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CHEMISTRY

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Abstract

Full Text

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V. K. KHAIRULLIN

REACTION OF ETHYLDICHLOROPHOSPHINE

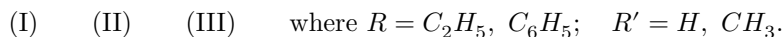
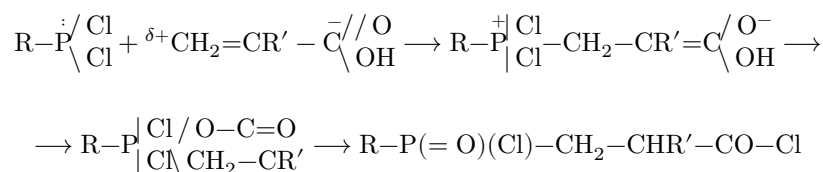
WITH α, β -UNSATURATED ACIDS

(Presented by Academician B. A. Arbutov, 16 XI 1964)

Recently A. A. Petrov and co-workers studied the condensation reaction of glycolphosphorous acids with α, β -unsaturated ketones (1). In October 1964 the same authors (2) reported the condensation of the aforementioned acid chlorides with various conjugated heteroatomic systems, including acrylic and methacrylic acids. The constants and properties of the substances obtained are not given by the authors. When we were studying the reactions of acid chlorides of trivalent phosphorus acids, the work of A. A. Petrov was not known to us.

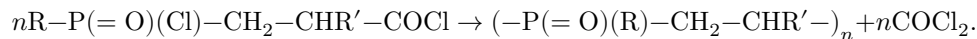
The present paper reports on the interaction of aryl- and alkyl-dichlorophosphines with acrylic and methacrylic acids. The reaction of equimolecular amounts of ethyldichlorophosphine and acrylic or methacrylic acid proceeds with the evolution of heat. Phenyl-dichlorophosphine reacts with acrylic acid on heating. As a result of these reactions, the acid chlorides of 4-oxo-4-chloro-4-phosphacarboxylic acids are obtained.

The reaction proceeds according to the scheme (3):



The unshared pair of electrons of phosphorus attacks the β -carbon atom of the α, β -unsaturated acid. An intermediate bipolar ion (I) is formed, which passes into the 1 : 1 adduct (II), which rearranges into the acid chloride of 4-oxo-4-chloro-4-phosphacarboxylic acid (III).

Distillation of the acid chlorides of 4-oxo-4-chloro-4-phosphacarboxylic acids is accompanied by considerable decomposition with liberation of phosgene:



Therefore the yields of the products are low. However, if the reaction products are subjected to fractionation in an apparatus for film distillation, the yields of the acid chlorides increase considerably.

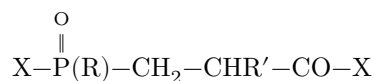
The constants of the acid chlorides of 4-oxo-4-chloro-4-phosphapropionic, 2-methyl-4-oxo-4-chloro-4-phosphapropionic, and 4-oxo-4-chloro-4-phenyl-4-phosphabutyrac acids are presented in Table 1, Nos. 3, 4, 8.

Hydrolysis of the chloroanhydrides (Table 1, Nos. 3, 4) with water gave the corresponding acids (Table 1, Nos. 1, 2).

Reactions of the chloroanhydrides of 4-oxo-4-chloro-4-phosphacarboxylic acids with alcohols in the presence of triethylamine in ether give the corresponding

Table 1

Derivatives of 4-oxo-4-hydroxy-4-phosphacarboxylic acids

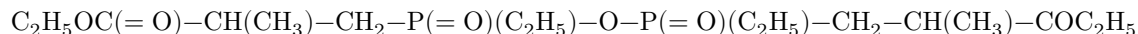


No.	X	R	R'	B.p., °C (pres- sure, mm Hg)	d_4^{20}	n_D^{20}	MR_D , cal- found	P, %, cu- found	Cl, %, cu- found	Yield, %			
1	OH	C ₂ H ₅ H	a)	—	—	—	—	18.30	18.22	—	—	84.5	
2	OH	C ₂ H ₅ CH ₃	b)	—	—	—	—	16.69	17.20	—	—	92.5	
3	Cl	C ₂ H ₅ H		118- 120 (0.22)	1.3412	1.4935	44.01	43.87	15.22	15.25	34.72	34.93	62.5
4	Cl	C ₂ H ₅ CH ₃		116- 117 (0.2)	1.2817	1.4875	48.75	48.49	14.49	14.27	32.51	32.67	37.2
5	OCH ₃	C ₂ H ₅ H		103- 104 (0.22)	1.1480	1.4510	45.54	45.92	15.68	15.95	—	—	57.5
6	OC ₂ H ₅	C ₂ H ₅ H		116- 118 (0.22)	1.0761	1.4550	55.06	55.15	13.62	13.94	—	—	54.5

No.	X	R	R'	B.p., °C (pres- sure, mm Hg)	d_4^{20}	n_D^{20}	MR_D , cal- MR_D , cu- found	P, %, P, cal- %, found	Cl, %, Cl, cal- %, found	Yield, %			
7	OC ₂ H ₅	C ₂ H ₅	H ₃ CH ₂	86-87 (0.07)	1.05361	1.44405	59.56	59.78	12.96	13.11	—	50.0	
8	Cl	C ₆ H ₅	H	114-116 (0.002)	1.38401	1.55955	58.61	58.74	13.00	12.34	29.00	28.24	10.5
9	OCH ₂	C ₂ H ₅	Cl	237 (0.002) c)	1.36681	1.49708	83.08	83.86	7.63	7.98	37.53	36.55	46.5

a) M.p. 99.5°. b) M.p. 40–43°. c) At this temperature the product distilled over with considerable decomposition.

esters (Table 1, Nos. 5, 6, 7). It should be noted that during distillation of the crude reaction products, thick, oily liquids remain in the distillation flask. In the case of the reaction of 2-methyl-4-oxo-4-chloro-4-phosphacaproyl chloride with ethyl alcohol, the anhydride of ethyl 2-carbethoxyisopropylphosphinic acid was isolated from this residue:



B.p. 175–177° at 0.1 mm Hg; d_4^{20} 1.1383; n_D^{20} 1.4670; MR_D found 97.10; calculated 96.24.

$\text{C}_{16}\text{H}_{32}\text{O}_7\text{P}_2$. Found, %: C 48.23; H 8.25; P 15.52
Calculated, %: C 48.23; H 8.10; P 15.55

The product is titrated by two equivalents of alkali.

The chloroanhydride of 4-oxo-4-chloro-4-phosphacapronic acid with epichlorohydrin also gives the 1,3-dichloroisopropyl ester (Table 1, No. 9).

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CITED LITERATURE

1. N. A. Razumova, A. A. Petrov, DAN, **158**, 907 (1964).
2. A. A. Petrov, N. A. Razumova, A. Kh. Voznesenskaya, ZhOKh, **34**, 3512 (1964).
3. G. Kamai, V. A. Kukhtin, DAN, **109**, 91 (1956).

Note: Figure translations are in progress. See original paper for figures.

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