REACTION OF ALKYL ETHYLPHOSPHONOCHLORIDITES OR ARYLPHOSPHONOCHLORIDITES WITH ACRYLAMIDE AND METHACRYLAMIDE

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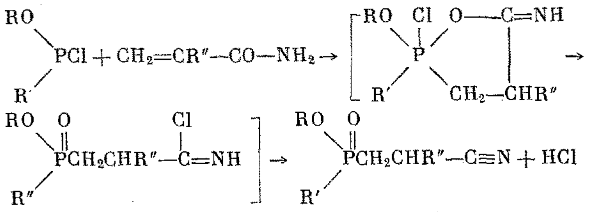
The reaction of alkyl phenylphosphonochloridites and p-tolyphosphonochloridites with acrylamide has been reported previously [1]. Continuing a study in this direction, we have investigated the reaction of alkyl ethyl-, phenyl-, and p-tolyphosphonochloridites with acrylamide and methacrylamide. The reactions of the chloridites mentioned with acrylamide take place more readily than with methacrylamide, which is probably due to the comparatively high polarizability of acrylamide. The reaction apparently takes place with an original nucleophilic attack of the tricoordinated phosphorus atom on the β-carbon atom of the α,β-unsaturated amide with the formation of an intermediate product of 1,4-addition. The latter, undergoing the second stage of the Arbuzov reaction, eliminates hydrogen chloride and is converted into the ester of an alkyl- or aryl-β-cyanoalkylphosphinic acid



(I)—(VIII)

R = alkyl; R′ = C_2H_5, C_6H_5, $p\text{-}CH_3\text{—}C_6H_4$; R″ = H or CH_3

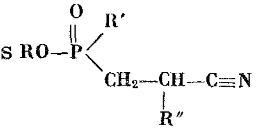
The IR spectra of compounds (I)-(VIII) have absorption bands in the ~2250 cm^{-1} region characteristic for the C≡N group. The IR spectrum of α-methyl-α-trichloromethylethyl β-cyanoethyl(ethyl)phosphinate (I) (Fig. 1A) contains absorption bands of the following groups: P–O–C 1020 cm^{-1}, P=O 1210 cm^{-1}, C≡N 2240 cm^{-1}. The IR spectrum of α-methyl-α-trichloromethylethyl β-cyanoisopropyl(phenyl)phosphinate (VI) (Fig. 1B) contains, besides the absorption bands mentioned for compound (I), frequencies in the 1450, 1580, and 3050 cm^{-1} region characteristic for the benzene ring. The characteristics of compounds (I)-(VIII) are given in Table 1.

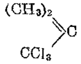
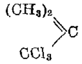
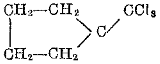
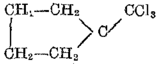
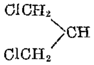
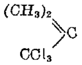
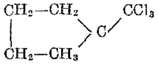
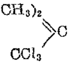
EXPERIMENTAL

Esters of Ethyl- and Aryl-β-cyanoalkylphosphinic Acids (I)-(VIII). A four-necked flask with a stirrer, thermometer, and calcium chloride tube was filled with dry CO_2 and charged with 0.1 mole of an alkyl ethylphosphonochloridite. Then 0.1 mole of acrylamide was added in portions. The temperature of the reaction mixture rose. Then the contents of the flask were stirred for 16-20 h with the temperature being raised gradually to 60-80°, until the evolution of HCl had ceased. After a first vacuum distillation, the esters were generally contaminated with an amorphous deposit. Consequently they were filtered through a glass filter and redistilled in vacuum.

The esters of the aryl-β-cyanoalkylphosphinates (V)-(VIII) were obtained similarly. Compound (VI) crystallized after distillation and compounds (I) and (II) on storage.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, pp. 2334-2336, October, 1969. Original article submitted March 31, 1969.

TABLE 1. Esters of Alkyl- and Aryl-β-cyanoalkylphosphinic Acids  $RO-P(=O)(R')-CH_2-CH(R'')-C\equiv N$

Compound No.	R	R′	R″	Empirical formula	Yield, %	Bp, °C (p, mm Hg)	Mp, °C	d_4^{20}	n_D^{20}	Found/calculated, %				
										MR	C	H	N	P
I	 $(CH_3)_2C(CCl_3)$	C_2H_5	H	$C_9H_{15}Cl_3NO_2P$	60,8	150—152 (0,05)	49	1,3285	1,4965	67,47/67,92	35,00/35,32	4,89/4,93	4,34/4,57	11,80/11,20
II	 $(CH_3)_2C(CCl_3)$	C_2H_5	CH_3	$C_{10}H_{17}Cl_3NO_2P$	59,1	140—145 (0,05)	67	—	1,4940	—	36,92/37,33	5,30/5,32	—	9,90/9,63
III		C_2H_5	H	$C_{11}H_{17}Cl_3NO_2P$	58,9	155—160 (0,05)	—	1,3437	1,5135	74,30/74,96	39,14/39,79	5,47/5,45	4,33/4,18	9,36/9,32
IV		C_2H_5	CH_3	$C_{12}H_{19}Cl_3NO_2P$	52,7	158 (0,05)	—	1,2981	1,5080	79,45/79,57	39,50/38,76	5,68/5,53	4,18/4,04	9,40/8,95
V	 $(ClCH_2)_2CH$	C_6H_5	CH_3	$C_{13}H_{16}Cl_2NO_2P$	54,3	157—161 (0,05)	—	1,2952	1,5420	77,73/77,92	—	—	4,36/4,37	9,80/9,67
VI	 $(CH_3)_2C(CCl_3)$	C_6H_5	CH_3	$C_{14}H_{17}Cl_3NO_2P$	50,5	170—172 (0,05)	88	—	1,5350	—	45,59/45,69	4,57/4,65	3,85/3,81	8,94/8,44
VII		C_6H_5	CH_3	$C_{16}H_{19}Cl_3NO_2P$	47,2	188 (0,05)	—	1,3166	1,5430	94,79/94,45	48,35/48,56	5,53/4,84	3,50/3,54	7,82/7,82
VIII	 $(CH_3)_2C(CCl_3)$	p-CH_3—C_6H_4	CH_3	$C_{15}H_{19}Cl_3NO_2P$	56,4	180—183 (0,05)	—	1,2827	1,5340	92,70/92,03	47,67/47,16	5,30/5,01	4,01/3,66	8,23/8,10

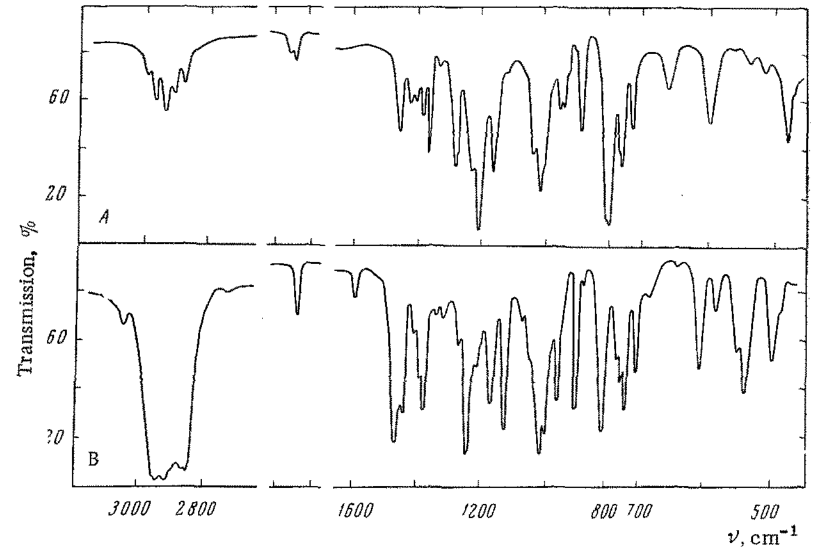


Fig. 1. IR spectra: A) α-Methyl-α-trichloromethylethyl β-cyanoethyl(ethyl)phosphinate (I); B) α-methyl-α-trichloromethylethyl β-cyanoisopropyl(phenyl)propionate (VI) (taken in paraffin oil).

CONCLUSIONS

The reaction of alkyl ethylphosphonochloridites and arylphosphonochloridites with acrylamide and methacrylamide forms esters of ethyl- and aryl-β-cyanoalkylphosphinic acids.

LITERATURE CITED

1. V. K. Khairullin, M. A. Vasyanina, and A. N. Pudovik, Izv. Akad. Nauk SSSR, Ser. Khim., 1967, 1603.