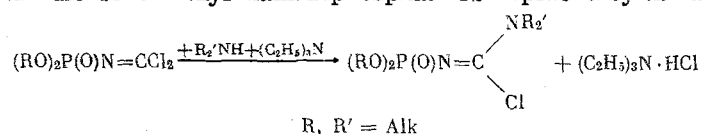


REACTION PRODUCTS OF DICHLOROMETHYLENAMIDES
OF DIALKYLPHOSPHORIC ACIDS WITH AMINES AND
ACETIC ANHYDRIDE

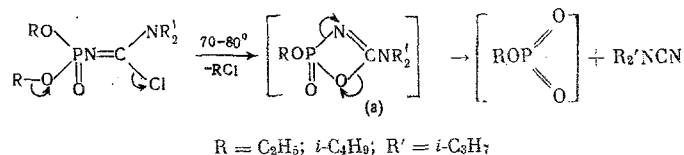
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UDC 542.91;547.1'118

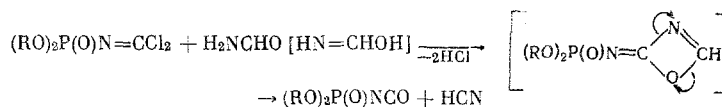
The dichloromethylenamides of dialkylphosphoric acids $(RO)_2P(O)N=CCl_2$ are formed in good yields when the esters of isothiocyanatophosphoric acid are treated with chlorine. The compounds are stable during distillation and storage [1]. The acid chloride of the N-phosphorylated iminocarbamic acid is formed when one chlorine atom in the dichloromethylenamidophosphate is replaced by the amino group



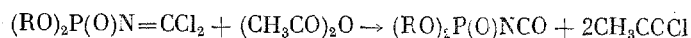
In contrast to the dichloromethylenamides of dialkylphosphoric acids, the acid chlorides of the N-phosphorylated iminocarbamic acids proved to be compounds that are thermally unstable. Even at 70°C they cleave alkyl halide to apparently form intramolecular condensation products, which decompose at this temperature into the cyanodiisopropylamine were isolated when the acid chloride of N-diisobutoxyphosphorylimino-N'-diisopropylcarbamic acid $(i-C_4H_9O)_2P(O)N=C[N(C_3H_7-i)_2]Cl$ is heated at 70-80°. Analogous products were obtained when the acid chloride of N-diethoxyphosphorylamino-N'-diisopropylcarbamic acid was heated. As a result, on the basis of the isolated products the process for the intramolecular condensation of the acid chloride of an iminocarbamic acid can be depicted by the following scheme



The cyclic ester-amide (a) that is formed at 70-80° as a result of intramolecular condensation decomposes into the cyanodialkylamine and metaphosphoric acid ester (an intense peak at 2200 cm⁻¹, which belongs to the vibrations of the C≡N group, was detected in the IR spectrum of the product before distillation). The metaphosphoric acid ester was not isolated in the pure state. It decomposes when its distillation is attempted, which is in agreement with the data on the thermal instability of these compounds. The secondary cyclic ester-amides of the N-phosphorylated iminocarbamic acids are apparently formed when formamide (in the iso-form) reacts with the dichloromethylenamides of the dialkylphosphoric acids. HCN is evolved when these ester-amides are cleaved during heating, and the esters of isocyanatophosphoric acid [2] are formed in approximately 60% yields



We found that the same compounds can be obtained in 75-80% yields by the reaction of acetic anhydride with the dichloromethylenamides of dialkylphosphoric acids



Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of Academy of Sciences of the USSR. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 6, pp. 1398-1399, June, 1974. Original article submitted June 25, 1973.

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EXPERIMENTAL METHOD

Acid Chloride of N-Diisobutoxyphosphorylimino-N'-diisopropylcarbamic Acid. To an ether solution of 14.18 g of $(i\text{-C}_4\text{H}_9\text{O})_2\text{P}(\text{O})\text{N}=\text{CCl}_2$ was added at -50° an ether solution of a mixture of 4.91 g of diisopropylamine and 4.91 g of triethylamine. After removal of the salts and solvent we obtained 15.2 g (88%) of $(i\text{-C}_4\text{H}_9\text{O})_2\text{P}(\text{O})\text{N}=\text{C}[\text{N}(\text{C}_3\text{H}_7\text{-}i)_2]\text{Cl}$ as a mobile liquid; n_D^{20} 1.4704; d_4^{20} 1.0564. Found: P 9.05; N 7.91; Cl 9.24%; MR 93.73. $\text{C}_{15}\text{H}_{32}\text{ClN}_2\text{O}_3\text{P}$. Calculated: P 8.74; N 7.90; Cl 10%; MR 93.92. The absorption bands of the P=O (1260) and C=N (1640 cm^{-1}) bonds are present in the IR spectrum of the acid chloride.

The acid chloride (13.7 g) was heated at $70\text{--}100^\circ$ for 1 h, and then the $t\text{-C}_4\text{H}_9\text{Cl}$ (3 g, 84%) was removed in vacuo. Distillation of the residue gave 2.3 g (48%) of $(i\text{-C}_3\text{H}_7)_2\text{NCN}$ [3] with bp $78.5\text{--}80$ (10 mm); n_D^{20} 1.4262; d_4^{20} 0.8727. In the IR spectrum the $\text{C}\equiv\text{N}$ group appears as an intense band at 2200 cm^{-1} .

The acid chloride of N-diethoxyphosphorylimino-N'-diisopropylcarbamic acid decomposes in a similar manner when heated.

Diethyl Ester of Isocyanatophosphoric Acid. A mixture of 11.65 g of $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{N}=\text{CCl}_2$ and 5.11 g of $(\text{CH}_3\text{CO})_2\text{O}$ was heated at $90\text{--}100^\circ$ for 6 h. Fractional distillation gave 7 g (80%) of $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{NCO}$ with bp $70\text{--}72^\circ$ (2 mm); n_D^{20} 1.4205; d_4^{20} 1.1805. Found: P 17.16; N 7.91%; MR 38.43. $\text{C}_5\text{H}_{10}\text{NO}_4\text{P}$. Calculated: P 17.32; N 7.82%; MR 38.79. The bands of the NCO (2290 cm^{-1}) and P=O (1280 cm^{-1}) groups are observed in the IR spectrum. Besides $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{NCO}$, CH_3COCl was isolated in 51% yield. The synthesis of $(i\text{-C}_4\text{H}_9\text{O})_2\text{P}(\text{O})\text{NCO}$ in 75% yield was accomplished in a similar manner; bp $73\text{--}74^\circ$ (1 mm); n_D^{20} 1.4265; d_4^{20} 1.0603. Found: P 13.26; N 5.66%; MR 56.86. $\text{C}_9\text{H}_{18}\text{NO}_4\text{P}$. Calculated: P 13.19; N 5.95%; MR 57.26. The bands of the NCO (2280 cm^{-1}) and P=O (1295 cm^{-1}) groups are present in the IR spectrum.

CONCLUSIONS

1. The acid chlorides of N-dialkoxyphosphorylated iminodialkylcarbamic acids form unstable intramolecular condensation products, which decompose into the cyanodialkylamine and metaphosphoric acid ester.

2. When reacted with acetic anhydride the dichloromethylenamides of dialkylphosphoric acids form the esters of isocyanatophosphoric acid.

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