INVESTIGATIONS IN THE FIELD OF DIOLS AND CYCLIC ETHERS. II

The Reaction of Butane-1,3-Diol Cyclic Sulphate with Hydrogen Chloride

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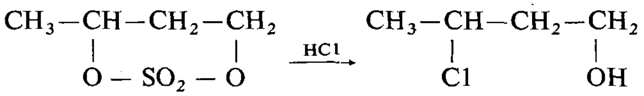
The authors report their investigations on the study of chemical transformations in butane-1,3-diol cyclic sulphate subjected to the effect of hydrogen chloride. As a result of the reaction, 3-chloro-butanol-1 (II), and 4-chloro-butanol-2 (III) were formed.

In a previous communication we have dealt [1] with a chemical transformation of butane-1,3-diol, taking place on effect of acetyl chloride. In accordance with SEARLES and his coworkers' statements [2], on applying the method of gas-liquid chromatography we pointed out that the reactions result in formation of two isomeric chloroacetates. All the results and statements concerning the similar transformations of 2-methyl-oxetane made it necessary to carry out the investigations described in the present paper.

LICHTENBERGER and his coworkers [3—7] have far reachingly dealt with the synthesis and chemical changes of cyclic sulphates. In the course of their work they examined the cleavage of cyclic sulphates of 1,3-diols by hydrogen halide acids. They have stated that as a result of the change, 1,3-halohydrins are formed [3—6]. According to their investigations, starting from butane-1,3-diol, 3-chloro-butanol-1 was formed:

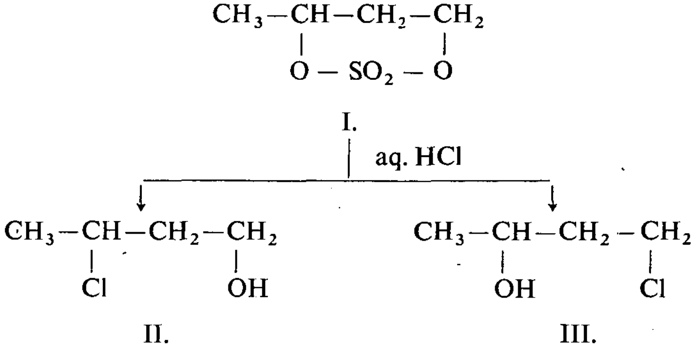


$$\begin{array}{c}\mathrm{CH_3-CH-CH_2-CH_2}\\ \quad|\qquad\qquad\quad|\\ \mathrm{O-SO_2-O}\end{array} \xrightarrow{\mathrm{HCl}} \begin{array}{c}\mathrm{CH_3-CH-CH_2-CH_2}\\ \qquad|\qquad\qquad\quad|\\ \qquad\mathrm{Cl}\qquad\qquad\mathrm{OH}\end{array}$$

I. II.

The reaction was carried out in a sealed tube, on effect of heating in a water-bath. The yield is 50%. The physical constants of the formed chlorohydrin agree with the data published by VERHULST [8]. It is fairly probable that the chlorohydrin synthesized by VERHULST is the mixture of two isomers.

In the course of the study chemical changes of diols relying upon data from literature and on our own observations, it appeared necessary to begin the study of cleavage reactions of butane-1,3-diol cyclic sulphate. The present paper deals with the transformation effected by hydrogen chloride. The gas-liquid chromatography was used in these investigations. Varying the experimental conditions it can be stated that by the reaction of a cyclic sulphate and hydrogen chloride, a pure chlorohydrin isomer cannot be formed, but only the mixture of two isomers (II + III).



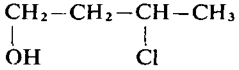
$$\underset{\mathrm{O}-\mathrm{SO_2}-}{\mathrm{CH_3-CH}}-\underset{\mathrm{O}}{\mathrm{CH_2-CH_2}} \xrightarrow{\text{aq. HCl}} \mathrm{CH_3-\underset{Cl}{CH}-CH_2-\underset{OH}{CH_2}} + \mathrm{CH_3-\underset{OH}{CH}-CH_2-\underset{Cl}{CH_2}}$$

The reaction was carried out with aqueous hydrochloric acid solution by boiling in water-bath. Heating under atmospheric pressure, 14% of (II) and 86% of (III) formed. Under similar conditions but carrying out the procedure in a saleed tube, the yield is ~80% of (II) and ~20% of (III).

In order to evaluate the chromatograms, (II) and (III) were prepared. The synthesis of (II) was done by the reduction of *β*-chlorobutyraldehyde with $LiAlH_4$, and that of (III) by SONDHEIMER and WOODWARD's method [9]. Tables I and II give physical constants of (II) and (III) found in the literature.

Table I

Physical Constans of



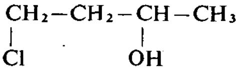
$$\mathrm{\underset{OH}{CH_2}-CH_2-\underset{Cl}{CH}-CH_3}$$

	Boiling Point °C	(Hg mm)	Density gr/cm³	$n_D^{t°C}$	R_{M_D} found	calcd.	Ref.
1.	67–8	(15)	$6{,}0622^{20}_{4}$	$1{,}4446^{20}$	—	—	8[a]
2.	71	(17)	$6{,}0650^{17}_{4}$	$1{,}44436^{15}$	27,40	27,06	3[b]
3.	75–6	(23)	$1{,}0671^{20}_{4}$	$1{,}4441^{20}$	27,04	27,06	10[b]
4.	66–8	(15)	—	$1{,}4396^{27}$	—	—	11[b]
5.	83,6–85	(32)	$1{,}0626^{20}_{4}$	$1{,}4420^{20}$	27,03	27,06	12
6.	74	(16)	—	$1{,}4398^{25}$	—	—	2
7.	—	—	$1{,}06218^{20}_{4}$	$1{,}44464^{20}$	—	—	17

a — likely mixture of (II) and (III)
b — certain mixture of (II) and (III)

Table II

Physical Constans of



$$\mathrm{\underset{Cl}{CH_2}-CH_2-\underset{OH}{CH}-CH_3}$$

	Boiling point °C	(Hg mm)	Density gr/cm³	$n_D^{t°C}$	R_{M_D} found	calcd.	Ref.
1.	67	(20)	—	$1{,}4408^{20}$	—	—	9
2.	63,7–64	(15)	1,0686	$1{,}4430^{20}$	26,93	27,06	12
3.	61	(10)	—	$1{,}4440^{20}$	—	—	2

Results of measurements[1]

Fig 1 shows the chromatogram of 3-chloro-butanol-1 (II), Fig 2 that of 4-chloro-butanol-2 (III) and Fig. 3 represents the chromatogram of the mixture of the two compounds.

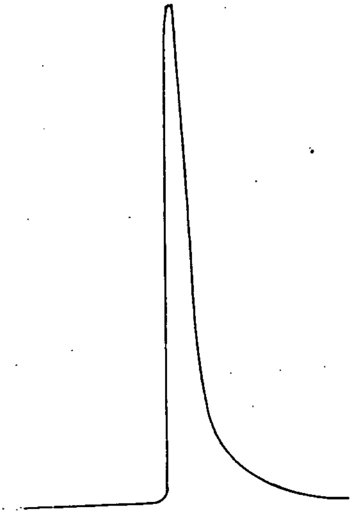


Fig. 1

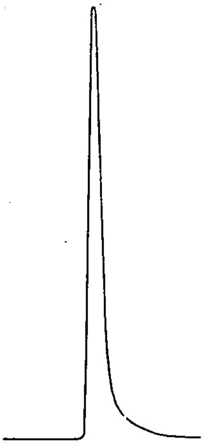


Fig. 2

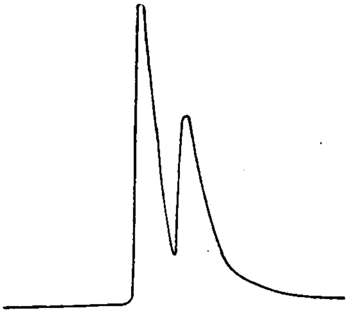


Fig. 3

It can be seen that the time of rupture of (III) is shorter than that of (II), and a relatively good separation can be attained even on applying a short column.

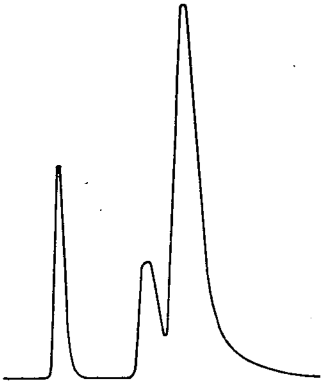


Fig. 4

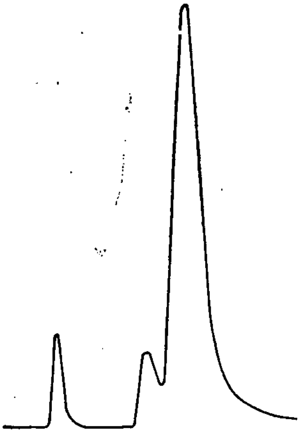


Fig. 5

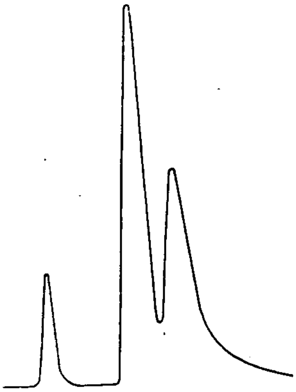


Fig. 6

[1] To the quantitative comparison of the curves, the measures of Figs. 1, 3, 4, 5, 6, 10 should be multiplied by 2, and those of Figs. 2, 7, 8, 9, 10, 11, 12 by 3.

Fig. 4 shows the chromatogram of the reaction product (IV), of the cyclic sulphate and hydrogen chloride, performing the reaction in a sealed tube. Fig. 5 represents the chromatogram of mixtures of the latter with (II), while Fig. 6 these with (III).

During the tranformation a substance with lower b. p. was also formed in a relatively great amount. We supposed that under the conditions of the reaction, 1,3-dichlorobutane (VI) can also be formed. With the purpose of identification, 1,3-dichlorobutane was prepared from butane-1,3-diol by VOGEL's method [14], applied for the synthesis of 1,4-dichlorobutane. Fig. 7. shows the chromatogram of 1,3-dichlorobutane (VI), while that of the mixture of (IV + VI) is given in Fig. 8.

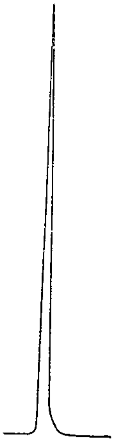


Fig. 7

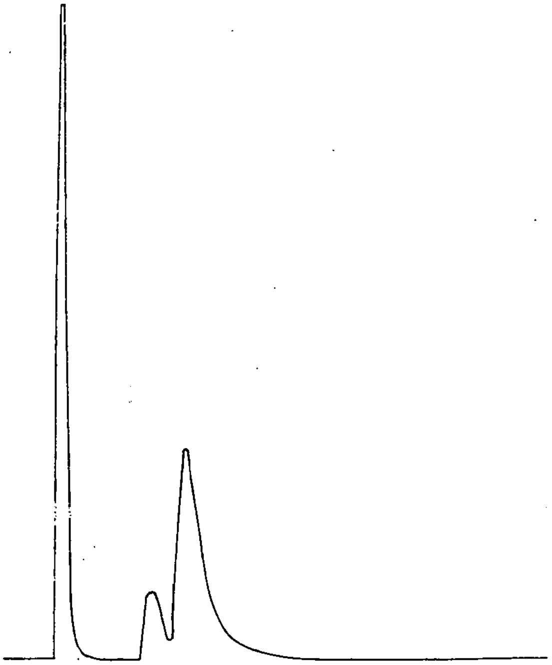


Fig. 8

From these chromatograms it can be stated that the cleavage of a cyclic sulphate by hydrogen chloride under pressure yields $\sim 80\%$ of (II) and $\sim 20\%$ of (III) (calculated for (IV)—(VI)). The transformation is accompanied by formation considerable amount of 1,3-dichlorobutane.

Fig. 9 represents the chromatogram of the product (V) of reaction between butane-1,3-diol cyclic sulphate and hydrogen chloride, under atmospheric pressure. Figure 10 contains the chromatogram of mixture of (II + V), and Fig. 11 that of (III + V).

From the evalution of the chromatograms it appears that the cleavage of butane-1,3 diol cyclic sulphate under the aforementioned conditions, besides a relatively small amount of 4-chloro-butanol-2 ($\sim 30\%$) mostly results in 3-chloro-butanol-1 ($\sim 70\%$).

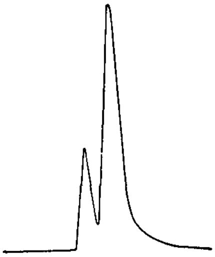


Fig. 9

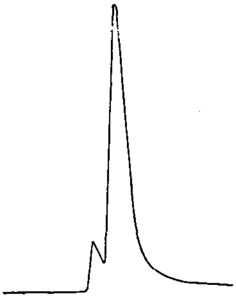


Fig. 10

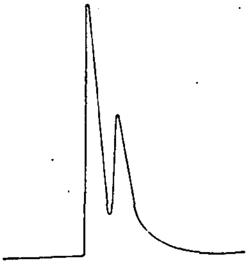


Fig. 11

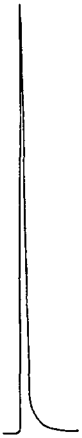


Fig. 12

In oder to estimate the relative retardations the chromatogram of *n*-butanol (VII) was also taken-up under similar conditions (Fig. 12).
Relative retardations (*r*) were calculated by the method as described by Schay [15], measuring the corresponding distances:

$$r_{\mathrm{II,\,VII}} = \frac{48}{8{,}7} = \underline{5{,}5} \qquad r_{\mathrm{III\ VII}} = \frac{37{,}5}{8{,}7} = \underline{4{,}3}$$

$$r_{\mathrm{III,\,VII}} = \frac{18{,}6}{8{,}7} = \underline{2{,}1}$$

Experimental

Butane-1,3-diol cyclic sulphate was synthesized according to the method described by J. and R. Lichtenberger (3). 90 g (1 mole) butane-1,3-diol (produced by Chemische Werke Hüls) was dissolved in 400 ml of chloroform and with cooling and stirring, 1000 g (20%) of oleum was added dropwise to the mixture during 2 hours. The temperature was maintained between 0—10°C. After pouring it on 1500 g ice and separation the aqueous layer was extracted with 3 × 300 ml chloroform. The combined organic phases were washed with water, saturated $NaHCO_3$ solution and water again. After drying over anhydrous K_2CO_3, the chloroform mixture was distilled in water-bath, condensed to 500 ml and purified three times with charcoal After distilling the whole of the chloroform, the residue cryallizes when cooling. Recrystallizing it from ethanol the m. p. is 45°C. Yield: 76 g (50%).

Less amount (20 g) of butane-1,3-diol cyclic sulphate can be distilled under vacuum heating it carefully. The loss is 20—30%. B. p.: 133—140°C (2—5 Hg mm); n_D^{20} : 1,4321.

According to our observations butane-1,3-diol cyclic sulphate cannot be distilled in large amount, because it easily decomposes by intensive gas evolution.
Reaction of butane-1,3-diol cyclic sulphate with aqueous HCl

a) 10 g cyclic sulphate was heated in a sealed tube in water bath for 40 min with 25 ml of aqueous HCl solution of 1,18 density. After cooling, 100 ml water was added and the mixture extracted with ether three times. Thereafter the mixture was washed with $NaHCO_3$, dried over anhydrous K_2CO_3 and distilled. 4 g (57%) of (IV) was yielded.
Bp.: 78—80°C (25 mm); n_D^{20}: 1,4428;
Analysis: Calculated for C_4H_9ClO:

C: 44,25; H: 8,34; Cl: 32,66%.
Found C: 44,14; H: 8,24; Cl: 34,56%.

The chlorine content increased due to the presence of 1,3-dichlorobutane.

b) Starting from the formed amount the reaction mixture was kept under reflux current for 40 minutes. The yield was 3,25 g (46%) of (V).
Bp.: 74—76°C (25 mm); n_D^{20}: 1,4446;
Analysis:

Found: C: 44,73; H: 7,78; Cl: 32,29%.

From data of analysis and from the chromatogram of the product it appears that (V) is contaminated by another product, having higher boiling point and it does not contain chlorine. Since it has no importance as regard to the study of the main process, we did not deal with its identification.

3-chloro-butanol-1 (*II*) was synthesized by hydrogenation of *β*-chlorobutyraldehyde [13 –] with $LiAlH_4$, starting from 300 g of crotonaldehyde. The yield was 25—30%. Bp.: 80—82°C (28 Hg mm). n_D^{20}: 1,4428;
Analysis:

Found: C: 44,23; H: 8,44; Cl: 32,28%.

4-chloro-butanol-2 (*III*) was synthesized according to SONDHEIMER and WOODWARD's method [9.]

Bp.: 64—65°C; (15 Hg mm); n_D^{20}: 1,4412;

Analysis:

Found: C: 44,49; H: 8,31; Cl :32,67%.

1,3-dichlorobutane (*VI*) [14].
Bp.: 136°C (756 Hg mm); n_D^{20}: 1,4428;

Analysis: Calculated $C_4H_8Cl_2$:

C: 37,82; H: 6,35; Cl: 55,83%.
Found: C: 38,10; H: 6,48; Cl: 55,48%.

Gas-liquid chromatography investigations were carried out by a *Willy Giede GCHF 18/2 Type* apparatus.

Experimental conditions:

1. Carrier: thermolyt (grain size 0,2—0,4 mm).
2. Liquid phase: dioctylphtalate. Its amount on the carrier: 20%.
3. Length of the column: 1 m. Inner diameter: 6 mm.
4. Temperature: 120°C.
5. Carrier gas: 300 ml H_2/min.
6. Pressure: 0,3 atm.
7. Detector strom : 140 mA.
8. Sensitivity: 2 (end deflection — 3,8 mV).
9. Paper velocity: 600 mm/hour.
10. Sample: 0,005—0,02. ml,

The quantitative evaludtion of the transformationproduct was carried out by planimetric determination of the chromatograms and by the determination of the mixture of known amount of (II) and (III).

Charge of the column

Thermolyt charge containing 20% dioctylphtalate was prepared according to the methods generally applied. Dioctylphtalate of corresponding amount was dissolved in absolute ether. With stirring the etheric solution, measured quantity of thermolyte of the corresponding grain size was introduced. The ether was allowed to evaporate with slow stirring and the filled column was placed into the gas chromatograph and kept in a H_2 current at 100°C.

MILLER's paper [16], dealing with the same field appeared after the completion of our experimental work (on 25 August, 1962). He claims that butane-1,3-diol cyclic sulphate results in two chlorohydrin isomers [73% (II) and 27% (III)] on heating with concentrated HCl in water bath.

ИЗУЧЕНИЕ ХИМИЧЕСКИХ ПРЕВРАЩЕНИЙ ДИОЛОВ, И ОРГАНИЧЕСКИХ ОКИСЕЙ III.

РЕАКЦИЯ ЦИКЛИЧЕСКОГО СУЛЬФАТА БУТАНДИОЛА-1,3 С ХЛОРИСТЫМ ВОДОРОДОМ

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Авторы изучали химические превращения циклического сульфата бутандиола-1,3 происходящие под влиянием хлористово водорода. В результате реакции 3-хлоробутанол-1 (II) и 4-хлоробутанол-2 (III) были получены в зависящем от экспериментальных условий изменяющем отношении.

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