ON THE REACTION OF SOME ARYLALKOXYCHLOROPHOSPHINES WITH ACRYLAMIDE

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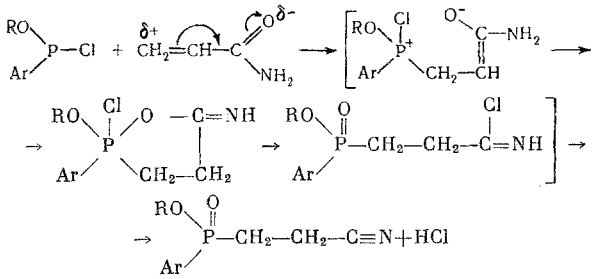
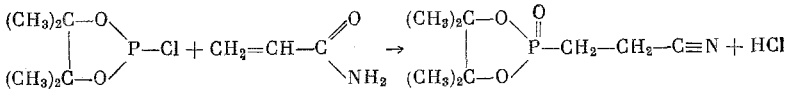
Continuing our investigation of the reaction of acyl chlorides of phosphorus acids with amides of unsaturated carboxylic acids, we studied the reaction of phenyl and p-tolylalkoxychlorophosphines and the acyl chloride of tetramethylethyleneglycolphosphonous acid with acrylamide. Mixing of the reagents leads to evolution of heat and HCl with formation of the corresponding acrylic esters of aryl-β-cyanoethylphosphonic acid



where Ar = C_6H_5 or p-CH_3–C_5H_4, and R is chloro-substituted alkyl. Figure 1 gives the IR spectrum of the 1-trichloromethylcyclopentyl ester of phenyl-β-cyanopropylphosphonic acid (II). The spectrum was obtained in a UR-10 spectrometer; drops of the substance were placed between KBr plates. The spectrum contains the following absorption bands: ν (C≡N) 2250 cm^{-1}, ν (P=O) 1250 cm^{-1}, ν [P(O)–OC] 1040 cm^{-1}, double bonds of the benzene ring 1600 cm^{-1}, the bond linking the carbon atom of the benzene ring with the phosphorus atom 1450 cm^{-1}, and ν (=C–H) 3060 cm^{-1}.

In the reaction of the acyl chloride of tetramethylethyleneglycolphosphorous acid with acrylamide the glycol ring is retained and we obtain the tetramethylethyleneglycol ester of β-cyanoethylphosphonic acid



EXPERIMENTAL

Preparation of Tert-(1,1,1-trichloro)butyl Ester of Phenyl-β-cyanoethylphosphonic Acid. 24 g of the acyl chloride of phenyl-tert-(1,1,1-trichloro)butoxyphosphonous acid

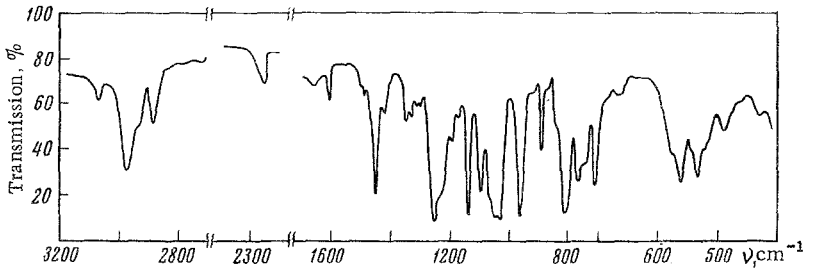


Fig. 1. Infrared spectrum of the 1-trichloromethylcyclopentyl ester of phenyl-β-cyanoethylphosphonic acid (II).

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TABLE 1. Esters of Aryl-β-cyanoethylphosphonic Acid $R-O-\overset{O}{\overset{\|}{P}}(Ar)-CH_2-CH_2-C\equiv N$

Cpd. No.	Ar	R	Yield, %	bp, °C (p, mm Hg)	mp, °C	d_4^{20}	n_D^{20}	MR found	MR calculated	Found, % N	Found, % P	Empirical formula	Calculated, % N	Calculated, % P
I	C_6H_5	$(CH_3)_2CH-CCl_2-C$	47,4	198—199 (0,001)	66—67	—	1,5400	—	—	3,84	8,71	$C_{13}H_{15}Cl_3NO_2P$	3,94	8,73
II	C_6H_5	$CH_2-CH_2-C(CCl_3)-CH_2-CH_2$	20,0	190—192 (0,001)	64—65	—	1,5460	—	—	3,62	7,86	$C_{15}H_{17}Cl_3NO_2P$	3,67	8,13
III	C_6H_5	$Cl-CH_2-CH_2-CH_2-CH_2-C$	20,1	179—180 (0,001)	—	1,2745	1,5410	63,52	63,83	5,04	12,13	$C_{11}H_{18}ClNO_3P$	5,43	12,19
IV	p-$CH_3-C_6H_4$	$(CH_3)_2CH-CCl_2-C$	48,2	197—198 (0,001)	73—74	—	1,5360	—	—	3,82	8,18	$C_{14}H_{17}Cl_3NO_2P$	3,79	8,40

and 5.4 g of acrylamidewere placed in a four-necked flask with a stirrer, thermometer, dropping funnel, reflux condenser and a calcium chloride tube. The mixture was stirred and the temperature rose to 50°. Vigorous evolution of hydrogen chloridewas observed. To complete the reaction the mixture was heated at 130° for 5 h. Distillation gave 8.5 g of the tert-(1,1,1-trichlorobutyl ester of phenyl-β-cyanoethylphosphonic acid (see Table 1, compound I); it was a thick viscous liquid which dissolves in acetone and crystallizes when left to stand.

Preparation of 1-Trichloromethylcyclopentyl Ester of Phenyl-β-cyanoethylphosphonic Acid. 25.9 g of phenyl-1-trichloromethylcyclopentoxychlorophosphine and 5.4 g of acrylamide were placed in the above-described apparatus; the temperature of the reaction mixture rose to 60°, accompanied by vigorous evolution of hydrogen chloride. The reaction mixture was heated at 110° for 5 h and then fractionated in a film distillation apparatus at coil temperature 250° and pressure 0.001 mm Hg. Redistillation of the distillate from an Arbuzov flask gave 5.7 g of the 1-trichloromethylcyclopentyl ester of phenyl-β-cyanoethylphosphonic acid; it was a thick syrup which eventually crystallized (compound II).

Preparation of the β-Chloroethyl Ester of Phenyl-β-cyanoethylphosphonic Acid. 18.95 g of the acyl chloride of phenyl-β-chloroethoxyphosphonic acid and 6.1 g of acrylamide were placed in the apparatus. The temperature rose to 80°C and vigorous evolution of hydrogen chloride was observed. To complete the reaction the mixture was heated at 130° for 5 h. The reaction mixture was then distilled twice; we obtained 4.4 g of the β-chloroethyl ester of phenyl-β-cyanoethylphosphonic acid (compound III).

Preparation of the Tert-(1,1,1-trichloro)butyl Ester of p-Tolyl-β-cyanoethylphosphonic Acid. By reacting 25 g of p-tolyl-tert-(1,1,1-trichloro)butoxychlorophosphine with 5.4 g of acrylamide we obtained 13.3 g of tert-(1,1,1-trichloro)-butyl ester of p-tolyl-β-cyanoethylphosphonic acid; it was a thick syrup which eventually crystallized (compound IV).

Preparation of the Tetramethylethyleneglycol Ester of β-Cyanoethylphosphonic Acid. 20.05 g of tetramethylethyleneglycolphosphonous chloride [1] was placed in the four-neck flask and 7.81 g of acrylamide added; during this process the mixture was stirred and cooled with cold water to keep the temperature below 80°. After addition of all the acrylamide the reaction mixture was stirred at room temperature for 2 h and then distilled. We obtained 5.48 g (23.1% of the theoretical yield) of the tetramethylethyleneglycol ester of β-cyanoethylphosphonic acid; the bp was 179° (0.001 mm) and n_D^{20} 1.4642, which agrees with [2].

CONCLUSIONS

1. The reaction of arylalkoxychlorophosphines with acrylamide leads to evolution of HCl and formation of alkyl esters of aryl-β-cyanoethylphosphonic acid.

2. Tetramethylethyleneglycolphosphonous chloride reacts with acrylamide to form the tetramethylethyleneglycol ester of β-cyanoethylphosphonic acid, the glycol ring being retained.

LITERATURE CITED

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2. A.N. Pudovik and G.A. Golitsyna, Zh. obshch. khimii, 34, 876 (1964).