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Abstract

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ON ESTERS OF ETHYL-β-CHLOROVINYLPHOSPHINIC ACID

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Recently we reported the synthesis and certain properties of derivatives of ethylvinylphosphinic acid ([1]). In particular, it was noted that the acid chloride of ethylvinylphosphinic acid adds bromine, which qualitatively proves the unsaturation of the vinyl group. However, upon proceeding to quantitative measurement, we encountered the fact that the weight gain of the product from the interaction of the acid chloride of ethylvinylphosphinic acid with an equimolecular amount of bromine was approximately one half of that calculated. The main fraction isolated by slow distillation of the product in vacuo, according to the molecular refraction found, corresponded closely to that calculated for the acid chloride of ethyl-β-bromovinylphosphinic acid. The ethyl ester, obtained by treating the product with ethanol in absolute ether in the presence of pyridine, also corresponded, by analyses and molecular refraction, to the ethyl ester of ethyl-β-bromovinylphosphinic acid.

We believe that as a result of bromination the acid chloride of ethyl-α,β-dibromoethylphosphinic acid is formed; however, the latter is a product of low stability and, already upon removal of the light fractions under vacuum at 50°, eliminates hydrogen bromide with formation of the acid chloride of ethyl-β-bromovinylphosphinic acid.

$$C_2H_5P(=O)(Cl)(CH{=}CH_2) + Br_2 \rightarrow C_2H_5P(=O)(Cl)(CHBrCH_2Br) \xrightarrow{-HBr}$$

$$\longrightarrow \underset{(I)}{C_2H_5P(=O)(Cl)(CH{=}CHBr)} \quad \text{or} \quad \underset{(II)}{C_2H_5P(=O)(Cl)(CBr{=}CH_2)}$$

Although we leave open the question of choosing one or the other structure, we give preference to the first variant, with the halogen atom located at the β-carbon atom, since both steric and thermodynamic factors in this case should determine greater stability of the molecule. The chlorination reaction of the acid chloride of ethylvinylphosphinic acid was studied more thoroughly. Contrary to what has been said above, the chlorination product, the acid chloride of ethyl-α,β-dichloroethylphosphinic acid, proved to be a stable product and distilled in vacuo without any signs of decomposition. Nevertheless, the tendency

toward elimination of hydrogen chloride is still expressed in the high, almost quantitative yield of the acid chloride of ethyl-β-chlorovinylphosphinic acid in the reaction of catalytic dehydrochlorination of the acid chloride of ethyl-α,β-dichloroethylphosphinic acid over a mixture of calcined barium carbonate and activated charcoal at 330–350°.

Esters of ethyl-β-chlorovinylphosphinic acid were synthesized by the generally accepted method, i.e., by interaction of the acid chloride with the corresponding alcohols in absolute ether, in the presence of an organic base (pyridine). All of them are colorless, readily mobile liquids, possessing a very faint odor and not miscible (with the exception of the methyl and ethyl esters) with water.

Subsequent chlorination of ethyl-β-chlorovinylphosphinic acid chloride, as was to be expected ([2]), is difficult. Thus, after 3-hour chlorination of 39 g of the latter, the greater part of the starting product was recovered from the reaction mixture, and ethyl-α,β,β-trichloroethylphosphinic acid chloride was isolated in only 22% yield. The constants of all the products obtained are given in Table 1.

A communication concerning certain derivatives of β-chlorovinylphosphinic acid ([3]) contains no data on their polymerization. At the same time, it seemed of interest to study the tendency toward polymerization of the vinyl group containing, on the one hand, an organophosphorus

Table 1

Products	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	P, %, found	P, %, calc.	Halogen, %, found	Halogen, %, calc.	Yield, %
$C_2H_5P(O)(C_6H_4Br)Cl$	108–110/10	1,5265	1,6478	40,60	41,30	–	–	–	–	–
$C_2H_5P(O)(OC_2H_5)(C_6H_4Br)$	97,5–98/10	1,4840	1,3750	46,95	47,31	13,45	13,62	34,91	35,20	40
$C_2H_5P(O)(C_6H_4Cl)Cl$	132–133/10	1,5100	1,4240	43,85	43,74	14,65	14,76	50,98	50,80	82
$C_2H_5P(O)(OC_2H_5)(C_6H_4Cl)$	105–107/3	1,4745	1,2410	49,39	49,31	–	–	32,00	32,50	30
$C_2H_5P(O)(CH_2Cl)Cl$	92–94/10	1,4965	1,5080	38,48	38,41	17,70	17,88	40,68	41,00	85
$C_2H_5P(O)(CHCl_2)Cl$	135–140/10	1,5220	1,5160	48,91	48,61	12,60	12,70	57,60	58,20	22
$C_2H_5P(O)(OC_2H_5)(CH_2Cl)$	82–86/12	1,4550	1,1870	39,43	–	–	–	21,38	21,00	51

Products	B.p., °C/mm	n_D^{20}	d_4^{20}	MR_D, found	MR_D, calc.	P, %, found	P, %, calc.	Halogen, %, found	Halogen, %, calc.	Yield, %
$C_2H_5P(O)(OC_2H_5)CH{=}CHCl$	85–89/10	1,4625	1,1260	44,65	44,05	—	—	19,86	19,42	63
$C_2H_5P(O)(OC_3H_7\text{-}n)CH{=}CHCl$	106–112/12	1,4610	1,1084	48,45	48,67	—	—	18,15	18,00	44
$C_2H_5P(O)(OC_3H_7\text{-}i)CH{=}CHCl$	93–94/3	1,4575	1,1050	48,03	48,20	—	—	17,80	18,20	73
$C_2H_5P(O)(OC_4H_9\text{-}n)CH{=}CHCl$	112–115/11	1,4610	1,0760	56,60	53,29	—	—	16,42	16,80	55
$C_2H_5P(O)(OC_4H_9\text{-}i)CH{=}CHCl$	108–106/12	1,4590	1,0870	52,95	53,29	—	—	17,00	16,80	41
$C_2H_5P(O)(OC_6H_5)CH{=}CHCl$	122–132/3	1,5305	1,1900	59,41	58,92	—	—	15,60	15,30	38
$C_2H_5P(O)(OC_6H_5)CH{=}CHBr$	114–115/3	1,5240	1,4110	58,88	54,06	15,54	15,74	—	—	35

radical and, on the other hand, a halogen atom, in particular chlorine, and to compare these data with the results obtained in the polymerization of ethylvinylphosphinic acid esters. Among the saturated esters, the methyl, ethyl, and butyl esters of ethyl-β-chlorovinyl- and the ethyl ester of ethyl-β-bromovinylphosphinic acids were studied. Polymerization was carried out in sealed ampoules in the presence of 2% amounts of benzoyl peroxide at a temperature of 100–150°.

However, after prolonged heating (for 10 days), no appreciable change in the viscosity of the products was observed, whereas esters of ethylvinylphosphinic acid, as already reported earlier, under these conditions polymerized into viscous syrupy masses and even lost their property of flow (at room temperature). On the basis of what has been said, it may be assumed that peroxide polymerization of saturated esters of vinylphosphinic acid with introduction of a halogen into the β-position is hindered. We are partly inclined to see the reason for this in additional shielding of the double bond by the halogen atom.

A different picture was expected and, in fact, obtained in the polymerization of allyl esters of ethylvinyl- and ethyl-β-chlorovinylphosphinic acids. Studies by Toy and Cooper ([4]), as well as by one of the authors jointly with Kukhtin ([5]), showed that the rate of polymerization of allyl esters of phosphorus acids increases with the introduction of electronegative groups. In accordance with

this, in studying the polymerization of the allyl esters indicated by us, using as initiator 2% amounts of benzoyl peroxide, dinitrile of 2-azo-bis-isobutyric acid (porophor), and diazoaminobenzene, in the first two cases a sharp increase in the polymerization rate of the allyl ester of ethyl-β-chloroethylphosphinic acid was observed. Whereas the former, already within 30 min at 40°, polymerized into a wax-like mass, the allyl ester of ethylvinylphosphinic acid, after 4 hours of heating at 40°, retained its original consistency, and only with an increase in temperature to 80° after 1 hour formed a wax-like mass. A contradictory result was obtained in the case of initiation with diazoaminobenzene. The contents of the ampoule with the allyl ester of ethylvinylphosphinic acid, after 10 hours of heating (4 hours at 40° and 6 hours at 80°), lost the property of flow, whereas the allyl ester of ethyl-β-chlorovinylphosphinic acid only slightly increased its viscosity. This circumstance requires additional investigation.

Experimental Part

Acid chloride of ethyl-α,β-dichloroethylphosphinic acid (I). Chlorine was passed into the acid chloride of ethylvinylphosphinic acid (80 g), cooled to −10°, with vigorous stirring, at a rate allowing the temperature of the reaction mass to be maintained within the range up to +5°. The end of the reaction was determined by the cessation of the rise in temperature upon removal of cooling. The gain in weight of the contents of the flask was 50 g. The crude product was poured into an Arbuzov flask, freed from excess chlorine by suction, and distilled in vacuo. 100 g of substance (I) was obtained.

Acid chloride of ethyl-β-chlorovinylphosphinic acid (II). 75 g of substance (I) was passed through a quartz tube filled with a layer of barium carbonate and then a layer of activated charcoal. The temperature in the tube furnace was maintained within 330–350°. As a result, after distillation on a 25-cm herringbone dephlegmator, 50 g of substance (II) was isolated.

Allyl ester of ethyl-β-chlorovinylphosphinic acid (III). A mixture of 400 ml of absolute ether, 11 g of allyl alcohol, and 14 g of pyridine was cooled to −10°. With vigorous stirring

31 g of (II) was added dropwise from a dropping funnel. After the addition was complete, the mixture was heated to the boiling point of the ether and kept at this temperature for 2 hours, after which it was again cooled and filtered from pyridine hydrochloride. However, during distillation traces of pyridine hydrochloride were detected; therefore, after the first distillation the product was treated with an equal volume of cold 5% soda solution and then with an equal volume of distilled water. The lower layer on distillation gave 20 g of (III).

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