REACTION OF CHLOROPHOSPHINES WITH β-CHLOROACRYLIC ACID

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Previously we had made a systematic study of the reactions of alkyl- and aryldichlorophosphines [1-13], and of other acid chlorides of trivalent phosphorus acids [14-17], with α,β-unsaturated acids, which reactions lead to the formation of the acid chlorides of phosphorylated carboxylic acids. In the present paper we report on the reactions of methyl-, ethyl-, and phenyldichlorophosphine with β-chloroacrylic acids and the results of a thermographic study of some reactions of a similar type.

The reactions of methyl-, ethyl-, and phenyldichlorophosphine with cis-β-chloroacrylic acid, which is a stronger acid than acrylic acid, but has an electron-acceptor substituent attached to the β-carbon atom, begin at 52-53°C (Fig. 1), and are accompanied by the liberation of HCl and the formation of the acid chlorides of either alkyl- or aryl-(β-chloroformylvinyl)phosphinic acids:

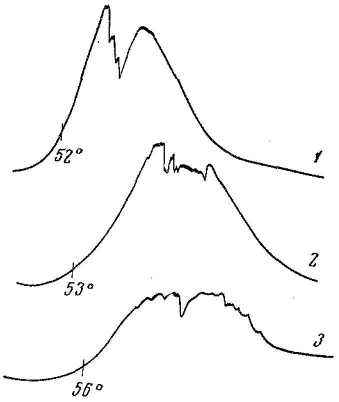

Fig. 1

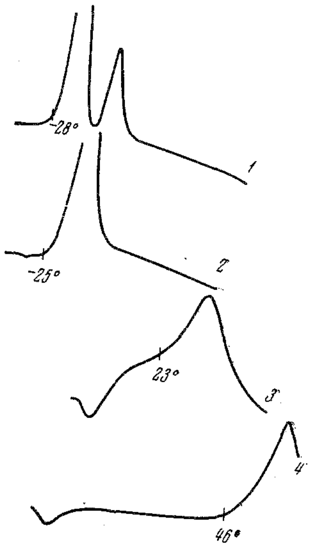

Fig. 2

Fig. 1. Thermograms of reactions: 1) of methyldichlorophosphine; 2) of ethyldichlorophosphine; 3) of phenyldichlorophosphine with cis-β-chloroacrylic acid.

Fig. 2. Thermograms of reactions: 1) of methyldichlorophosphine; 2) of ethyldichlorophosphine; 3) of phenyldichlorophosphine; 4) of chloromethyldichlorophosphine with acrylic acid.

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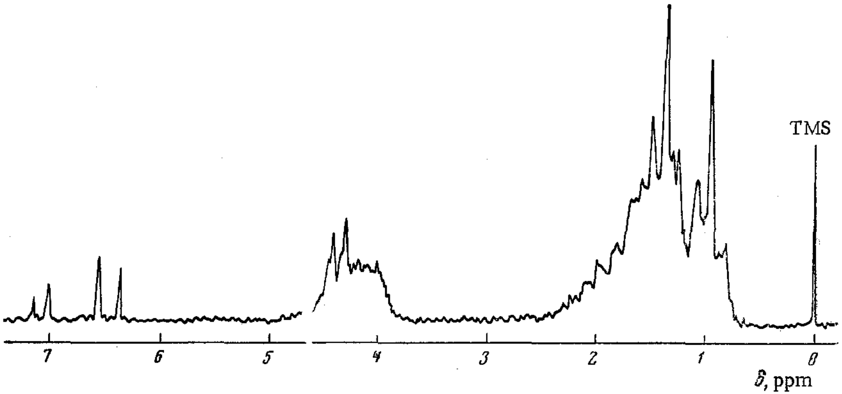
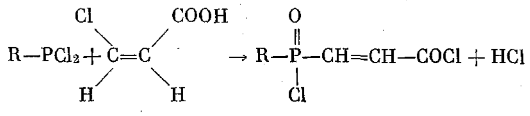


Fig. 3. NMR spectrum of ester (III).



$$\underset{\text{H}}{\overset{\text{Cl}}{\text{R—PCl}_2+\text{C}}}=\underset{\text{H}}{\overset{\text{COOH}}{\text{C}}}\rightarrow \text{R—}\underset{\text{Cl}}{\overset{\text{O}}{\overset{\|}{\text{P}}}}\text{—CH=CH—COCl}+\text{HCl}$$

$R=CH_3$ (I), C_2H_5, C_6H_5

As by-product is formed 16-20% of the acid chloride of trans-β-chloroacrylic acid. Its formation is associated with the presence of the trans-isomer as impurity in the cis-β-chloroacrylic acid [18]. Actually, the reaction of ethyldichlorophosphine with trans-β-chloroacrylic acid, contaminated with the cis-isomer, leads to the formation of 65% of the acid chloride of trans-β-chloroacrylic acid and only 10% of the acid chloride of ethyl-(β-chloroformylvinyl)phosphinic acid. As a result, the spatial structure of the β-chloroacrylic acid also exerts an important influence on the direction of the reactions.

Previously [19] the theory was expressed that the dialkylchlorophosphines when reacted with α, β-unsaturated acids fulfill the role of electrophilic components. The authors extended their concept also to the alkylchlorophosphines, since the latter are more electrophilic reagents than the dialkylchlorophosphines.

In order to obtain additional data on the mechanism of the reactions of alkyl- and aryldichlorophosphines with α,β-unsaturated acids we made a thermographic study of a number of reactions of this type. The differential heat curves were recorded on a modernized Kurnakov NTR-63 pyrometer. The thermocouples were Chromel–Alumel, and the standard was Nujol. A heating rate of 0.9 deg/min was maintained with the aid of a linear heating sensing element. A Stepanov glass vessel served as the cell for running the reactions. In order to exclude the reaction of the substances while being mixed, the vessel, after adding the acrylic acid, was cooled by immersion in liquid air, and then the chlorophosphine was added. After this the vessel was placed in the furnace, which was cooled below the temperature of the start of reaction, in order to record the thermogram. In the reactions with the β-chloroacrylic acids the recording was conducted from room temperature.

From the thermograms (Fig. 2, 1 and 2) it can be seen that the methyl- and ethyldichlorophosphines are the most active in the reaction with acrylic acid (the temperature at which the reaction starts is −28 and −25°, respectively). Two exothermic effects are observed in the thermogram for the reaction of methyldichlorophosphine with acrylic acid (1), the first of which apparently corresponds to the formation of the intermediate complex, while the second corresponds to its decomposition. The alternation of the exothermic and endothermic effects in the reaction of ethyldichlorophosphine with acrylic acid (2) is probably caused by the solution of the acrylic acid, and also by the partial liberation of HCl. Phenyldichlorophosphine begins to react with acrylic acid at 23°. Curve 3 shows the total heat effect. The reaction of chloromethyldichlorophosphine with acrylic acid begins at 46°. From Fig. 2 it can be seen that when the electron-donor substituents in the dichlorophosphines are replaced by electron-acceptor substituents their activity in the reaction with acrylic acid decreases, and consequently in these reactions they cannot fulfill the role of electrophilic components.

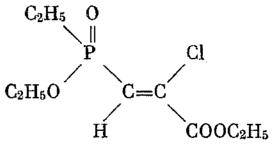
The acid chloride of ethyl-(β-chloroformylvinyl)phosphinic acid was converted to the ethyl ester of ethyl-(β-carbethoxyvinyl)phosphinic acid [20]. Chlorination of the ester gave the ethyl ester of ethyl-(α,β-dichloro-β-carbethoxyethyl)phosphinic acid (II). In its IR spectrum (ν, cm^{-1}) are present the

TABLE 1

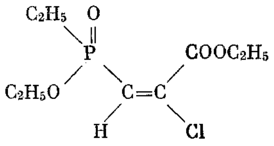
Compound No.	Formula	Yield, %	Bp, °C (p, mm of Hg)	d_4^{20}	n_D^{20}	Found/calculated				
						MR	C, %	H, %	Cl, %	P, %
I	$CH_3\underset{Cl}{P}(O)-CH=CH-COCl$	37,6	110(0,05)	1,4416	1,5160	39,17/39,69	25,31/25,69	2,95/2,69	38,20/37,91	16,83/16,56
II	$C_2H_5\underset{OC_2H_5}{P}(O)CHCl-CHCl-COOC_2H_5$	97,2	—	1,2643	1,4740	64,71/64,89	37,17/37,14	5,90/5,82	24,82/24,38	11,21/10,64
III	$C_2H_5\underset{OC_2H_5}{P}(O)-CH=CCl-COOC_2H_5$	90,1	140—142 (0,06)	1,1873	1,4740	60,27/59,56	42,60/42,45	6,81/6,33	13,70/13,92	12,12/12,16
IV	$C_2H_5\underset{Cl}{P}(O)-CH=CCl-COOC_2H_5$	80,5	130(0,04)	1,3100	1,4980	54,90/54,82	34,69/34,32	4,96/4,52	28,22/28,12	12,84/12,64
V	$C_2H_5\underset{OH}{P}(O)-CH=CCl-COOC_2H_5$	100,0	—	1,2730	1,4945	51,25/51,11	36,97/37,10	5,19/5,34	15,91/15,64	13,17/13,67
VI	$C_2H_5\underset{OC_4H_9}{P}(O)-CH=CCl-COOC_2H_5$	70,0	151—153 (0,04)	1,1307	1,4690	69,68/69,69	46,87/46,73	7,38/7,13	12,33/12,54	10,80/10,95

absorption bands of the groups: P—O—C (1040), P=O (1250), and C=O (1760). Treatment of ester (II) with triethylamine results in the cleavage of HCl and the formation of the ethyl ester of ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic acid (III), the structure of which is in agreement with its IR spectrum (ν, cm^{-1}): P—O—C (1035), P=O (1225), C=C (1595) C=O (1730).

In order to determine the position of the chlorine in ester (III) we took its NMR spectrum (Fig. 3). The NMR spectrum was recorded at room temperature on an RYa-2303 spectrometer at an operating frequency of 60 MHz. The internal standard was tetramethylsilane ($\delta_{TMS} = 0$). Two doublets of different intensity, with chemical shifts of $\delta = 6.38$ and 7.02 ppm, testify to the presence of two isomers. The values of the spin–spin coupling constants, $J_{PH} = 10.2$ and 9.6 Hz, corroborate the fact that in both isomers the proton is found in the α-position with respect to the phosphorus atom. Apparently, the isomers differ in the position of the chlorine atom and the carbethoxyl grouping with respect to the phosphoryl group


(IIIa)

and


(IIIb)

The value of the spin–spin coupling constant $2J_{PH}$ for such an arrangement of the proton is found to be in agreement with the literature data [21].

The treatment of ester (III) with PCl_5 in CCl_4 gave the acid chloride of ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic acid (IV), in whose IR spectrum are retained the absorption bands of the groups: P—O (1230 cm^{-1}), C=C (1598 cm^{-1}) and C=O (1740 cm^{-1}), while the band of the P—O—C group disappears, and the absorption band of the P—Cl bond (550 cm^{-1}) appears. The hydrolysis of acid chloride (IV) gave ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic acid (V) [IR spectrum (ν, cm^{-1}): P=O (1230), C=C (1598), C=O (1735), P(O)OH (2100-2320, 2560-2800 v.w.)]. Acid chloride (IV) when reacted with butanol gives the butyl ester of ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic acid (VI). The constants of compounds (II)-(VI) are given in Table 1.

EXPERIMENTAL METHOD

Reaction of Methyldichlorophosphine with cis-β-Chloroacrylic Acid. In a four-necked flask, fitted with a stirrer, thermometer, dropping funnel and a calcium chloride tube, filled with dry CO_2, was placed 5.3 g of cis-β-chloroacrylic acid. With cooling in a mixture of ice and water, 5.8 g of methyldichlorophosphine was added in drops at such a rate that the temperature of the reaction mixture did not exceed 30°. The reaction mixture was stirred for 3 h without cooling; the evolution of HCl was observed. Distillation gave 1.35 g of the acid chloride of trans-β-chloroacrylic acid with bp. 40° (0.06 mm); 111° (760 mm); n_D^{20} 1.4913 [18], and 3.5 g of the acid chloride of methyl-(β-chloroformylvinyl)phosphinic acid (I).

Reaction of Ethyldichlorophosphine with cis-β-Chloroacrylic Acid. In a similar manner, the reaction of 5.3 g of cis-β-chloroacrylic acid with 6.5 g of ethyldichlorophosphine in 50 ml of absolute benzene gave 1 g (16%) of the acid chloride of trans-β-chloroacrylic acid and 7 g (70%) of the acid chloride of ethyl-(β-chloroformylvinyl)phosphinic acid with bp. 110° (0.06 mm); d_4^{20} 1.3581; n_D^{20} 1.5140. The constants and its IR spectrum are identical with the constants and IR spectrum of the acid chloride of ethyl-(β-chloroformylvinyl)phosphinic acid, which was described by us previously [22].

Reaction of Ethyldichlorophosphine with trans-β-Chloroacrylic Acid. To 10.6 g of trans-β-chloroacrylic acid with mp 79-81.5° [18], contaminated with the cis-isomer, dissolved in 50 ml of benzene, in a CO_2 atmosphere, was added 13.1 g of ethyldichlorophosphine in drops. The reaction mixture was heated at 60° for 3 h, and then the benzene was distilled off. Distillation of the residue gave 8.5 g of low-boiling fraction and 2.1 g (10.5%) of the acid chloride of ethyl-(β-chloroformylvinyl)phosphinic acid with bp. 110° (0.06 mm); d_4^{20} 1.3580; n_D^{20} 1.5138. Redistillation of the low-boiling fraction gave 8.2 g (65.6%) of the acid chloride of trans-β-chloroacrylic acid with bp. 111-113°; n_D^{20} 1.4913.

Reaction of Phenyldichlorophosphine with cis-β-Chloroacrylic Acid. The reaction of 5.3 g of cis-β-chloroacrylic acid with 9 g of phenyldichlorophosphine in 50 ml of absolute benzene gave 1.25 g (19%) of the acid chloride of trans-β-chloroacrylic acid and 6.3 g (52%) of the acid chloride of phenyl-(β-chloroformylvinyl)phosphinic acid with bp. 140° (0.04 mm); d_4^{20} 1.3880; n_D^{20} 1.5790. The constants coincide with the literature data [13].

Reaction of Ethyldichlorophosphine with Acrylic Acid in Acrylonitrile Solution. From the reaction products of 13.1 g of ethyldichlorophosphine and 7.2 g of acrylic acid in 35 g of acrylonitrile was isolated 33.5 g of acrylonitrile and 20.2 g of crude acid chloride of ethyl-(β-chloroformylethyl)phosphinic acid with d_4^{20} 1.3392; n_D^{20} 1.4958 [20].

Ethyl Ester of Ethyl-(α,β-dichloro-β-carbethoxyethyl)phosphinic Acid (II). With stirring and cooling to −15°, into a solution of 55 g of the ethyl ester of ethyl-(β-carbethoxyvinyl)phosphinic acid [22] in 100 ml of CCl_4 was passed a stream of dry chlorine until the temperature of the reaction mixture ceased to rise. The solvent was removed in the vacuum of a water-jet pump. The residue represents ester (II).

Ethyl Ester of Ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic Acid (III). To 70 g of (II) in 300 ml of absolute benzene was added 24.7 g of triethylamine in drops. After stirring for 6 h, the triethylamine hydrochloride (36 g) was filtered, and the benzene was distilled off. Distillation of the residue gave 56.5 g of ester (III).

Acid Chloride of Ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic Acid (IV). To 40 g of ester (III) in 50 ml of CCl_4 was added 33 g of PCl_5. The temperature of the reaction mixture rose from room temperature up to 60°. After 1 h at 60° the formed ethyl chloride and phosphorus oxychloride, and also the solvent were removed in vacuo, while the residue was distilled. We obtained 31 g of acid chloride (IV).

Ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic Acid (V). To 8 g of acid chloride (IV) was added 0.6 g of water. Here the evolution of HCl was observed and the temperature of the reaction mixture rose up to 60°. The HCl was removed at 0.04 mm. We obtained 7.3 g of acid (V).

Butyl Ester of Ethyl-(β-chloro-β-carbethoxyvinyl)phosphinic Acid (VI). To 6 g of acid chloride (IV) in 50 ml of absolute benzene was added in drops a mixture of 1.9 g of butanol and 2.5 g of triethylamine. The reaction mixture was stirred at room temperature for 2 h. The triethylamine hydrochloride (3.5 g) was filtered, and the benzene was distilled off. Distillation of the residue in vacuo gave 5.8 g of ester (VI).

CONCLUSIONS

1. The reactions of methyl-, ethyl-, and phenyldichlorophosphine with cis-β-chloroacrylic acid lead to the formation of the acid chlorides of methyl-, ethyl-, and phenyl-(β-chloroformylvinyl)phosphinic acid.

2. With trans-β-chloroacrylic acid the reaction proceeds with the formation of the acid chloride of trans-β-chloroacrylic acid.

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