REACTION OF PHOSPHORUS PENTACHLORIDE WITH SOME α-HYDROXY-CARBOXYLIC ACIDS

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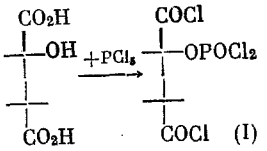
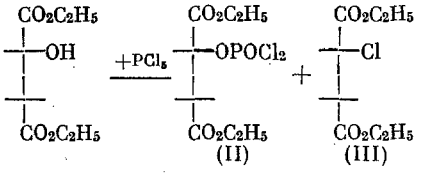
Despite the apparent simplicity of the reaction of PCl_5 with 2,2,2-trichlorolactic acid, a united opinion regarding the nature of the obtained product is lacking. According to [1], the latter is O-(2,2,2-trichloro-1-chloroformylethyl) dichlorophosphate, and not 1,2,2,2-tetrachloropropionyl chloride, as was stated previously [2].

Actually, when PCl_5 was reacted with another α-hydroxycarboxylic acid, namely D,L-malic acid, we obtained O-[1,2-di(chloroformyl)ethyl] dichlorophosphate (I) as the main product.



(I)

Along with O-[1,2-di(ethoxycarbonyl)ethyl] dichlorophosphate (II), we were able to detect 1-chloro-1,2-di(ethoxycarbonyl)ethane (III) when PCl_5 is reacted with diethyl malate.



The main reaction products are respectively O-[2-chloro-1,2-di(chloroformyl)ethyl] dichlorophosphate (IV) and O-[2-chloro-1,2-di(methoxycarbonyl)ethyl] dichlorophosphate (VII) when PCl_5 is reacted with D-tartaric acid and its dimethyl ester. The NMR spectra confirm the nonequivalence of the methine protons in (IV) (δ, ppm): 5.77 g (CH_A); 5.33 g (CH_B), $^3J_{H_ACCH_B} = {}^3J_{H_BCCH_A} = 3.75$, $^3J_{POCHA} = 12.9 = {}^4J_{POCCH_B} = 1.6$ Hz, and in (VIII): 4.88 g (CH_A); 5.51 g (CH_B), $^3J_{H_ACCH_B} = {}^3J_{H_BCCH_A} = 5$, $^3J_{POCH_A} = 12$, $^4J_{POCCH_B} = 2.25$ Hz, and also the nonequivalence of the methyl protons in (VIII): 3.83 and 3.89 ppm. Chlorophosphate (VII) is relatively stable when heated, whereas (IV) easily cleaves HCl to give O-[1,2-di(chloroformyl)vinyl] dichlorophosphate (V). The NMR spectrum of the latter has two signals with δ 6.93 and 7.56 ppm (1H, ratio ~9:1), which are apparently caused by the presence of a mixture of geometric isomers. The treatment of (IV) with methanol in the presence of triethylamine results in the cleavage of dimethyl phosphate and the formation of 1-chloro-1,2-di(methoxycarbonyl)ethylene (VI). The NMR spectrum of (VI) consists of two pairs of singlets of nonequivalent methyl (3.79 and 3.89 ppm) and methine protons (6.27 and 7.09 ppm, ratio 1:4). A completely identical NMR spectrum was obtained for the thermal decomposition product of O-[2-chloro-1,2-di(methoxycarbonyl)ethyl]phosphoric acid (VIII), which is formed by the reaction of (VI) with AcOH. (See scheme on following page).

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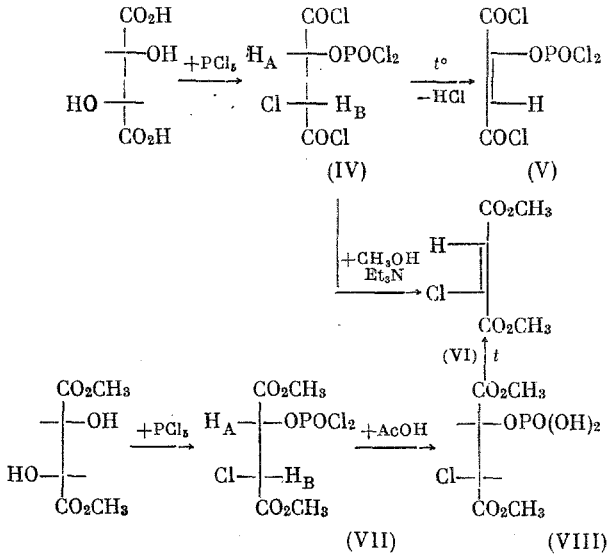
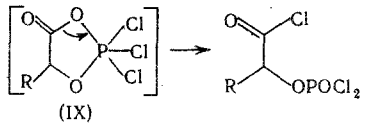
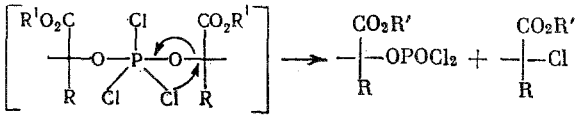


The results of studying the reaction of PCl_5 with the D,L-malic and D-tartaric acids, and also their esters, are in full agreement with the assumption that the PCl_5 reacts first with the alcoholic hydroxyl of the α-hydroxycarboxylic acid to give the corresponding alkoxytetrachlorophosphorane. Taking into account the ability of α-hydroxycarboxylic acids to form spirophosphoranes when reacted with cyclic chlorophosphites and PCl_3 [3], it may be assumed that when an equimolar ratio of the reactants or an excess of PCl_5 is used the unstable cyclic dioxytrichlorophosphorane (IX) is formed, the decomposition of which leads to the O-(1-chloroformylalkyl) dichlorophosphate. Naturally, the possibility of forming the acyl halide via the intermolecular reaction of the carboxyl group with PCl_5 is not excluded here. This possibly is the specific reason for the reaction of PCl_5 with trichlorolactic acid [1].



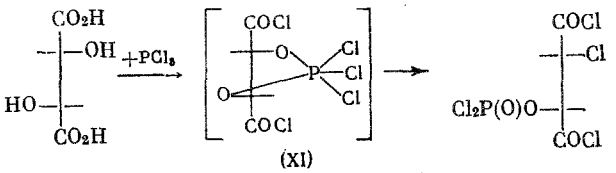
(IX)

With an excess of the α-hydroxy acid or its ester the initially formed tetrachlorophosphorane can react with the hydroxy group of another acid molecule to give the dialkoxytrichlorophosphorane (X). The latter on decomposition gives a mixture of the corresponding 1-substituted alkanecarboxylic acid derivatives.



(X)

The presence of an αdiol grouping in the hydroxy acid molecule (like, for example, in D-tartaric acid and its ester) makes it possible to form the cyclic dioxytrichlorophosphorane (XI), the decomposition of which leads to the 1,2-disubstituted 2-chloroethyl dichlorophosphates.



(XI)

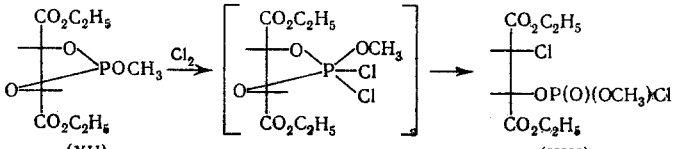
The possibility of the intermediately formed dioxytrichlorophosphorane (XI) decomposing in this manner is indirectly confirmed by the formation of O-methyl O-[2-chloro-1,2-di(ethoxycarbonyl)ethyl] chlorophosphate (XIII) via the chlorination of 2-methoxy-4,5-dimethoxycarbonyl-1,3,2-dioxaphospholane (XII). The intermediate formation of the dihalophosphorane in this reaction is entirely probable, especially if it is considered that one

TABLE 1. Properties of Reaction Products of PCl_5 with α-Hydrocarboxylic Acids and Their Esters

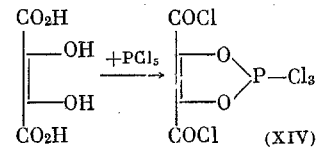
α-Hydroxycarboxylic acid (ester)	Mole ratio of hydroxy compound and PCl_5	Main reaction products	Yield, %	Empirical formula	bp, °C (p, mm of Hg)	n_D^{20}	δ_{31P}, ppm	Found / Calculated, % C	H	P	Cl
D,L-Malic acid	0,31	(I)	64,1	$C_4H_5Cl_3O_4P$	90—92 (0,15)	1,4930	—10	16,75 / 16,67	1,11 / 1,04	10,35 / 10,76	49,46 / 49,31
Diethyl D,L-malate	0,22	(II) (III)*	22,7 36,5	$C_8H_{15}Cl_2O_6P_2$	116—117 (0,20) 74—76 (0,15)	1,4568 1,4430	—7 —	31,27 / 31,27	4,06 / 4,23	9,78 / 10,10	24,88 / 23,12
D-Tartaric acid	0,27	(IV)	85,0	$C_4H_2Cl_6O_4P$	98—100 (0,07)	1,5015	—12	14,76 / 14,88	0,63 / 0,62	9,64 / 9,61	54,63 / 55,04
Dimethyl D-tartrate	0,64	(VII)	44,7	$C_6H_8Cl_3O_6P$	123—125 (0,05)	1,4746	—10	23,01 / 22,97	2,62 / 2,55	9,79 / 9,89	33,88 / 33,97
Dihydroxymaleic acid	0,24	(XIV)	36,3	$C_4Cl_5O_4P$	97—98 (0,02)	1,4575	26	15,10 / 14,98	—	9,75 / 9,67	54,62 / 55,38

*Found: C 46.28; H 6.47; Cl 17.47%. $C_8H_{13}O_4Cl$. Calculated: C 46.04; H 6.23; Cl 17.03%.

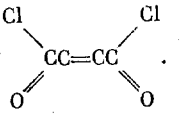
of the known methods for the synthesis of triaroxydihalophosphoranes is the halogenation of triaryl phosphites [4, 5].



The possible formation of dioxychlorophosphorane (XI) is also supported by the fact that when PCl_5 was reacted with dihydroxymaleic acid we were able to obtain 2,2,2-trichloro-4,5-di-(chloroformyl)-1,3,2-dioxa-4-phospholene (XIV). The structure of (XIV) was confirmed by the



elemental analysis data and the IR spectra: 1620 (C=C) and 1785 cm^{-1} (C=O). Absorption bands are completely absent in the 3100-3500 cm^{-1} region, which indicates the absence of alcohol and carboxyl hydroxyls. The NMR spectrum shows the absence of protons, and δ_{31P} + 26 ppm. At the present time a total of only two members of the dioxytrichlorophosphoranes has been characterized [6, 7], and the values of the chemical shifts (26, and 26.5 ppm) given for them coincide with those found by us. It may be assumed that the relative stability of the cyclic trichlorophosphorane (XIV) is caused by the presence of the conjugated system



EXPERIMENTAL METHOD

The NMR spectra were recorded on a Varian-60 spectrometer for 30% solutions in CCl_4 relative to TMS. The ^{31}P NMR spectra were recorded on an NR-2303 spectrometer relative to 85% H_3PO_4.

Reaction of PCl_5 with D,L-Malic Acid. With stirring, 10 g of D,L-malic acid was added to a suspension of 50 g of PCl_5 in 200 ml of abs. benzene. The mixture was stirred at 40° until the HCl evolution ceased. The mixture after cooling to ~25° was evaporated in vacuo, the excess PCl_5 was filtered, and the residue was distilled. We obtained 13.8 g of (I) as a clear colorless oil. Infrared spectrum (ν, cm^{-1}): 1740 (C=O), 1300 (P=O), 580 (P—Cl). NMR spectrum (δ, ppm): 5.68 m (1H), $^3J_{HCCH}$ = 5.1, J_{POCH} = 13.2 Hz and 3.76 d (2H), $^3J_{HCCH}$ = 5.1 Hz.

The reaction of PCl_5 with the other α-hydroxy acids, or their ester, was run in a similar manner in benzene. In the case of the D-tartaric

and dihydroxymaleic acids the reaction mixture was stirred at 60° for 3 h; in the case of dimethyl tartrate the mixture was refluxed for 2 h. The mole ratios of the reactants, the properties of the obtained products, and the elemental analysis results are given in Table 1.

O-[1,2-Di(chloroformyl)vinyl] dichlorophosphate (V). After 20 g of (IV) was heated at 120-135° for 25 h the residue was distilled. We obtained 5.67 g (32%) of (V), bp 33° (0.02 mm). δ_{31P} + 10 ppm. Found: C 17.11; H 0.43%. $C_4HCl_4O_4P$. Calculated: C 16.78; H 0.35%.

1-Chloro-1,2-di(methoxycarbonyl)ethylene (VI). With stirring, to a solution of 5.6 g of MeOH and 17.7 g of Et_3N in 200 ml of abs. ether at −10° was added in drops a solution of 11.3 g of (IV) in 20 ml of ether. After removing the solvent from the filtrate the residue was distilled. We obtained 2.1 g (33%) of (VI) as a colorless viscous oil, bp 60-62° (0.06 mm); n_D^{20} 1.4722. Found: C 40.29; H 3.90; Cl 19.97%. $C_6H_7ClO_4$. Calculated: C 40.34; H 3.32; Cl 19.89%. Infrared spectrum (ν, cm^{-1}): 1750 (C=O), 1310 (P=O), 1640 (C=C), 770 (C—Cl).

O-[2-Chloro-1,2-di(methoxycarbonyl)ethyl]phosphoric Acid (VIII). A mixture of 14.4 g of (VII) and 4.2 g of AcOH was refluxed for 2 h, and the obtained crystals were filtered and washed with abs. ether. We obtained 7.3 g (58%) of (VIII), mp 108-110°. Found: C 26.16; H 3.60; P 13.22%. $C_6H_{10}ClO_8P$. Calculated: C 26.03; H 3.61; P 12.83%. Infrared spectrum (ν, cm^{-1}): 1290 (P=O), 1730 (C=O), 2700 (P—OH). δ_{31P} 17 ppm.

O-Methyl O-[2-chloro-1,2-di(ethoxycarbonyl)ethyl] Chlorophosphate (XIII). Chlorine was passed into a solution of 11.8 g of (XII) in 130 ml of abs. $CHCl_3$ until a permanent yellow-green color appeared (~3.5 h). After removal of the solvent in vacuo the residue was distilled. We obtained 5 g (31%) of (XIII) as a clear colorless oil, bp 140-142° (0.14 mm): n_D^{20} 1.4623. δ_{31P} − 6 ppm. Found: C 27.00; H 3.50; P 10.27%. $C_7H_{11}Cl_2O_7P$. Calculated: C 27.18; H 3.56; P 10.03%.

CONCLUSIONS

The reaction of PCl_5 with the D,L-malic and D-tartaric acids gives the O-[1,2-di-(chloroformyl)ethyl] and O-[2-chloro-1,2-di(chloroformyl)ethyl] dichlorophosphates, while reaction with dihydroxymaleic acid gives 2,2,2-trichloro-4,5-di(chloroformyl)-1,3,2-dioxa-4-phospholene.

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