enins), XI, and in a total synthesis of the sex hormone equilenin, XII. In the latter case the procedures have been refined so that the racemic form of the hormone can be prepared in about 28% over-all yield in eight steps from 1-keto-7-methoxy-1,2,3,4-tetrahydrophenanthrene, IIIa. The steps involve formylation (step 1) followed by treatment with hydroxylamine (step 2) to produce an isoxazole Va, which is isomerized with alkoxide and methylated (step 3) to give the cyano ketone VIIa. Condensation of VIIa with dimethyl succinate in the presence of potassium *t*-butoxide (step 4) affords, in one operation, 15-carbomethoxy-14,15-dehydroequilenin methyl ether, VIIIa ($R' = CH_3$), which is hydrolyzed (step 5) to the free acid IXa, and decarboxylated (step 6) to give 14,15-dehydroequilenin methyl ether, Xa. Hydrogenation of Xa (step 7) followed by demethylation (step 8) gives *dl*-equilenin XII, which on resolution affords *d*-equilenin, identical with the natural product.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE PITTSBURGH PLATE GLASS CO., COLUMBIA CHEMICAL DIVISION]

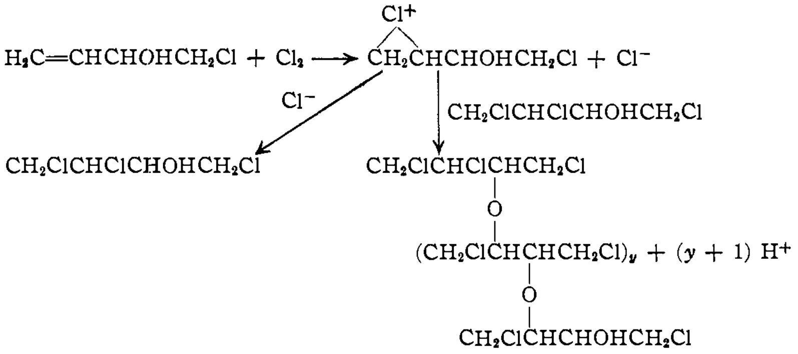
Some Reactions of Butadiene Monochlorohydrin, 1-Chloro-3-buten-2-ol

BY W. E. BISSINGER, R. H. FREDENBURG, R. G. KADESCH,[1] F. KUNG, J. H. LANGSTON,[2] H. C. STEVENS AND F. STRAIN

The recent availability of 1-chloro-3-buten-2-ol (I) from the hypochlorination of butadiene[3,4] has prompted us to investigate some of the typical reactions associated with the functional groups in this compound. Our studies have involved (1) chlorination of the double bond to form a trichlorobutanol and dehydrohalogenation of the latter to a dichloroepoxybutane, (2) conversion of the chlorohydrin to chloromethylvinyl ketone, (3) hydrolysis of the chlorohydrin to erythrol, 2-butene-1,4-diol and aldehydic products, (4) reaction of the chlorohydrin with sodium cyanide to form a butadiene cyanohydrin and dehydration of the cyanohydrin to cyanobutadiene, (5) hydrogenation of the butadiene cyanohydrin to butylene cyanohydrin and its hydrolysis and dehydration, (6) reaction of the chlorohydrin with formaldehyde to produce a formal and attempted reaction of this formal with metal cyanides and magnesium, and (7) phosgenation of the chlorohydrin to chloroformate and carbonate esters.

Discussion

Chlorination of 1-Chloro-3-buten-2-ol (I).—We have observed the addition of chlorine to 1-chloro-3-buten-2-ol (I) to be complicated considerably by side reactions, as is also apparently the case with allyl alcohol.[5] In our experiments polymeric ethers were obtained along with the expected 1,3,4-trichlorobutan-2-ol (II). This is understandable on the basis of a two-stage mechanism for halogen addition such as the one suggested by Bartlett and Tarbell[6] for bromine addition to stilbene in methyl alcohol. For the present case the reactions may be formulated as



Chlorine and hydroxyl analyses of the viscous polyether fraction indicated an average value of y of about 0.21.

As expected from the formulated mechanism, increase in the chloride ion concentration prevailing during the chlorine addition increased the yield of the trichlorobutanol and decreased the formation of ether. Thus, direct chlorination of I in carbon tetrachloride gave a 47% yield of 1,3,4-trichlorobutan-2-ol with approximately 43% of polyether. Saturation of the carbon tetrachloride with hydrogen chloride increased the yield of trichlorobutanol to 63%, while chlorination in concentrated hydrochloric acid gave this product in 77% yield. In the latter preparations polyether formation was correspondingly reduced (see Experimental section).

Dehydrochlorination of II using sodium hydroxide proceeded easily, giving practically quantitative yields of dichloroepoxybutane (III) probably consisting of a mixture of the two possible iso-

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[4] Kadesch, THIS JOURNAL, **68**, 41 (1946).

[5] Williams, *Trans. Am. Inst. Chem. Engrs.*, **37**, 171 (1941).

[6] Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

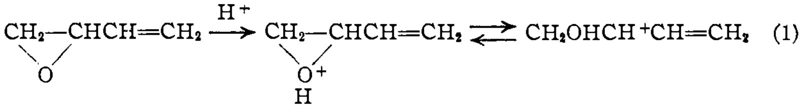
meric compounds. The proportion of the two isomers in the mixture was not determined.

Attempted Oxidation of I; Preparation of Chloromethyl Vinyl Ketone.—Although descriptions of bromovinyl[7] and chlorovinyl[8] methyl ketones have appeared in the literature, chloromethyl vinyl ketone (IV), isomeric with the latter, has not been reported. Attempts were made to convert I directly into IV by a variety of oxidation methods including electrolysis, treatment with reagents such as chromic acid, selenium dioxide, ceric sulfate, ferric chloride, aluminum *t*-butoxide–acetone mixture, cobaltous acetate–acetaldehyde mixture, as well as by dehydrogenation over copper chromite. None of these methods was satisfactory, although in some cases IV was probably formed in minor quantities. A less direct route to IV was then sought through the debromination of 1-chloro-3,4-dibromobutan-2-one, a derivative of I, prepared by Petrov[3] by bromination of I followed by oxidation of the resulting 1-chloro-3,4-dibromobutan-2-ol with chromic acid. Our attempt to debrominate the 1-chloro-3,4-dibromobutan 2-one with zinc[9] failed to give any of IV, but treatment with sodium iodide[10] resulted in a 55% yield of chloromethyl vinyl ketone (IV).

Hydrolysis of I.—The very slow rate of hydrolysis of I in water and dilute acid solutions, as well as the extremely rapid conversion of I to 3,4-epoxy-1-butene in high yields by dilute aqueous sodium hydroxide has previously been reported from this Laboratory.[11] Further studies, here described, show that the hydrolysis of I by hot sodium bicarbonate solutions proceeds rapidly and that yields as high as 50% of the theoretical of 3,4-epoxy-1-butene may be isolated early during this hydrolysis, despite relatively rapid hydration of the epoxide under these conditions. Epoxide formation is thus an intermediate step through which at least a major proportion of the hydrolysis proceeds, not only in alkaline solutions, but also in nearly neutral sodium bicarbonate solutions.

The hydrolysis of I with a 10% excess of 5% sodium bicarbonate solution gave a 40% yield[12] of erythrol, a 16% yield of 3,4-epoxy-1-butene and a 6% yield of *trans*-2-butene-1,4-diol along with some aldehydic materials not recovered.

While the formation of 2-butene-1,4-diol was somewhat unexpected, its occurrence probably was the result of an allylic rearrangement produced by slightly acidic conditions developed during the hydrolysis and involving the carbonium ion, $CH_2OHCH^+CH{=}CH_2$. This ion probably originated from either or both of the following reactions: (1) an acid-catalyzed, unimolecular ring opening of the 3,4-epoxy-1-butene, or (2) from the reaction of erythrol with a proton.

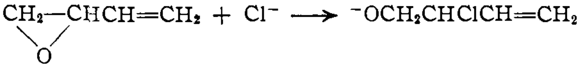


$$CH_2{-}CHCH{=}CH_2 \xrightarrow{H^+} CH_2{-}CHCH{=}CH_2 \rightleftarrows CH_2OHCH^+CH{=}CH_2 \quad (1)$$

$$CH_2OHCHOHCH{=}CH_2 + H^+ \longrightarrow CH_2OHCH^+CH{=}CH_2 + H_2O \quad (2)$$

$$CH_2OHCH^+CH{=}CH_2 \longleftrightarrow CH_2OHCH{=}CHCH_2^+ \xrightarrow{H_2O}$$
$$CH_2OHCHOHCH{=}CH_2 + CH_2OHCH{=}CHCH_2OH + H^+$$

To secure further information on reaction (1), a brief study was made of the influence of different conditions of acidity and alkalinity upon the tendency for formation of 2-butene-1,4-diol. Also, we were especially interested in observing the effect of chloride ion on the course of this hydration since Brönsted,[13] *et al.*, have found that epoxides add chloride ion to form chlorohydrins much more readily than water is added, over the same *p*H range as that existing in the hydrolysis of I with aqueous sodium bicarbonate. Such an opening of the epoxide ring by chloride ion could serve as a third explanation for the formation of 2-butene-1,4-diol. Thus, through an addition of chloride ion to 3,4-epoxy-1-butene some 2-chloro-3-buten-1-ol could be formed.



$$CH_2{-}CHCH{=}CH_2 + Cl^- \longrightarrow {}^-OCH_2CHClCH{=}CH_2$$

$$^-OCH_2CHClCH{=}CH_2 + H_2O \rightleftarrows HOCH_2CHClCH{=}CH_2 + OH^-$$

By an S_N^1 type[14a,b] hydrolysis, this chlorohydrin could yield 2-butene-1,4-diol through rearrangement.[15] Another mechanism considered along this same line, involved an abnormal[16] addition of chloride ion to 3,4-epoxy-1-butene, forming 1-chloro-2-buten-4-ol, which on hydrolysis[14b] could yield 2-butene-1,4-diol. This last mechanism seemed less probable because no definite proof of abnormal additions could be found despite the intensive investigations by Young and co-workers.[16] The effect of chloride ion on the hydration of 3,4-epoxy-1-butene in essentially neutral and in alkaline solutions

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[7] Nield, *ibid.*, **67**, 1145 (1945).

[8] Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 487 (1938); *C. A.*, **32**, 7891 (1938); German Patent 642,147; *C. A.*, **30**, 1735 (1936).

[9] Rohm, *Ber.*, **34**, 573 (1901).

[10] Winstein and Young, THIS JOURNAL, **61**, 1646 (1939).

[11] Kadesch, *ibid.*, **68**, 46 (1946).

[12] Other hydrolyses of I using saturated sodium bicarbonate solutions gave 55–65% yields of erythrol.

[13] Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929), found that over a *p*H range of 4.0 to 8.5 the uncatalyzed addition of chloride ion to epoxides was twenty to twenty-six times faster than the uncatalyzed addition of water. At lower *p*H values the much more rapid acid-catalyzed chloride addition and hydration reactions predominated.

[14] (a) This is probable since a close analog, 3-chloro-1-butene, hydrolyzes solely by the S_N^1 mechanism even in the presence of sodium hydroxide. Young and Andrews, *ibid.*, **66**, 421 (1944). (b) The rapid rates of hydrolysis of 2-chloro-3-buten-1-ol and 1-chloro-2-buten-4-ol have previously been described by Kadesch.[11]

[15] This rearrangement would also involve the resonating ion, $CH_2OHCH^+CH{=}CH_2 \longleftrightarrow CH_2OHCH{=}CHCH_2^+$, as shown above.

[16] Young, Roberts and Winstein, THIS JOURNAL, **64**, 2157 (1942).

was investigated in the experiments, the results of which are summarized in Table I.

TABLE I

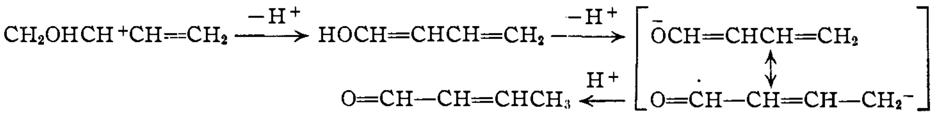
EFFECT OF CHLORIDE ION ON THE HYDRATION OF 3,4-EPOXY-1-BUTENE(C_4H_6O)

Hydration medium	Concentration, moles/liter			Yields, %	
	C_4H_6O	NaCl	Na_2CO_3	Erythrol	1,4-Diol
H_2O	1.00	0.0	0.0	74	15
$H_2O + NaCl$	0.60	.66	.0	63	4
$H_2O + Na_2CO_3$	1.00	.00	.05	81	0
$H_2O + Na_2CO_3 + NaCl$	1.00	1.00	.05	67	0

These data show that the formation of 2-butene-1,4-diol depends on the acidity of the hydrating medium, but is independent of the presence of chloride ion. Evidently, the rearrangement involved in the formation of 2-butene-1,4-diol is extremely sensitive to very small concentrations of hydrogen ion. For example, in the first two experiments described in Table I, the *p*H of the solutions was but slightly below 7.0 yet 4–15% of the 1,4-diol was formed. That the chloride ion entered into the reaction in some manner not yet fully understood was evidenced by the reduced yields of butenediols and the odor of crotonaldehyde and its condensation products in those reaction mixtures where sodium chloride was used, both in the neutral and alkaline solutions.

The formation of 2-butene-1,4-diol through the occurrence of reaction (2) is a possibility, due to slightly acidic conditions resulting from the carbon dioxide produced during the bicarbonate hydrolysis of I. In connection with this, we have observed that erythrol undergoes an allylic rearrangement forming 2-butene-1,4-diol in the presence of dilute hydrochloric acid. Under the conditions employed, the mixture of products formed was much richer in erythrol (65%) than in 2-butene-1,4-diol (5%). These results are in agreement with those obtained for the crotyl alcohol–methylvinylcarbinol system in which the secondary alcohol was the predominating isomer in the presence of acids.[17]

Along with the formation of 2-butene-1,4-diol from the rearrangement of erythrol by dilute acids some crotonaldehyde was also formed. This probably involved prototropic changes stemming from the intermediate carbonium ion, CH_2OHCH^+-$CH{=}CH_2$.[18]



$$CH_2OHCH^+CH{=}CH_2 \xrightarrow{-H^+} HOCH{=}CHCH{=}CH_2 \xrightarrow{-H^+} \left[\begin{array}{c}\bar{O}CH{=}CHCH{=}CH_2 \\ \updownarrow \\ O{=}CH{-}CH{=}CH{-}CH_2^-\end{array}\right] \xrightarrow{H^+} O{=}CH{-}CH{=}CHCH_3$$

The cyclic sulfite[19] and carbonate[20] esters of some 1,2-glycols previously reported have not included the similar esters of erythrol. We have obtained erythryl sulfite (V) in 86% yield by the alcoholysis of dimethyl sulfite with erythrol. By a similar reaction with diethyl carbonate, a 95% yield of erythryl carbonate (VI) resulted. When heated with benzoyl peroxide the erythryl sulfite evolved sulfur dioxide and eventually formed a tarry mass. Erythryl carbonate, on the other hand, polymerized to a colorless, hard, brittle resin.

Reaction of I with Sodium Cyanide.—Reaction of I with 25% aqueous sodium cyanide[21] resulted in a 74% yield of butadiene cyanohydrin (VII) together with an 8% yield of 3,4-epoxy-1-butene. Judging by the behavior[22,23] of 3,4-epoxy-1-butene and other oxides we expected the cyanohydrin, VII, to be a mixture of 2-cyano-3-buten-1-ol and 1-cyano-3-buten-2-ol, mainly the latter. One isomer seemed to predominate since an α-naphthylurethan with a very sharp melting point was obtained in 70% yield from VII.

A proposed synthesis of 1-cyano-3-buten-2-ol for comparison with VII involved the treatment of the Grignard reagent from the formal of I with cyanogen bromide. Reaction of I with paraformaldehyde gave rise to the formal of I in 32% yield but attempts to prepare the Grignard compound from the formal failed. The formal also failed to react with sodium cyanide[24] and cuprous cyanide.

The butadiene cyanohydrin, VII, was hydrogenated smoothly without reduction of the cyano or hydroxyl groups to a butylene cyanohydrin, VIII, which also formed an α-naphthylurethan derivative in high yield and with a sharp melting point. For comparison with VIII we attempted unsuccessfully to prepare CH_3CH_2-$CHOHCH_2CN$, 3-hydroxyvaleronitrile, by a Reformatsky reaction between propionaldehyde and bromoacetonitrile. The previous synthesis[25] of the desired material from 1-bromo-2-hydroxybutane and potassium cyanide suffers from the ambiguity resulting from possible formation of intermediate oxide.

Heating of VIII with sulfuric acid produced as the principal product a material in 39% yield which appeared to be γ-valerolactone. While this reaction is being investigated further, the results indicate that the cyano group in the

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[17] Hearne, U. S. Patent 2,373,956; *C. A.*, **39**, 4081 (1945).

[18] These steps were proposed by Dr. P. D. Bartlett.

[19] Majima and Simanuki, *Proc. Imp. Acad.* (*Japan*), **2**, 544 (1926); Carlson and Cretcher, THIS JOURNAL, **69**, 1954 (1947).

[20] Vorländer, *Ann.*, **280**, 187 (1894); Allpress, *J. Chem. Soc.*, **125**, 2259 (1924); Steimmig and Wittwer, U. S. Patent 1,907,891; *C. A.*, **27**, 3721 (1933).

[21] Nutting, Britton, *et al.*, U. S. Patent 2,311,636; *C. A.*, **37**, 4407 (1943).

[22] See ref. 4. Also, later, unpublished results by Drs. P. D. Bartlett and S. D. Ross have shown that the addition of methanol to 3,4-epoxy-1-butene under alkaline conditions produces a mixture containing substantial amounts of both isomers, 1-methoxy-3-buten-2-ol and 2-methoxy-3-buten-1-ol.

[23] Chitwood and Freure, THIS JOURNAL, **68**, 680 (1946), on the other hand, found that primary monoethers of propylene glycol were formed almost exclusively in the base-catalyzed alcoholysis of propylene oxide.

[24] Hass and Marshall, *Ind. Eng. Chem.*, **23**, 252 (1931).

[25] Levene and Haller, *J. Biol. Chem.*, **76**, 415 (1928).

main component of VII is attached to a terminal carbon atom as expected.

Butadiene cyanohydrin, VII, was quite resistant to dehydration by heating with phosphorus pentoxide, sodium bisulfate, orthophosphoric acid, or metaphosphoric acid, in liquid phase reactions, the maximum yield of cyanobutadiene obtained being 17%. Vapor phase dehydration over alumina, however, was more successful giving a 40% yield of a cyanobutadiene (X).

Phosgenation of I.—Although the phosgenation of I was slow and complete conversion was difficult, the 1-chloro-3-buten-2-yl chloroformate (XI) was obtained in reasonably good yields employing reaction temperatures of 20–25°. In the presence of pyridine, the reaction of I with phosgene readily produced its carbonate ester, bis-(1-chloro-3-buten-2-yl)-carbonate (XII), recovered in 80% yield.

Experimental

1. **Chlorination of 1-Chloro-3-buten-2-ol (I).**—The 1-chloro-3-buten-2-ol was prepared by the addition of hypochlorous acid to butadiene as described by Kadesch.[4]

a. **Chlorination under Anhydrous Conditions.**—Fifty-three grams (0.50 mole) of 1-chloro-3-buten-2-ol was dissolved in 125 ml. of carbon tetrachloride and 35.5 g. (0.50 mole) of chlorine was bubbled through the solution at −5 to +5°. After flushing with air to remove hydrogen chloride, the carbon tetrachloride was removed at reduced pressure and the remaining product distilled through a 1.0 × 15-cm. Vigreux column. The 1,3,4-trichlorobutan-2-ol, 41.8 g. (47% yield) was collected at 86–93° (mostly at 93°) at 4 mm., n^{20}D 1.5047.

The very viscous residue, 31.8 g., remaining from the distillation contained 53.9% of chlorine and 4.9% of free hydroxyl groups (acetyl chloride–pyridine method) and showed no unsaturation toward bromine. A cryoscopic determination of the average molecular weight in benzene gave a value of 360. These analytical results and the molecular weight correspond approximately to an average value of *y* in the polyether, $C_6H_6Cl_3O(C_4H_6Cl_2O)_yC_4H_6Cl_2OH$, of 0.21. Calculated for *y* equal to 0.21 in this formula: Cl, 55.2; OH, 4.9; mol. wt., 347.

When this experiment was repeated except that the carbon tetrachloride solution was saturated (5% by weight) with dry hydrogen chloride before chlorination, 56.1 g. (63% yield) of trichlorobutanol, b. p., 93–96° at 4 mm., n^{20}D 1.5042, along with a 24.8 g. residue of chlorinated polyether was obtained.

Anal. Calcd. for $C_4H_7Cl_3O$: Cl, 60.0. Found: Cl, 59.5.

b. **Chlorination in Hydrochloric Acid Solution.**—A solution of 53 g. (0.50 mole) of 1-chloro-3-buten-2-ol in 71 g. of concentrated hydrochloric acid was chlorinated as in (a). The mixture separated into two phases during chlorination. After the reaction was complete, the aqueous phase was separated and the hydrochloric acid distilled off at 30 mm., 6 g. of oil remaining. This oil was combined with the main oil layer which was then distilled. The fraction (69.9 g.) boiling at 97–114° at 5 mm. was collected and analyzed for total chlorine to determine the relative amounts of butadiene dichlorohydrin[26] (resulting through hypochlorination) and trichlorobutanol.

Anal. Calcd. for $C_4H_7Cl_3O$: Cl, 60.0; for $C_4H_8Cl_2O_2$: Cl, 44.6. Found: Cl, 58.2.

The yield of 1,3,4-trichlorobutan-2-ol thus calculated was 61.7 g. (70% yield) while that of butadiene dichlorohydrin was 8.2 g. (10% yield). The polyether (distillation residue) amounted to 5.8 g.

In a modified procedure, 21.2 g. (0.20 mole) of 1-chloro-3-buten-2-ol and 14.2 g. (0.20 mole) of chlorine were added simultaneously and at equivalent rates to 150 g. of concentrated hydrochloric acid. The mixture was extracted with carbon tetrachloride after which the aqueous acid was again treated with 1-chloro-3-buten-2-ol and chlorine and extracted as above. This procedure was repeated until three moles of each reactant had been introduced. Distillation of the aqueous layer gave 64.1 g. of material, b. p. 90–120° at 4 mm., containing 52.4% of chlorine. Based on this analysis, 32.5 g. of trichlorobutanol and 31.6 g. of butadiene dichlorohydrin was present in the aqueous phase. A polyether residue of 4.9 g. remained. Distillation of the carbon tetrachloride extract gave 393 g. of a trichlorobutanol fraction, b. p. 90–115° at 4 mm. containing 59.4% chlorine. A polyether residue of 29.8 g. remained. Calculated on the basis of the chlorine analyses of these two distillates, the final yield of 1,3,4-trichlorobutan-2-ol (II) amounted to 77% while 10% of butadiene dichlorohydrin was formed.

2. **Dehydrochlorination of 1,3,4-Trichlorobutan-2-ol (II).**—To 64.5 g. (0.36 mole) of 1,3,4-trichlorobutan-2-ol was added 79.8 g. (0.39 mole) of 20% sodium hydroxide over a period of ten minutes at room temperature. After stirring for one hour, analysis of the aqueous layer for chloride ion showed 97.7% reaction. The oil layer was then distilled, the main fraction, 37.3 g. (96% yield) of dichloroepoxybutanes (III) being collected at 96–100° at 45 mm., n^{20}D 1.4749.

Anal. Calcd. for $C_4H_6Cl_2O$: Cl, 50.3. Found: Cl, 48.9.

3. **Preparation of Chloromethyl Vinyl Ketone (IV).** a. **Bromination of 1-Chloro-3-buten-2-ol.**—The procedure described by Petrov[3] was followed. A solution of 320 g. (3.0 moles) of 1-chloro-3-buten-2-ol in 450 ml. of chloroform was treated with 480 g. (3.0 moles) of bromine at 10–25° over a one-hour period. Fractionation of the product through a 2.0 × 43-cm. packed column yielded 673 g. (84% yield) of 1-chloro-3,4-dibromobutan-2-ol, b. p. 126–129° at 10 mm., n^{20}D 1.5635.[27]

b. **Oxidation of 1-Chloro-3,4-dibromobutan-2-ol.**—The general procedure described by Petrov[3] was followed here except for a few minor improvements. A solution of 250 g. (2.50 moles) of chromic anhydride in 250 ml. of water was added to 666 g. (2.50 moles) of 1-chloro-3,4-dibromobutan-2-ol with stirring at 25–50° over a fifteen-minute period. Over twenty minutes a solution of 375 g. (3.75 moles) of concentrated sulfuric acid in 250 ml. of water was added to the above mixture with cooling to keep the temperature below 50°. The mixture was stirred for 1.66 hours at 50–70°, then diluted with 500 ml. of water and 500 ml. of chloroform. The organic layer was washed with aqueous sodium bisulfite, water, and dried. On fractionation through a 2.0 × 43-cm. packed column, the 1-chloro-3,4-dibromobutan-2-one, 492 g. (74% yield) was collected at 112–114° at 10 mm., n^{20}D 1.5544.[28]

c. **Oxidation of 1,3,4-Trichlorobutan-2-ol.**—When 44.5 g. (0.25 mole) of 1,3,4-trichlorobutan-2-ol (59.4% chlorine) was oxidized with acidified chromic anhydride exactly as above, 31 g. (71% yield) of 1,3,4-trichlorobutan-2-one, b. p. 89–90° at 10 mm., n^{20}D 1.4968 was obtained. The material was very lachrymatory.

Anal. Calcd. for $C_4H_5Cl_3O$: Cl, 60.7. Found: Cl, 61.4.

Efforts to prepare both a semicarbazone and a 2,4-dinitrophenylhydrazone of this compound were unsuccessful; only a tarry mass formed with 2,4-dinitrophenylhydrazine while no solid product precipitated with semicarbazide.

d. **Debromination of 1-Chloro-3,4-dibromobutan-2-one to Chloromethyl Vinyl Ketone (IV).**—Two hundred

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[26] One typical butadiene dichlorohydrin, 1,4-dichlorobutan-2,3-diol, has b. p. 152° at 30 mm., Henninger, *Ann. chim.*, [6] **7**, 228 (1886).

[27] Petrov[3] reported b. p. 129–130° at 10 mm., n^{20}D 1.5610 for 1-chloro-3,4-dibromobutan-2-ol.

[28] Petrov[3] reported b. p. 132–133° at 25 mm., n^{20}D 1.5540, for 1-chloro-3,4-dibromobutan-2-one.

and twenty-five grams (1.50 moles) of sodium iodide in 1000 ml. of acetone was added over thirty minutes to a stirred solution of 227 g. (0.97 mole) of 1-chloro-3,4-dibromobutan-2-one in 500 ml. of acetone at 30°. After stirring an additional thirty minutes the sodium bromide was filtered off and the filtrate was diluted to about 2000 ml. with acetone. After chilling overnight in Dry Ice, the cold mixture was filtered to remove the iodine. The solution was then distilled through a 2.0 × 43-cm. packed column in the presence of a little hydroquinone, removing the acetone at 20–29° at reduced pressure. The main product, 66 g., was collected at 37° at 10 mm.; a residue of 57 g. remained. To remove traces of iodine from the product it was dissolved in chloroform and stirred with 30 g. of mercury[29] for one hour and then redistilled. The colorless lachrymatory distillate, 49 g. (55% yield) of chloromethyl vinyl ketone (IV) had the following constants: m. p. −43 to −30°; b. p. 37–39° at 10 mm., 70° at 60 mm., 89–90° at 140 mm.; $n^{20}\mathrm{D}$ 1.4675; d^{20}_4 1.2604.

Anal.[30] Calcd. for C_4H_5OCl: C, 45.93; H, 4.78; Cl, 33.97. Found: C, 45.68; H, 5.07; Cl, 33.76; Br, 0.78.

An attempt was made to dechlorinate 1,3,4-trichlorobutan-2-one by the same procedure as described above. While a small amount of the chloroketone may have resulted, the reaction did not proceed readily.

4. **Hydrolysis of 1-Chloro-3-buten-2-ol to Erythrol.**—A mixture of 320 g. (3.0 moles) of 1-chloro-3-buten-2-ol and 277.2 g. (3.3 moles) of sodium bicarbonate in 5000 ml. of water contained in a 10-liter flask, fitted with a reflux condenser to which was connected a Dry Ice trap, was heated on the steam-bath for five and one-half hours, after which time carbon dioxide evolution had ceased. Collected in the Dry Ice trap was 33.7 g. (16% yield) of 3,4-epoxy-1-butene, b. p. 63–66°, $n^{20}\mathrm{D}$ 1.4132.[4] The reaction mixture was distilled to dryness, the salt cake extracted with ethyl alcohol and the alcohol extract distilled through a 1.0 × 25-cm. Vigreux column. The erythrol, 106 g. (40% yield), was collected at 74–80° at 2 mm., $n^{20}\mathrm{D}$ 1.4608.[31] On continued distillation a higher boiling fraction, 15.4 g. (6% yield), $n^{20}\mathrm{D}$ 1.4755, b. p. 104–105° at 2 mm. was obtained. This compound was identified as *trans*-2-butene-1,4-diol by its freezing point of 24–25°, and by the melting point (132–133°) of its dibromide.[32] As a further derivative the 1,4-bis-(methyl carbonate) ester was prepared as follows: 2.0 g. (0.023 mole) of the above 2-butene-1,4-diol was mixed with 4.0 g. (0.05 mole) of pyridine and 20 ml. of ether and while stirring at −4°, 4.4 g. (0.046 mole) of methyl chloroformate was added. The product was poured into water, washed with hydrochloric acid and water and dried. On removing the ether, the solid 2-butene-1,4-bis-(methyl carbonate), 2.5 g. (53% yield) crystallized. Recrystallized from hot water the white plates melted at 68–69°. The corresponding bis-(methyl carbonate) ester of erythrol was similarly prepared; it distilled at 95–97° at 1 mm., $n^{20}\mathrm{D}$ 1.4290, but did not solidify on standing at room temperature.

A mixture of 32 g. (0.38 mole) of sodium bicarbonate and 39.1 g. of an aqueous 84.2% solution of 1-chloro-3-buten-2-ol (0.308 mole of pure I) in 500 ml. of water was rapidly heated in a flask to which was attached a 1.5 × 30-cm. Vigreux column, a downward condenser, a receiver and a Dry Ice trap. Evolution of carbon dioxide and distillation started within ten minutes. During the next ten minutes the vapor temperature increased from 50 to 98°. The distillate and the contents of the Dry Ice trap were then combined, separated from a small aqueous layer and redistilled. The 3,4-epoxy-1-butene fraction, b. p. 60–70°, $n^{20}\mathrm{D}$ 1.4160, weighed 9.8 g. (0.14 mole) while 3.2 g. (0.03 mole) of 1-chloro-3-buten-2-ol was recovered unchanged on continued distillation. The yield of 3,4-epoxy-1-butene, based on unrecovered I, was 50%.

5. **Butenediols from 3,4-Epoxy-1-butene and Sodium Chloride Solutions.**—A mixture of 75.6 g. (1.08 mole) of 3,4-epoxy-1-butene and 70.8 g. (1.20 mole) of sodium chloride in 1800 ml. of water was heated under reflux on a steam-bath for three and one-half hours, during which time the solution had become homogeneous and refluxing had stopped. After distilling off the water (the odor of crotonaldehyde was noticed), the solid residue was extracted with ethyl alcohol and the extract distilled through a 1.5 × 30-cm. Vigreux column at 2 mm., yielding 60 g. (63% yield) of erythrol, b. p. 82–90°, $n^{20}\mathrm{D}$ 1.4615 and 4 g. (4% yield) of 2-butene-1,4-diol, b. p. 100–104°, $n^{20}\mathrm{D}$ 1.4720. The 1,4-diol fraction was converted to its 1,4-bis-(methyl carbonate) ester as before; the recrystallized solid melted at 69°.

In a similar experiment a mixture of 70.0 g. (1.0 mole) of 3,4-epoxy-1-butene[33] and 1000 ml. of distilled water was refluxed for three and one-half hours. After one-half hour of heating, the oil layer and odor of 3,4-epoxy-1-butene had disappeared. On distillation as before a 74% yield of erythrol and a 15% yield of 2-butene-1,4-diol (m. p. 19–23°) was obtained.

A mixture of 70.0 g. (1.0 mole) of 3,4-epoxy-1-butene[33] and 5.3 g. (0.05 mole) of sodium carbonate was similarly refluxed with 1000 ml. of distilled water for three and one-half hours. The odor of 3,4-epoxy-1-butene was evident after three hours but had disappeared after three and one-half hours. On distillation an 81% yield of erythrol, b. p. 80–81° at 2 mm., $n^{20}\mathrm{D}$ 1.4615, but no 2-butene-1,4-diol, was obtained. A semisolid residue of 1.8 g. remained in the flask.

A mixture of 70.0 g. (1.0 mole) of 3,4-epoxy-1-butene,[33] 58.5 g. (1.0 mole) of sodium chloride and 5.3 g. (0.05 mole) of sodium carbonate in 1000 ml. of distilled water was refluxed for three and one-half hours as before. Considerable gummy material, resembling aldol in odor, was present. On distillation much of this by-product steam distilled. The yield of erythrol, b. p. 84–86° at 2 mm., $n^{20}\mathrm{D}$ 1.4612, was 67%. No 2-butene-1,4-diol was present. A tarry residue of 4.3 g. remained.

6. **Stability of Erythrol to Acids and Bases.**—A 10-g. sample of erythrol ($n^{20}\mathrm{D}$ 1.4618) and 0.50 g. (5%) of anhydrous sodium carbonate was heated at 145–150° for four hours and then distilled, giving 9.5 g. (95% recovery) of erythrol, b. p. 62–70° at 1 mm., $n^{20}\mathrm{D}$ 1.4618. There was no fore-run or organic residue.

A solution of erythrol (23.5 g.) in water (40 ml.) with 1.2 g. of added sodium carbonate was refluxed for six and one-half hours, then distilled. No fore-run or organic residue was obtained and a 96% recovery of erythrol resulted. A Schiff test for aldehydes was negative.

A solution of 60 g. of erythrol and 1.0 g. of concentrated hydrochloric acid in 250 ml. of water (*p*H 1.6) was refluxed for three hours, then distilled from a Claisen flask with a Dry Ice trap attached to the receiver. After first removing the water at atmospheric pressure, the distillate obtained consisted of 39.2 g. (65%) of unchanged erythrol, b. p. 72–77° at 1 mm., $n^{20}\mathrm{D}$ 1.4615, and 2.6 g. (5% yield) of 2-butene-1,4-diol, b. p. 110–120° at 1 mm., $n^{20}\mathrm{D}$ 1.4749.

Anal. Calcd. for $C_4H_6(OH)_2$: unsaturation equivalent, 44.0. Found: unsaturation equivalent, 44.0.

Collected in the Dry Ice trap was 3.3 g. (7% yield) of crotonaldehyde, $n^{20}\mathrm{D}$ 1.4432, identified by its 2,4-dinitrophenylhydrazone, m. p. 185–186°. This derivative of known crotonaldehyde melted at 186° and a mixed melting point with the above derivative showed no depression.

7. **Preparation of Erythryl Sulfite (V).**—A mixture of 17.6 g. (0.20 mole) of erythrol and 22.0 g. (0.20 mole) of dimethyl sulfite was heated in a modified Claisen flask to

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[29] King, "Organic Syntheses," Coll, Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 402.

[30] Analysis by Dr. Carl Tiedcke, Laboratory of Microchemistry, New York, N. Y.

[31] Prévost, *Compt. rend.*, **183**, 1293 (1926), reported b. p. 94° at 12 mm., $n^{20}\mathrm{D}$ 1.4627, for erythrol.

[32] Prévost[31] reported m. p. 25°, b. p. 131° at 12 mm., $n^{20}\mathrm{D}$ 1.4772, for *trans*-2-butene-1,4-diol and m. p. 132.5–133° for its dibromide.

[33] This sample of 3,4-epoxy-1-butene contained 0.02% of total chlorine and less than 0.01% of easily hydrolyzable chlorine as determined by shaking the sample with dilute sodium hydroxide followed by titration for chloride ion by the Volhard method.

120° whereupon a strong reaction ensued. Within twenty minutes 13.6 g. (theory, 12.8 g.) of a methanol fraction, b. p. 65–66°, was collected. Distillation of the residue gave 18.2 g. (86% yield) of erythryl sulfite (V), b. p. 56–58° at 3 mm., n^{20}D 1.4588.

Anal. Calcd. for $C_4H_6SO_3$: S, 23.9. Found: S, 23.9.

Two grams of erythryl sulfite was heated with 5% by weight of added benzoyl peroxide at 70° for seventy-two hours. Sulfur dioxide was evolved and a black gelatinous mass not completely soluble in acetone was obtained.

8. **Preparation of Erythryl Carbonate (VI).**—Four grams of sodium was dissolved in a mixture of 400 g. (4.5 moles) of erythrol and 802 g. (6.8 moles, 50% excess) of diethyl carbonate. The reaction flask was attached to a 1.3 × 43-cm. Vigreux column and heated at 110–130° for four and one-half hours, removing the ethyl alcohol as formed at 77–78°. Distillation of the residue gave 492 g. (95% yield) of erythryl carbonate (VI), b. p. 102–106° at 5 mm., n^{20}D 1.4487.

Anal. Calcd. for $C_4H_6CO_3$: saponification equivalent, 57.0. Found: sapn. equiv., 57.7.

When heated with 5% by weight of added benzoyl peroxide for fifteen hours at 70° this ester gave a colorless, hard, brittle polymer, insoluble in acetone and chloroform but soluble in hot ethylene carbonate. The polymer softened at about 110°.

9. **Preparation of Butadiene Cyanohydrin (VII) from 1-Chloro-3-buten-2-ol.**—A mixture of 160 g. (1.5 moles) of 1-chloro-3-buten-2-ol (I) and 105 g. (2.14 moles) of sodium cyanide in 1100 ml. of water was heated at 50–60° with stirring for two and one-half hours. Titration for chloride ion showed the reaction to be complete. The dark-red reaction mixture was extracted five times with 300-ml. portions of ethyl ether, after which the extract was dried over anhydrous sodium sulfate and distilled through a 15-plate Fenske column. An 8% yield of 3,4-epoxy-1-butene was isolated by distillation but no I was recovered. The butadiene cyanohydrin (VII), 107 g. (74% yield), was collected at 132–133° at 30 mm., n^{20}D 1.4559.

Anal. Calcd. for C_5H_7ON: N, 14.4; hydroxyl, 17.5. Found: N, 14.3; hydroxyl, 16.8.

The solubility of the butadiene cyanohydrin in water at 25° was 14.6 g. per 100 g. of water. Its partition coefficient between ether and water at room temperature was 5.6.

The α-naphthylurethan of VII was prepared in 70% yield by heating a mixture of 1.01 g. (0.0104 mole) of VII and 1.93 g. (0.0114 mole) of α-naphthyl isocyanate on the steam-bath for fifty hours, after which the derivative was recrystallized from benzene–petroleum ether. A total of 1.74 g., m. p. 112.5–113.5°, was obtained.

10. **Hydrogenation of Butadiene Cyanohydrin to Butylene Cyanohydrin (VIII).**—A solution of 14.1 g. (0.145 mole) of butadiene cyanohydrin in 20 ml. of dioxane was hydrogenated in a Parr apparatus at 25° using palladium black. On distillation through a 6-plate Fenske column, the butylene cyanohydrin (VIII), 11.6 g. (82% yield), distilled at 126–129° at 30 mm., n^{20}D 1.4348–1.4350. Unsaturation analysis by the bromate–bromide method showed the presence of not more than 0.5% of unsaturation, calculated as butadiene cyanohydrin.

Anal. Calcd. for C_5H_9ON: hydroxyl, 17.2. Found: hydroxyl, 16.5.

The α-naphthylurethan of VIII was prepared as above in 60–70% yield, m. p. 105–106°. A mixture of the α-naphthylurethans of VII and VIII mix-melted at 101–102°.

The butylene cyanohydrin (VIII) was hydrolyzed and dehydrated as follows: To 23.8 g. (0.23 mole) of concentrated sulfuric acid was added 6.7 g. (0.067 mole) of VIII while stirring and cooling below 65°. The mixture was then heated to 155° over a period of twenty minutes, cooled, 8 ml. of water was added and the mixture was refluxed for six hours. The product was diluted with 40 ml. of saturated salt solution and extracted five times with 10 ml. portions of ether. Distillation of the ether extract through a 0.6 × 6.0-cm. Vigreux column gave 2.6 g. of material, b. p. 79–80° at 10 mm., n^{20}D 1.4351, m. p. −37 to −35°. When titrated with standard sodium hydroxide, the neutralization equivalent was 1100.

Anal. Calcd. for γ-valerolactone[34]: saponification equivalent, 100. Found: saponification equivalent, 98.

11. **Formal of I; bis-(1-Chloro-3-buten-2-oxy)-methane.**—Following the procedure of Adams and Adkins[35] the formal of I was prepared from 213 g. (2.0 moles) of I, 30 g. (1.0 mole) of paraformaldehyde and 4 g. of ferric chloride. The bis-(1-chloro-3-buten-2-oxy)-methane (IX), 71 g. (32% yield) distilled at 117–121° at 10 mm., n^{20}D 1.4737.

Anal. Calcd. for $C_9H_{14}O_2Cl_2$: Cl, 31.5; unsaturation equivalent, 56.2. Found: Cl, 31.9; unsaturation equivalent, 56.1.

When a mixture of IX and sodium cyanide was heated in aqueous alcohol solution under the conditions described by Hass and Marshall[24] for reaction with *n*-amyl chloride, none of the desired nitrile was formed. Similarly, a mixture of IX and cuprous cyanide failed to undergo any reaction when heated at 110° for seven hours.

12. **Dehydration of Butadiene Cyanohydrin.**—The apparatus consisted of an inclined 2.5 × 37-cm. Pyrex pyrolysis tube heated by an electric furnace. The tube was fitted with a thermometer-well in the center. The first 6–9 inches of the tube was not packed and served as a preheater section. In the experiments summarized in Table II, the cyanohydrin was introduced through a dropping funnel over a one and one-half-hour period. Considerable carbonization on the tube packing was always noted. The pyrolyzate, consisting of two phases, was separated, the lower aqueous layer extracted with ether, and the extract combined with the oil layer. This was dried over sodium sulfate and distilled through a 0.8 × 25-cm. column packed with a stainless steel spiral. The cyanobutadiene (X) boiled at 61–63° at 50 mm., n^{20}D 1.4812.[36a,b]

TABLE II

VAPOR PHASE DEHYDRATION OF BUTADIENE CYANOHYDRIN

Catalyst	Cyanohydrin charged, g.	Temp., °C.	Cyanohydrin recovered, %	Yield[a] of C_4H_5CN, %
Silica gel (10–16 mesh)	35	320–350	28	13
Alumina (8–9 mesh)	46	325–345	0	25[b]
Alumina	153	290–320	27	40

[a] Yields are based on the cyanohydrin not recovered. [b] *Anal.* Calcd. for C_4H_5CN: N, 17.7. Found: N, 17.5.

13. **Preparation of Chloroformate of (I).**—Three hundred and nineteen grams (3.0 moles) of 1-chloro-3-buten-2-ol was placed in a three-necked flask fitted with thermometer, gas inlet tube, and a Dry Ice–acetone reflux condenser. Phosgene was passed into the flask until 396 g. (4.0 moles) had been added during a seven-hour period, the temperature being maintained at 20–25° by external heating when necessary. After standing overnight at room temperature, excess phosgene was removed by bubbling air through the mixture for one hour, after which the liquid product was washed with three 500-ml. portions of water. Distillation of the oil layer gave 339 g. (67% yield) of 1-chloro-3-buten-2-yl chloroformate (XI), b. p. 75–76° at 22 mm.

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(34) Beilstein, "Handbuch der organischen Chemie," Vol. XVII, Julius Springer, Berlin, 1933, p. 235, lists the following constants for γ-valerolactone: b. p. 83–84° at 13 mm., n^{17}D 1.4362, n^{22}D 1.4331, m. p. −31°.

(35) Adams and Adkins, THIS JOURNAL, **47**, 1358 (1925).

(36) (a) Coffman, *ibid.*, **57**, 1981 (1935), reported b. p. 65–68° 58 mm., n^{20}D 1.4880 for 1-cyano-1,3-butadiene. (b) Clifford and Long, U. S. Patent 2,328,890; *C. A.*, **38**, 1146 (1944), gave constants for 2-cyano-1,3-butadiene: b. p. 53–58° at 11 mm., n^{29}D 1.4435.

Anal. Calcd. for $C_5H_6O_2Cl_2$: Chloroformate Cl, 21.0. Found:[37] 20.1.

14. Preparation of Carbonate Ester of (I).—Phosgene was passed into a stirred mixture of 121 g. (1.13 moles) of 1-chloro-3-buten-2-ol and 182 g. (2.3 moles) of pyridine in 425 ml. of benzene while cooling to keep the temperature at 0–10°. After standing for four hours at room temperature, the pasty product was shaken with water and the benzene layer separated, washed with 5% hydrochloric acid, then with water, and finally dried over anhydrous sodium sulfate. On distillation 103 g. (79% yield) of bis-(1-chloro-3-buten-2-yl)-carbonate (XII), b. p. 116–121° at 4 mm., $n^{20}D$ 1.4726, was obtained.

Anal. Calcd. for $C_9H_{12}O_3Cl_2$: saponification equiv., 79.7; Cl, 29.7. Found: saponification equiv., 79.7; Cl, 30.0.

Acknowledgment.—The helpful suggestions of Dr. A. Pechukas during the course of this study are gratefully acknowledged.

Summary

1. A number of reactions involving the functional groups of butadiene monochlorohydrin, 1-chloro-3-buten-2-ol, have been carried out and the compounds obtained are described.

2. The presence of chloride ion was found to retard the formation of polyethers in the chlorination of butadiene monochlorohydrin, and enabled the isolation of 1,3,4-trichlorobutan-2-ol in 77% yield. This was dehydrohalogenated to produce a nearly quantitative yield of a product probably consisting of a mixture of two dichloroepoxybutanes.

3. Chloromethyl vinyl ketone was prepared and observed to be a lachrymatory, easily polymerizable liquid.

4. The hydrolysis of butadiene monochlorohydrin with aqueous sodium bicarbonate was found to produce erythrol, 3,4-epoxy-1-butene and 2-butene-1,4,-diol. Mechanisms most probable for the formation of the latter compound are discussed.

5. Erythrol was found to undergo rearrangement in acid medium, forming 2-butene-1,4-diol and crotonaldehyde.

6. The cyclic sulfite and carbonate esters of erythrol were formed readily by the alcoholysis of dimethyl sulfite and diethyl carbonate, respectively, with erythrol.

7. Aqueous sodium cyanide converted butadiene monochlorohydrin to butadiene cyanohydrin, probably a mixture of isomers in which one compound, believed to be 1-cyano-3-buten-2-ol, was predominant. Dehydration of the cyanohydrin to cyanobutadiene was rather difficult. Catalytic reduction of the butadiene cyanohydrin to butylene cyanohydrin proceeded smoothly without any simultaneous hydrogenation of the hydroxyl or cyano groups. Hydrolysis and dehydration of the saturated cyanohydrin appeared to give γ-valerolactone, the formation of which indicates a cyano group on the terminal carbon atom of butadiene cyanohydrin.

8. The formal of butadiene monochlorohydrin was prepared; the chlorine atoms in this formal were found to be very unreactive toward magnesium metal, sodium cyanide and cuprous cyanide.

9. The phosgenation of butadiene monochlorohydrin to its chloroformate, in the absence of hydrogen chloride acceptors, was relatively slow. With pyridine, the carbonate ester formed readily.

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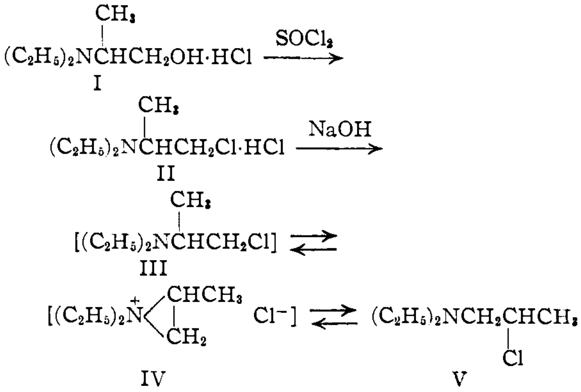
[37] This was determined by shaking a weighed sample with a 20% aqueous pyridine solution followed by Volhard determination of chloride ion.

[CONTRIBUTION FROM SMITH, KLINE AND FRENCH LABORATORIES AND THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Rearrangement of 1,2-Aminochloroalkanes

BY JAMES F. KERWIN, GLENN E. ULLYOT, REYNOLD C. FUSON AND CHARLES L. ZIRKLE[1]

In an earlier article[2] it was reported that when certain 2-hydroxyisopropyl sulfides were treated with hydrochloric acid the reaction involved rearrangement, yielding the corresponding normal chloropropyl sulfides. Although the expected 2-chloroisopropyl sulfides were not isolated, it seems certain that if formed they rearrange readily, the cyclic sulfonium chlorides being intermediates. We undertook to determine whether a similar rearrangement would occur in analogous nitrogen compounds. It was found that when the hydrochloride of 2-diethylamino-1-chloropropane (II), obtained from the corresponding amino alcohol hydrochloride (I) by treatment with thionyl chloride, was treated with alkali, the chloro amine isolated was the corresponding normal propylamine derivative (V).



$$\underset{\text{I}}{(C_2H_5)_2N\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2OH\cdot HCl} \xrightarrow{SOCl_2}$$

$$\underset{\text{II}}{(C_2H_5)_2N\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2Cl\cdot HCl} \xrightarrow{NaOH}$$

$$\underset{\text{III}}{[(C_2H_5)_2N\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_2Cl]} \rightleftarrows$$

$$\underset{\text{IV}}{\left[(C_2H_5)_2\overset{+}{N}\begin{matrix}/CHCH_3\\ |\\ \backslash CH_2\end{matrix}\;Cl^-\right]} \rightleftarrows \underset{\text{V}}{(C_2H_5)_2NCH_2\underset{\underset{\displaystyle Cl}{|}}{C}HCH_3}$$

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[1] Smith, Kline and French Laboratories Fellow, 1946–1947.

[2] Fuson, Price and Burness, *J. Org. Chem.*, **11**, 475 (1946).