INTERACTION OF EPICHLOROHYDRIN WITH PHOSPHORUS ACID CHLORIDES

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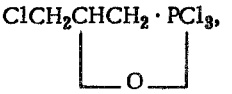
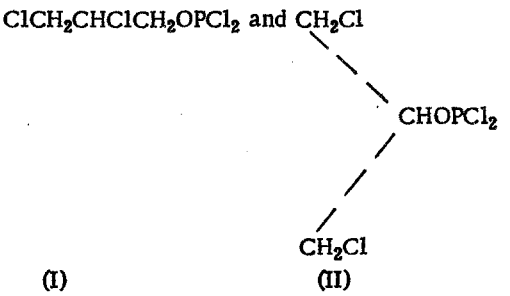
In 1879 Hanriot [1] described the addition product of phosphorus trichloride and epichlorohydrin  , but the structure of the product was not established. Kabachnik and Rossiiskaya [2] in 1946 determined the structure of the addition products of phosphorus trichloride and ethylene oxide, and on this basis came to the conclusion that two possible formulas exist for the product of Hanriot:

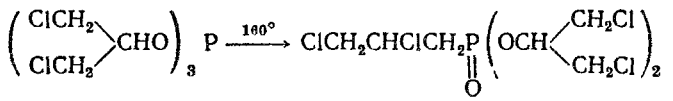


(I) (II)

By analogy with the addition product of epichlorohydrin and arsenic trichloride, the authors give preference to the second formula.

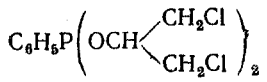
We have studied the interaction of epichlorohydrin with the chlorides of certain acids of phosphorus, namely: phosphorus trichloride, phenyldichlorophosphine, ethyldichlorophosphine, and methyldichlorophosphine oxide [dichloride of methylphosphonic acid]. Thereby the following results were obtained: The reaction between epichlorohydrin and phosphorus trichloride in equimolar ratio, in the presence of two or three drops of titanium tetrachloride, proceeds with considerable self-heating. Three fractions are obtained on distillation of the reaction products. Based on analytical data, and as we have established, the first fraction represents the dichloride of β,β'-dichloroisopropylphosphorous acid [β, β'-dichloroisopropoxydichlorophosphine]; it fumes strongly in air. The second fraction is the chloride of bis (β,β'-dichloroisopropyl) phosphorous acid [bis (β, β' -dichloroisopropoxy) chlorophosphine]. It also fumes in air, but more weakly. The third fraction is the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid. It will be shown below that the structures of these products actually correspond to the formulas named.

The interaction of epichlorohydrin with phosphorus trichloride in 3 : 1 mole ratio also proceeds with the evolution of heat. A thick yellow liquid is formed as a result of the reaction. During its vacuum distillation, the tris - (β,β'-dichloroisopropyl) phosphite formed in the reaction is isomerized into a derivative of pentavalent phosphorus, the bis (β,β'-dichloroisopropyl) ester of β, γ-dichloropropylphosphonic acid, according to a mechanism proposed by Kabachnik and Rossiiskaya [3] for tri-β-chloroethyl phosphite:

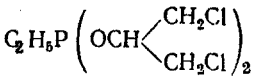


The isomerization occurs at a bath temperature ~ 160°C, and is accompanied by violent foaming of the material in the flask. The isomerization product is a transparent viscous liquid.

The reaction of epichlorohydrin with phenyldichlorophosphine and ethyldichlorophosphine in the presence of one or two drops of titanium tetrachloride proceeds with self-heating, especially strongly in the case of ethyldichlorophosphine. As a result of rearrangement of the reaction products, there are formed, respectively: 1) β,β'-dichloroisopropyl ester of β,γ-dichloropropylphenylphosphinic acid; 2) β,β'-dichloroisopropyl ester of β,γ-dichloropropylethylphosphinic acid. We had intended to isolate tris(β,β'-dichloroisopropyl) phosphite, the bis (β,β'-dichloroisopropyl) ester of phenylphosphonous acid:

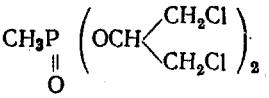


and the bis (β,β'-dichloroisopropyl) ester of ethylphosphonous acid:



by vacuum distillation at 0.02-0.05 mm; however, this was not successful, since the Arbuzov isomerization takes place at a bath temperature ~ 160°C for the first and second products and 150°C for the third product.

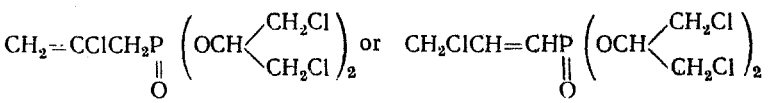
Epichlorohydrin enters into reaction with methyldichlorophosphine oxide[dichloride of methylphosphonic acid] on heating to 75-80°C. Subsequently the reaction proceeds with heat evolution, and only at the end is it again necessary to heat externally. The reaction product, the bis (β, β'-dichloroisopropyl) ester of methylphosphonic acid:



is a colorless, viscous liquid.

By the action of phosphorus pentachloride on the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid according to the methods of Kabachnik and Rossiiskaya[4] by the action of phosphorus pentachloride on the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid and on the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid in sealed tubes did not give the desired result.

The dehydrochlorination of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid by triethylamine in benzene solution by the method of Gefter [5] gave a colorless, viscous substance with b.p. 168-170°C (1 mm). The weight of the precipitated triethylamine hydrochloride that was formed during the dehydrohalogenation is evidence of the splitting of one HCl group. On this basis and from the analytical data, one of the following formulas can be ascribed to the product of dehydrochlorination:



In order to establish the structure of the products of interaction of epichlorohydrin with phosphorus acid chlorides, we performed a counter-synthesis: By the reaction between ethyldichlorophosphine and the α,γ-dichlorohydrin

of glycerin [1, 3-dichloroisopropanol], the bis (β,β'-dichloroisopropyl) ester of ethylphosphonous acid was obtained; this isomerized during vacuum distillation, and the β,β'-dichloroisopropyl ester of β,γ-dichloropropylethylphosphinic acid was isolated:

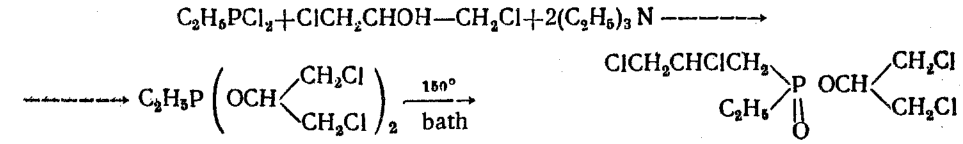


TABLE 1.

Method of preparation $ClCH_2CHClCH_2(C_2H_5)P(O)OCH(CH_2Cl)_2$	B.p., °C (p, mm Hg)	n_D^{20}	P, %		Cl, %	
			Calc.	Found	Calc.	Found
$C_2H_5PCl_2+\underset{O}{CH_2CH}CH_2Cl$	149—151 (0,05)	1,5055	9,8	9,57 9,96	44,88	44,61 44,47
$C_2H_5PCl_2+ClCH_2\underset{OH}{CH}CH_2Cl$	150—152 (0,05)	1,5057	9,8	9,62 9,91	44,88	44,69 44,58

A substance analogous in composition is formed, as was indicated previously, on the interaction of ethyldichlorophosphine with epichlorohydrin (direct synthesis).

A comparison of the physicochemical constants of the products of the direct and counter syntheses indicates that they are fully identical (Table 1). The infrared absorption spectra of the compounds compared also proved to be completely identical (Figs. 1 and 2). These data allow drawing the conclusion that the products of interaction of epichlorohydrin with phosphorus acid chlorides have an iso-structure. The physicochemical constants and analyses of the substances that we obtained are shown in Table 2.

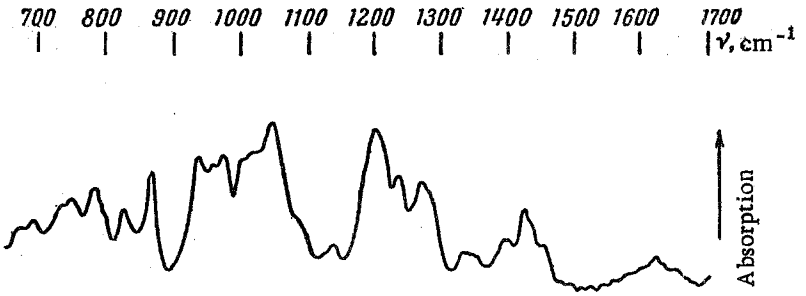


Fig. 1. IR absorption spectrum of β,β'-dichloroisopropyl ester of β, γ-dichloropropylethylphosphinic acid from direct synthesis.

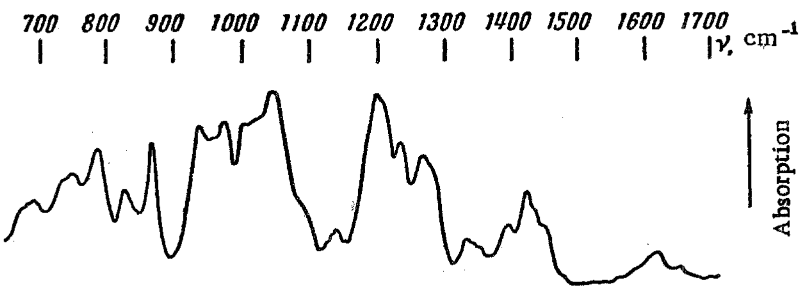


Fig. 2. IR absorption spectrum of β,β'-dichloroisopropyl ester of β, γ-dichloropropylethylphosphinic acid from counter synthesis.

TABLE 2.

Formula	B.p., °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR		P, %		Cl, %		Yield, %
				Found	Calc.	Found	Calc	Found	Calc.	
$ClCH_2CH(ClCH_2)OPCl_2$*	49—51 (1)	1,5222	1,5296	45,83	45,37	13,75 13,39	13,47	61,27 61,20	61,69	28
$(ClCH_2CH(ClCH_2)O)_2PCl$**	122—124 (1)	1,5183	1,4905	65,58	65,72	9,19 9,31	9,6	55,4 55,01	54,98	26
$ClCH_2CHClCH_2P(=O)(OCH(CH_2Cl)CH_2Cl)_2$***	170—172 (0,02)	1,5148	1,4823	84,38	83,39	7,28 7,03	7,46	51,12 51,38	51,27	47,5
$ClCH_2CHClCH_2C_6H_5P(=O)OCH(CH_2Cl)CH_2Cl$	179—181 (0,02)	1,5528	—	—	—	8,8 9,0	8,51	39,13 39,25	38,95	88
$CH_3P(=O)(OCH(CH_2Cl)CH_2Cl)_2$	127—129 (1)	1,4922	1,4391	64,43	64,86	9,25 9,38	9,75	44,56 44,8	44,6	75
$ClCH_2CHClCH_2C_2H_5P(=O)OCH(CH_2Cl)CH_2Cl$	149—151 (0,05)	1,5055	1,3768	68,14	68,34	9,57 9,96	9,8	44,61 44,47	44,88	54
$ClCH_2CH{=}CHP(=O)(OCH(CH_2Cl)CH_2Cl)_2$****	168—170 (1)	1,5102	—	—	—	7,83 7,68	8,18	46,55 46,83	46,84	47
$ClCH_2CHClCH_2P(=O)(Cl)OCH(CH_2Cl)CH_2Cl$	188—190 (8)	1,5168	—	—	—	9,27 9,42	9,6	55,44 55,8	54,98	43

* B. p., 75° (2 mm); d_4^{20} 1.4973; n_D^{20} 1.5195 [6].

** B. p. 135—137° (1 mm); d_4^{20} 1.4903; n_D^{20} 1.5189 [6].

*** B. p. 208—210° (2 mm); d_4^{20} 1.5018; n_D^{20} 1.5130 [6].

**** The other possible formula of this substance is $CH_2=CClCH_2P(=O)(OCH(CH_2Cl)CH_2Cl)_2$

EXPERIMENTAL

Synthesis of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylethylphosphinic Acid. In a four-necked flask with mechanical stirrer, reflux condenser, dropping funnel, thermometer, and CO_2 inlet tube, 20 g (0.21 mole) of epichlorohydrin was placed, and 2 drops of $TiCl_4$ was added. In a stream of CO_2, 13.1 g (0.1 mole) of ethyldichlorophosphine was added dropwise. Since the reaction takes place with heat evolution, the flask was cooled periodically in a water bath. The rate of dropping and the cooling were regulated to maintain the temperature in the flask at 50-55°C. At the end of the reaction, the mixture was stirred at room temperature for 4 hours. The product was vacuum distilled from an Arbuzov flask. At a bath temperature ~ 150°C isomerization was observed, accompanied by violent foaming of the material in the flask. Recovered 17 g (54% theor.) of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylethylphosphinic acid, with b.p. 149-151°C (0.05 mm); n_D^{20} 1.5055; d_4^{20} 1.3768. Found: P 9.57; 9.96; Cl 44.61; 44.47%: MR 68.13. $C_8H_{15}O_2PCl_4$. Calculated: P 9.8; Cl 44.88%; MR 68.34;

In the subsequent descriptions, all reactions between epichlorohydrin and phosphorus acid chlorides were carried out in the apparatus described above.

Synthesis of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylethylphosphinic Acid. [Counter-Synthesis] Synthesis of the ester by interaction of ethyldichlorophosphine with the α,γ-dichlorohydrin of glycerin [1,3-dichloroisopropanol] was carried out in the apparatus described above. The flask was charged with 13.1 g of ethyldichlorophosphine and 200 ml of dry ether. By means of the dropping funnel, in a CO_2 stream there was added a solution of 25.8 g of α,γ-dichlorohydrin of glycerin and 20.3 g of triethylamine in 100 ml of dry ether. The reaction mixture was cooled with snow–salt mixture. Stirring of the reaction products was continued 2 hours at room temperature. The precipitated triethylamine hydrochloride was filtered off, and the residue after removing the ether was vacuum distilled from an Arbuzov flask. At a bath temperature ~ 150°C, rearrangement took place (violent foaming of liquid). Recovered 15.4 g (49%) of a substance with b.p. 150–152° (0.05 mm); n_D^{20} 1.5057; d_4^{20} 1.3763. Found: P 9.62; 9.91; Cl 44.58; 44.69% MR 68.29. $C_8H_{15}O_2PCl_4$. Calculated: P 9.8; Cl 44.88%; MR 68.34.

Synthesis of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylphenylphosphinic Acid. Phenyldichlorophosphine 19 g and epichlorohydrin 21 g were taken for reaction. The product was vacuum distilled from an Arbuzov flask. During distillation, isomerization took place at a bath temperature ~ 160°C. Obtained 35 g (88% theor.) of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphenylphosphinic acid, with b. p. 179–181° (0.02 mm); n_D^{20} 1.5528. Found: P 8.8; 9.0; Cl 39.13; 39.25; C 40.4; 40.2; H 4.3; 4.2%. $C_{12}H_{15}O_2PCl_4$. Calculated: P 8.51; Cl 38.96; C 39.58; H 4.16%.

Interaction of Epichlorohydrin with Phosphorus Trichloride in 1 : 1 Ratio. Phosphorus trichloride 20 g and epichlorohydrin 13.5 g were taken for reaction. The reaction products were vacuum distilled from an Arbuzov flask. Obtained: 1) Dichloride of β,β'-dichloroisopropylphosphorous acid [β,β'-dichloroisopropoxydichlorophosphine], with b.p. 49-51° (1 mm); 9.5 g (28% theor.); n_D^{20} 1.5222; d_4^{20} 1.5296. Found: P 13.75; 13.39; Cl 61.27; 61.20%; MR 45.83. $C_3H_5OPCl_4$. Calculated: P 13.47; Cl 61.69%; MR 45.37. 2) chloride of bis (β,β'-dichloroisopropylphosphorous acid [bis (β,β'-dichloroisopropoxy) chlorophosphine], with b.p. 122-124° (1 mm); 12.2 g (26% theor.) n_D^{20} 1.5183; d_4^{20} 1.4905. Found: P 9.19; 9.60; Cl 55.01; 55.4%; MR 65.58. $C_6H_{10}O_2PCl_5$. Calculated: P 9.6; Cl 54.98%; MR 65.72. 3) bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid, with b.p. 170-172° (0.02 mm); 2.8 g (4.7% theor.); n_D^{20} 1.5148; d_4^{20} 1.4823. Found: P 7.28; 7.95; Cl 51.12; 51.38%; MR 84.38. $C_9H_{15}O_3PCl_6$. Calculated: P 7.46; Cl 51.27%; MR 83.89.

Interaction of Phosphorus Trichloride with Epichlorohydrin in 1 : 3 Ratio. Epichlorohydrin 70 g and phosphorus trichloride 35 g were taken for the synthesis. The reaction was conducted at 35-40°C. During distillation of the reaction products, isomerization occurred at a bath temperature ~ 160°C. Obtained 50 g (47.5 % theor.) of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid, with b.p. 170–172° (0.02 mm): n_D^{20} 1.5147; d_4^{20} 1.4820.

Synthesis of Chloride of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylphosphonic Acid. In a four-necked round-bottom flask with mechanical stirrer, reflux condenser, and thermometer, 20 g of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid was heated to 140°C. At this temperature, 20.5 g of phosphorus pentachloride was introduced in small portions. Then the reaction mixture was stirred 6 hours at a bath temperature of 150-155°C. The phosphorus oxychloride was distilled off, and the residue was vacuum fractionated from an Arbuzov flask in a stream of dry CO_2. After two distillations, there was obtained 6.5 g (43% theor.) of the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid, with b.p. 188–190°C. (8 mm); n_D^{20} 1.5168. Found: P 9.27; 9.42; Cl 55.44; 55.80%. $C_6H_{10}O_2PCl_5$. Calculated: P 9.6; Cl 54.98%.

Interaction of Bis (β,β'-Dichloroisopropyl) Ester of β,γ-Dichloropropylphosphonic Acid with Phosphorus Pentachloride, under Pressure. A mixture of 12.7 g of the bis (β,β'-dichloroisopropoyl) ester of β,γ-dichloropropylphosphonic acid and 13 g of phosphorus pentachloride was heated in a sealed tube at 145-150°C for 2 hours. After cooling, the contents of the tube was vacuum distilled. Obtained two fractions: 1) 30-68°C (8 mm) 6.7 g; 2) 185-188°C (8 mm) 7.2 g. On redistillation of the second fraction, obtained 5.4 g of a substance with b.p. 188-190°C (8 mm); n_D^{20} 1.5166. Found: P 9.19; 9.31; Cl 55.38; 55.72%. Based on the constants and the elemental analysis, the product obtained was the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid; yield 55% of theoretical.

Interaction of Chloride of β,β'-Dichloroisopropyl Ester of β,γ-Dichloropropylphosphonic Acid with Phosphorus Pentachloride, under Pressure. A mixture of 6.5 g of the chloride of the β,β'-dichloroisopropyl ester of β,γ-dichloropropylphosphonic acid and 4.5 g of phosphorus pentachloride was heated in a sealed tube for 8 hours at 165-170°c. The resulting transparent liquid was distilled from an Arbuzov flask. The reaction products were not successfully identified.

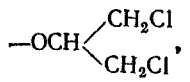
Dehydrochlorination of Bis (β,β'-Dichloroisopropyl) Ester of β,γ-Dichloropropylphosphonic Acid. A three-necked flask, fitted with a mechanical stirrer, reflux condenser, and thermometer, was charged with 18.5 g of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid, 9 g of triethylamine, and 40 ml of dry benzene. The reaction mixture was stirred with heating 3 hours at 30°C, 2 hours at 60°C, and 3 hours at 80°C, and was allowed to stand overnight. After filtering off the precipitate and removing the solvent by evaporating under vacuum, the filtrate was vacuum distilled from an Arbuzov flask. Recovered 2.8 g (47% theor.) of a substance with b.p. 168-170°C (1 mm); n_D^{20} 1.5102. Found: P 7.83; 7.68; Cl 46.55; 46.83%. Based on the elemental analysis, the substance corresponds to the formula $C_9H_{14}O_3PCl_3$, for which the calculated values are P 8.8, Cl 46.84%.

The authors express thanks to R. Shagidullin for taking the infrared absorption spectra of a number of the substances.

SUMMARY

1. Phosphorus acid chlorides react with epichlorohydrin according to the scheme proposed by Kabachnik and Rossiiskaya for the interaction of phosphorus trichloride with ethylene oxide.

2. It was established by a counter-synthesis method and by spectrum analysis that in the products of the addition of epichlorohydrin to phosphorus acid chlorides the ester groups have the iso-structure:



and not the linear structure $-OCH_2CHClCH_2Cl$.

3. At a bath temperature ~160°, tris (β,β'-dichloroisopropyl) phosphite undergoes the Arbuzov rearrangement, with the formation of the bis (β,β'-dichloroisopropyl) ester of β,γ-dichloropropylphosphonic acid.

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