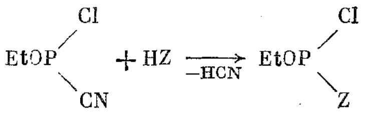
6. I. M. Aladzheva, P. V. Petrovskii, T. A. Mastryukova, and M. I. Kabachnik, Zh. Obshch. Khim., 50, 1442 (1980).
7. G. A. Gray, J. Am. Chem. Soc., 23, 7736 (1973).
8. N. A. Nesmeyanov, V. V. Mikulshina, and O. A. Reutov, J. Organomet. Chem., 13, 263 (1968).
9. A. I. Kol'tsov and G. M. Kheifits, Usp. Khim., 40, 1646 (1971).
10. M. Yu. Antipin, T. N. Sal'nikova, A. E. Kalinin, et al., Zh. Strukt. Khim., 19, 873 (1978).

REACTION OF TETRACOORDINATED PHOSPHORUS CHLOROCYANIDES WITH PROTON DONORS

A. N. Pudovik, G. V. Romanov, and
V. N. Nazmutdinova

UDC 542.91:547.1'118

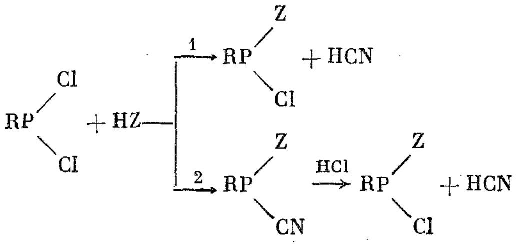
The development of a method for the synthesis of P(III) chlorocyanides [1] permitted us to study the relative reactivity of the chlorine atom and cyano group bound to one phosphorus atom. The reaction of ethyl chlorocyanophosphite with nucleophilic reagents such as alcohols, mercaptans and amines proceed under mild conditions with substitution of the CN group and the formation of trivalent phosphorus acid chlorides



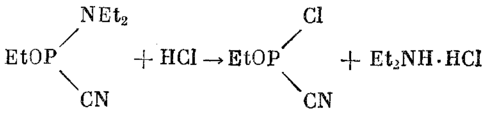
$Z = EtO, EtS, Et_2N.$

It is interesting to note that substitution of the chlorine atom occurs when the chlorophosphite molecule contains the NCO pseudohalide group in reactions with alcohols and amines [2].

We have previously found the facile substitution of the CN group by a chlorine atom in P(III) dicyanides by the action of HCl [1]. Hence, we may propose that chlorophosphites are formed in the reactions of chlorocyanophosphites with HZ either by the direct substitution of the cyano group (pathway 1) or through the intermediate substitution of the chlorine atom (pathway 2):



In order to clarify this question, experiments were designed to model the possible intermediate steps of this reaction. Thus, diethyl chlorophosphite was isolated in good yield upon bubbling dry HCl into diethyl cyanophosphite. However, the reaction of O-ethyl-N,N-diethylamidocyanophosphite with HCl proceeds with retention of the P—CN bond and substitution of the more basic Et_2N group.



A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, pp.1156-1157, May, 1987. Original article submitted July 8, 1986.

0568-5230/87/3605-1069$12.50

Thus, the reactions of chlorocyanophosphites with amines cannot be characterized by a mechanism with intermediate cleavage of the P—Cl bond. An analogous one-step reaction apparently also occurs in the reaction of the chlorocyanides with alcohols and mercaptans.

EXPERIMENTAL

The ^{31}P NMR spectra were taken on a KGU-4 NMR spectrum of 10.2 MHz relative to 85% H_3PO_4 as the external standard.

Diethyl Chlorophosphite. A sample of 0.69 g ethanol was added to 2.6 g ethyl chlorocyanophosphite in 30 ml benzene with stirring at 5-10°C. Distillation gave 2 g (80%) product with bp 55°C (15 mm), n_D^{20} 1.433, d_4^{20} 1.0693. Found: C, 30.85; H, 6.41; P, 19.79%. Calculated from $C_4H_{10}ClO_2P$: C, 30.67; H, 6.39; P, 19.81%. ^{31}P NMR spectrum (δ, ppm): 168 [3].

O-Ethyl-2-ethylchlorophosphite. A mixture of 2.7 g ethyl chlorocyanophosphite and 1.2 g EtSH was maintained for 3 h at 20°C. Distillation gave 2.9 g (87%) product with bp 64°C (15 mm), n_D^{20} 1.5116, d_4^{20} 1.2421. Found: C, 27.45; H, 5.84; P, 17.91%. Calculated for $C_4H_{10}ClOP$: C, 27.83; H, 5.80; P, 17.97% [3].

O-Ethyl-N-diethylamidochlorophosphite. A sample of 1.5 g diethylamine was added with stirring to 2.7 g ethyl chlorocyanophosphite in 30 ml benzene at 20°C. Spontaneous warming to 60°C occurred. Distillation gave 2.7 g (84%) product, bp 80°C (15 mm), n_D^{20} 1.4668; d_4^{20} 1.0406. Found: C, 39.10; H, 8.20; P, 16.60%. Calculated for $C_6H_{15}ClOP$: C, 39.24; H, 8.17; P, 16.89% [4].

Diethyl Chlorophosphite. Dry HCl was passed slowly through 2.2 g diethyl cyanophosphite for 1 h. Warming to 30-40°C occurred. The reaction endpoint was found by the disappearance of the ^{31}P NMR signal at 118 ppm. Distillation in vacuum gave 1.4 g (92%) product with bp 54°C (15 mm), n_D^{20} 1.4352; d_4^{20} 1.0742. Found: C, 30.65; H, 6.41; P, 19.83%. Calculated for $C_4H_{10}ClO_2P$: C, 30.67; H, 6.39; P, 19.81%. ^{31}P NMR spectrum (δ, ppm): 168 [3].

Ethyl Chlorocyanophosphite. Dry HCl was slowly passed through 3.2 g O-ethyl-N-diethylamidocyanophosphite and ^{31}P NMR spectra were taken until a signal appeared with δP 178 ppm. Distillation gave 1.8 g (62%) product with bp 35-36°C (15 mm), n_D^{20} 1.4560, d_4^{20} 1.2255. Found: C, 26.28; H, 3.57; P, 22.40%. Calculated for C_3H_5ClOP: C, 26.19; H, 3.64; P, 22.54%. ^{31}P NMR spectrum (δ, ppm): 100. Raman spectrum (ν, cm^{-1}): 2180 [1].

CONCLUSION

The reaction of P(III) chlorocyanides with alcohols, mercaptans and amines proceeds with the formation of the corresponding trivalent phosphorus acid chlorides.

LITERATURE CITED

1. G. V. Romanov, V. N. Nazmutdinova, and A. N. Pudovik, Izv. Akad. Nauk SSSR, Ser. Khim., 2654 (1983).
2. V. A. Shokol, Advances in the Chemistry of Organophosphorus and Organosulfur Compounds [in Russian], Vol. 3, Izd. Naukova Dumka, Kiev (1973), pp. 6-255.
3. A. I. Razumov, V. G. Liorber, V. V. Moskva, and Z. M. Khammatova, Tr. Kazansk. Khim. Tekhnol. Inst., 30, 265-270 (1962).
4. A. Zwierzak and A. Kariera, Tetrahedron, 23, 2243 (1967).