C_2H_5O)_2P(O)Cl$ in drops, and then the mixture was stirred at 38-40° for 1.5 h. We obtained 20 g (73%) of triethylamine hydrochloride, and 41.3 g (100%) of crude product as a dark brown liquid. Distillation of the crude product gave two fractions: I) bp 49-50° (10 mm); n_D^{20} 1.5235; d_4^{20} 0.9801; yield 2 g (20%). Found: C 81.25; H 5.13; N 13.25%; MR 31.13. C_7H_5N. Calculated: C 81.55; H 4.85; N 13.59%; MR 31.34. II) bp 124-125 (2 mm); n_D^{20} 1.4277. After redistillation, bp 127.5-128° (2.5 mm); n_D^{20} 1.4274; d_4^{20} 1.1903; yield 15 g (52%). Found: C 35.52; H 7.04; P 20.6%; MR 62.65. $C_8H_{20}O_7P_2$. Calculated: C 33.1; H 6.89; P 23.37%. MR 61.48.

As a result, fraction I is phenyl isocyanide, and fraction II is the ethyl ester of pyrophosphoric acid, which, based on the data of the IR spectra, is contaminated with formanilide.

CONCLUSIONS

1. A study was made of the reaction of the acid chlorides of acetic, butyric and isobutyric acids with the amide of diethylphosphoric acid, and of the acid chloride of diethylphosphoric acid with the amides of acetic, butyric and benzoic acids and with formanilide.

2. With the amide of diethylphosphoric acid the reaction proceeds with the formation of acylamidophosphates, while with the amides of acetic, butyric and benzoic acids and with formanilide the reaction goes with the formation of the ethyl ester of pyrophosphoric acid and the corresponding cyanides or phenyl isocyanide.

LITERATURE CITED

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