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Abstract

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ON THE MECHANISM AND COURSE OF THE ADDITION OF PHOSPHORUS TRICHLORIDE AND OTHER ACID CHLORIDES OF PHOSPHORUS ACIDS TO PROPYLENE OXIDE

The question of the mechanism of the reactions of phosphorus trichloride and of the acid chlorides of incomplete esters of phosphorus acids with α-oxides has, until recently, not been discussed in the literature. In studying the reactions of epichlorohydrin (1) and divinyl oxide (2) with the acid chlorides of dialkylphosphorous acids, we expressed the opinion that these reactions proceed with preliminary opening of the oxide ring by hydrogen chloride.

In the present study, using as examples the reaction of propylene oxide with phosphorus trichloride and with the acid chloride of dibutylphosphorous acid, we obtained new evidence confirming the proposed mechanism. It has been shown that these reactions proceed readily when the reagents, previously distilled, are mixed without special precautions for protection from atmospheric moisture. However, when a small amount of triethylamine is added to the reaction mixtures, these reactions do not occur. If thoroughly dried propylene oxide is added to the acid chloride of dibutylphosphorous acid distilled in vacuo in an atmosphere protected from moisture, no interaction between them is likewise observed.

Introduction into the reaction vessel of atmospheric air containing moisture, or addition to the reaction mixture of one or two drops of water, causes a vigorous reaction. The experiments carried out, together with those described earlier, make it possible to conclude that the first stage of the reactions under consideration is partial hydrolysis of the acid chlorides and interaction of the hydrogen chloride thereby formed with the α-oxide.

The oxonium ion formed upon addition of a proton to the oxide then, or directly, reacts with the chloride anion with formation of propylene glycol chlorohydrin, which subsequently reacts with the acid chloride; or, possibly, simultaneously with the chloride anion, molecules of the acid chloride also become involved in the reaction process.

With replacement of chlorine atoms by alkoxy groups, the basicity of the phosphorus atom decreases, which facilitates the reaction of the acid chloride with the oxide. As a result, a mixed ester of phosphorous acid is formed and hydrogen chloride is regenerated.

In both cases the course of opening of the oxide ring should be determined by the site of attack of the oxide ring by the chloride anion. As is known (3), upon interaction of hydrogen chloride with propylene oxide in an ethereal solution under cooling, the principal product formed is propylene glycol chlorohydrin with a secondary-alcohol group; the chlorohydrin with a primary-alcohol group is contained in the addition products only in a small amount ($\sim 10\%$). Thus, under the indicated conditions, opening of the oxide ring in propylene oxide under the action of hydrogen chloride occurs almost exclusively at the side of the primary carbon atom.

In accordance with our ideas on the mechanism of the reactions of oxides with acid chlorides of phosphorus acids, in their reactions with propylene oxide there should be formed mainly or exclusively mixed ···

esters of phosphorous acid containing chloropropyl radicals.

The literature contains contradictory data on the mode of addition of acid chlorides of phosphorus acids to propylene oxide. In the work of A. K. Efimova (^{4}), without any experimental evidence, it is assumed that rupture of the oxide ring under the action of phosphorus trichloride on propylene oxide occurs at the primary carbon atom. N. I. Shuikin and I. F. Bel' skii (^{5}), on the contrary, believe that rupture of the oxide ring in this reaction occurs at the secondary carbon atom; according to their data, the resulting esters of phosphorous acid contain unbranched β-chloropropyl radicals. In light of the available data, we considered it interesting and necessary to return to the study of this reaction and of the structure of the products formed.

The reactions of propylene oxide with phosphorus trichloride were carried out in ether solution and with cooling, at reagent ratios of 1 : 1, 2 : 1, and 3 : 1. In this way, in good yields, there were obtained, respectively, the dichloroanhydride of β-chloroisopropylphosphorous acid (I), the monochloroanhydride of β-chloroisopropylphosphorous acid (II), and tri-β-chloroisopropyl phosphite (III). The characteristics of these substances and of the compounds obtained from them are given in Table 1.

To determine the structure of the radicals entering into the products I—III obtained, the full phosphite was washed with water in the presence of a small amount of hydrochloric acid to give propylene glycol chlorohydrin. Both isomeric propylene glycol chlorohydrins of interest to us were synthesized by the methods described in the literature (^{3}, ^{6}) and had the following constants: 1-chloropropan-2-ol—b.p. 51° at 30 mm, d_4^{20} 1.1001, n_D^{20} 1.4358; 2-chloropropan-1-ol—b.p. 52° at 29 mm; d_4^{20} 1.0902; n_D^{20} 1.4363.

Fig. 1. IR transmission spectrum of propylene glycol chlorohydrin obtained by washing the full phosphite (III)

As can be seen from comparison of the constants, in view of their slight difference for the isomeric propylene glycol chlorohydrins, it is not possible to draw a definite conclusion about the structure of the chlorohydrin under investigation. However, this proved possible upon study of the infrared spectra of the chlorohydrin, investigation of the products of its oxidation, and a number of other data.

Stewart and co-workers (^{3}), in studying the IR absorption spectra of isomeric propylene glycol halohydrins, found that in the spectra of primary alcohols there is a characteristic absorption band at 980 cm^{-1}, whereas in the spectra of secondary alcohols there is a band at about 935 cm^{-1}.

As can be seen from Fig. 1, the spectrum of the chlorohydrin* obtained by washing the full phosphite (III) contains an intense absorption band at 941 cm^{-1}, also present in the prepared sample of 1-chloropropan-2-ol. The absorption at 984 cm^{-1}, characteristic of the primary alcohol 2-chloropropan-1-ol, is absent from it.

* The IR spectrum was recorded on a Hilger instrument.

IR spectra make it possible to conclude that a secondary alcohol group is present in the propylene glycol chlorohydrin under investigation. Chemical studies also lead to the same conclusion.

On oxidation with nitric acid of the chlorohydrin obtained by saponification of the phosphite, chloroacetic and acetic acids were isolated. The former, evidently, could have been formed only from the secondary alcohol 1-chloropropan-2-ol. No α-chloropropionic acid was found in the oxidation products. A reverse synthesis was carried out of dibutyl chloropropyl ester of phosphorous acid from dibutylphosphorous acid chloride anhydride and 1-chloropropan-2-ol (b.p. 86-88°/1.5 mm, n_D^{20} 1.4433; d_4^{20} 1.0198).

Table 1

Physical constants and analytical data of the synthesized compounds

No.	Formula of compound	Yield, %	b.p., °C/mm	d_4^{20}	n_D^{20}	P, % found	P, % calc.
I	$CH_3CHO(CH_2Cl)_2PCl_2$	60	65/13	1.3801	1.5060	15.95	15.84

No.	Formula of compound	Yield, %	b.p., °C/mm	d_4^{20}	n_D^{20}	P, % found	P, % calc.
II	$[CH_3CHO(CH_2Cl)]_2PCl$	45	88–89/2	1.2763	1.4820	12.03	12.22
III	$[CH_3CHO(CH_2Cl)]_3P$	85	98–99/0.03	1.2285	1.4710	9.22	9.94
IV	$[CH_3CHO(CH_2Cl)]_2P(S)Cl$	44	131–132/3	1.3424	1.5012	10.46	10.85
V	$[CH_3CHO(CH_2Cl)]_3P(S)$	74	117–119/0.04	1.2832	1.4885	9.08	9.01
VI	$CH_3CHO(CH_2Cl)P(OC_2H_5)_2$	60	84–85/10	1.0761	1.4355	14.43	14.43
VII	$CH_3CHO(CH_2Cl)P(O\text{-iso-}C_3H_7)_2$	40	97–98/10	1.0310	1.4310	11.71	12.35
VIII	$CH_3CHO(CH_2Cl)P(OC_3H_7)_2$	40	108–110/10	1.0353	1.4380	12.51	12.35
IX	$CH_3CHO(CH_2Cl)P(S)(OC_2H_5)_2$	50	73–75/0.04	1.1504	1.4613	12.78	12.57
X	$[CH_3CHO(CH_2Cl)]_2POC_2H_5$	20	118–119/10	1.1547	1.4520	11.63	11.77
XI	$CH_3CHO(CH_2Cl)P(OC_4H_9)_2$	41	87–88/1.5	1.0201	1.4430	11.22	11.44
XII	$\left.\begin{matrix}CH_3CHO\\CH_3CHO\end{matrix}\right\rangle POCH(CH_2Cl)CH_3$	93	78–80/3	1.1527	1.4546	14.76	14.57
XIII	$[CH_3CHO(CH_2Cl)]_2P(O)CH_2CHClCH_3$	65	145–146/3	1.2607	1.4700	9.51	9.94
XIV	$[CH_3CHO(CH_2Cl)]_2P(O)CH{=}CHCH_3$	75	134–135/2	1.2109	1.4698	11.42	11.27
XV	$(C_2H_5O)_2P(O)CH_2CHClCH_3$	55	77–78/1	1.1266	1.4400	14.44	14.43
XVI	$(C_2H_5O)_2P(O)CH{=}CHCH_3$	30	93–95/8	1.0532	1.4370	17.72	17.91
XVII	$CH_3CHO(CH_2Cl)P(O)(OC_2H_5)CH_2CHClCH_3$	60	113–114/1	1.1954	1.4550	11.65	11.77
XVIII	$(C_4H_9O)_2P(O)CH_2CHClCH_3$	75	122/2	1.0500	1.4425	11.87	11.44
XIX	$\left.\begin{matrix}CH_3CHO\\CH_3CHO\end{matrix}\right\rangle P(O)CH_2CHClCH_3$	80	131–134/0.5	1.2105	1.4616	14.69	14.62
XX	$\left.\begin{matrix}CH_3CHO\\CH_3CHO\end{matrix}\right\rangle P(O)CH{=}CHCH_3$	47	119–120/1	1.1402	1.4620	17.36	17.59

Its constants proved to be identical with those for the ester obtained as a result of the reaction of butyl alcohol with the dichloroanhydride of chloropropylphosphorous acid, obtained by addition of one molecule of phosphorus trichloride to propylene oxide (87-88° at 1.5 mm; n_D^{20} 1.4430; d_4^{20} 1.0201).

The proposed structure for the chlorohydrides and the complete phosphite obtained by addition to propylene oxide of phosphorus trichloride and other chloroanhydrides is also confirmed by studies of the structure of some products formed as a result of their chemical transformations. These reactions are also of independent interest. As compounds containing trivalent phosphorus, chlorohydrides I, II and complete phosphite III add sulfur. From II was obtained monochloroanhydride of di-(β-chloroisopropyl)-thiophosphorous acid (IV), and from III—tri-(β-chloroisopropyl)-thiophosphate (V) (Table 1).

On interaction of the chlorohydrides with alcohols in ether solution in the cold in the presence of a base, mixed esters of phosphorous acid are formed. From I were obtained the diethyl (VI), diisopropyl (VII), di-*n*-propyl (VIII) and di-*n*-butyl (XI) esters of phosphorous acid, and from II—ethyl di-(β-chloroisopropyl) phosphite (X). As a result of sulfur addition to VI, β-chloroisopropyl diethyl ester of thiophosphorous acid (IX) is formed. As a result of the reaction of the chloroanhydride of 2,3-butylene glycol phosphorous acid with propylene oxide was obtained

2,3-butyleneglycol β-chloroisopropyl ester of phosphorous acid (XII) was obtained.

Thermal isomerization of β-chloroalkyl esters of phosphorous acids into phosphinic esters is accompanied, as is known, by isomerization of the chloroalkyl radical participating in the transformation.

From esters III, VI, X, XI, and XII, upon heating them to 170-200°, the corresponding esters of β-chloro-*n*-propylphosphinic acid XIII, XV, XVII, XVIII, and XIX were obtained. As a result of dehydrochlorination of XIII, XV, and XIX, carried out by heating with triethylamine in benzene solution, esters of unsaturated phosphinic acids XIV, XVI, and XX were obtained. In the IR spectrum of XX there is an absorption band at 3010 cm^{-1}, characteristic of stretching vibrations of the =CH group, and absorption is absent in the region 3095-3075 cm^{-1}, characteristic of the $=CH_2$ group. On the other hand, in the 2,3-butyleneglycol ester of vinylphosphinic acid synthesized by us, both absorption bands are present. These results show that XX is the 2,3-butyleneglycol ester of propenylphosphinic acid and, consequently, the initial phosphorous acid ester contains a chloroisopropyl radical.

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