

THE REACTION OF $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ WITH MERCAPTANS

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In reactions of $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ with mercaptans in the presence of pyridine as a hydrogen chloride acceptor, the compounds $(\text{RS})_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ ($\text{R} = \text{C}_2\text{H}_5-, \text{C}_3\text{H}_7-, \text{C}_8\text{H}_{17}-$) were found to be the final products. The hitherto unknown $(\text{RS})_2\text{ClP}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ was also identified in the reaction mixture by ^{31}P NMR spectroscopy.

The study¹ of alcoholysis of trichlorophosphazene-N-(phosphoryl dichloride) revealed the formation of not only compounds of the type $(\text{RO})_n\text{Cl}_{3-n}\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_m(\text{OR})_{2-m}$ ($n = 1-3, m = 1, 2$) but also of $(\text{RO})\text{ClP}(\text{O})\text{NHP}(\text{O})\text{Cl}_2$ and their alcoholysis products. All the derivatives except $(\text{RO})_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}(\text{OR})$ were identified by ^{31}P NMR spectroscopy, although only $(\text{RO})\text{Cl}_2\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ and $[(\text{RO})_2\text{PO}]_2\text{NH}$ were isolated as the final reaction products.

The analogous reaction with mercaptans, which has not been so far studied, is the objective of the present work.

EXPERIMENTAL

Preparation of $(\text{C}_2\text{H}_5\text{S})_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$. An amount of 24.0 g of $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ in 200 cm³ of absolutized diethyl ether were mixed with 17.4 g of ethyl mercaptan at room temperature, and 22.2 g of pyridine (molar ratio about 1 : 3 : 3) in 120 cm³ of diethyl ether were added dropwise to the vigorously stirred solution within a period of 2.5 h, whereafter the mixture was stirred for another 3 h. The separated $\text{C}_2\text{H}_5\text{N.HCl}$ was filtered out, and diethyl ether was distilled off in a vacuum. An amount of 28.9 g of $(\text{C}_2\text{H}_5\text{S})_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$ (93.8% theory with respect to $\text{Cl}_3\text{P}=\text{N}-\text{P}(\text{O})\text{Cl}_2$) were obtained in the form of a gold-yellow viscous liquid. The propyl and octyl derivatives were also obtained in yields exceeding 90%.

The same results were also arrived at when using the starting reactant molar ratio 1 : 5 : 5. Attempted substitution of the two chlorine atoms in the $-\text{P}(\text{O})\text{Cl}_2$ group, performed by heating the reaction mixture with this reactant ratio in a sealed ampoule at 100°C, resulted in a destruction of the phosphazene skeleton. Replacement of alkyl mercaptan by its sodium salt gave a similar result even at room temperature. The reaction did not proceed at all if pyridine, the hydrogen chloride acceptor, was absent.

The mass spectrum was measured on a JEOL JMS-0156-2 instrument (ionization energy 75 eV). ^{31}P NMR spectra of the diethyl ether solutions were measured at 25°C on a BRUKER AM-400 FT spectrometer (161.978 MHz) using 85% phosphoric acid as the external standard.

For $(C_2H_5S)_3P=N-P(O)Cl_2$ (346.1) calculated: 20.82% C, 4.34% H, 20.50% Cl, 4.05% N, 17.92% P, 27.75% S; found: 21.00% C, 4.30% H, 19.21% Cl, 5.00% N, 17.60% P, 26.35% S. ^{31}P NMR (δ , ppm): 58.1 d, -11.8 d; $^2J(P, P) = 13.2$ Hz. The mass spectrum exhibited the following fragments m/z (%): 345 (12, M^+), 310 (4), 285 (88), 224 (100), 163 (2).

For $(C_3H_7S)_3P=N-P(O)Cl_2$ (388.1) calculated: 27.84% C, 5.41% H, 18.28% Cl, 3.61% N, 15.98% P, 24.75% S; found: 28.12% C, 5.50% H, 18.67% Cl, 4.70% N, 15.25% P, 24.01% S. ^{31}P NMR (δ , ppm): 56.3 d, -9.6 d; $^2J(P, P) = 9.4$ Hz.

For $(C_8H_{17}S)_3P=N-P(O)Cl_2$ (598.3) calculated: 48.17% C, 8.53% H, 11.86% Cl, 2.34% N, 10.37% P, 16.06% S; found: 49.00% C, 8.70% H, 12.21% Cl, 3.29% N, 8.86% P, 16.09% S. ^{31}P NMR (δ , ppm): 56.5 d, -9.5 d; $^2J(P, P) = 10.2$ Hz.

RESULTS AND DISCUSSION

The ^{31}P NMR spectra of reaction mixtures of $Cl_3P=N-P(O)Cl_2$ with ethyl mercaptan at molar ratios higher than 1 : 5, scanned applying proton decoupling, exhibited a pair of doublets with shifts of $\delta = 58.1$ and -11.8 ($^2J(P, P) = 13.2$ Hz). Without proton decoupling, the doublet with the former shift was split into a multiplet comprising 14 bands ($^3J(H, P) = 17.2$ Hz) whereas the doublet with the latter shift remained unchanged. This suggests that the reaction product is $(C_2H_5S)_3P=N-P(O)Cl_2$; this assumption is also born out by elemental analysis as well as the mass spectrum. The results for propyl and octyl mercaptans were analogous.

Preparation of $(C_2H_5S)_2ClP=N-P(O)Cl_2$ and $(C_2H_5S)Cl_2P=N-P(O)Cl_2$ was attempted by altering the reaction conditions. The molar ratio of the reactants was varied over the range of 1 : 0.8 to 1 : 2 and temperature, over the range of 20 to $-10^\circ C$. The ^{31}P NMR spectra exhibited invariably three pairs of doublets. Those with shifts of $\delta = 0$ and -13.6 ($^2J(P, P) = 17.4$ Hz) were due to the unreacted $Cl_3P=N-P(O)Cl_2$, whereas two doublets belonged to the reaction product, $(C_2H_5S)_3P=N-P(O)Cl_2$; the last pair of doublets displayed shifts of $\delta = 50.2$ and -11.3 ($^2J(P, P) = 15.7$ Hz), the former splitting into 10 bands in the non-decoupled spectrum. This suggests that these doublets belong to $(C_2H_5S)_2ClP=N-P(O)Cl_2$, whose isolation from the reaction mixture, however, failed. ^{31}P NMR spectroscopy also failed to prove the occurrence in the reaction mixture of $(C_2H_5S).Cl_2P=N-P(O)Cl_2$, which ought to be the first-step intermediate.

In conclusion, the results indicate that $Cl_3P=N-P(O)Cl_2$ reacts with mercaptans in a manner different from the reaction with alcohols. Although in both reactions it is the chlorine atoms in the $=PCl_3$ group that react preferentially, the reaction with mercaptans involves no formation of imido-bis(phosphoric acid) derivatives or compounds with more than three RS- groups in the phosphazene molecule.

REFERENCES

1. Riesel L., Pfützner A.: Z. Chem. 20, 98 (1980).

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