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

Reaction of 3,4-Epoxy-1-butene with Methanol. Direction and Mechanism of Ring Opening

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The addition of various substances of the type HX to unsymmetrical α-epoxides generally proceeds to give the alcohol with the greatest degree of branching at the carbinol carbon atom.[1] This course has been observed in reactions with a wide variety of reagents such as anions, X^- (alkoxides, phenoxides, organic and inorganic salts, and various carbanions), derived from HX and reactive molecules with an unshared electron pair (amines, ammonia, mercaptans and hydrogen sulfide). The same behavior has been exhibited in many acid-catalyzed reactions of hydrogen halides, alcohols, phenols and organic acids.

This consistent behavior of epoxides during ring opening is illustrated by the reactions with alcohols catalyzed by alkali hydroxides or sodium[2] and catalyzed by acids.[2c,3] Phenols react in the same way in the form of phenoxides[4] or when acid catalyzed.[2b,4a,5]

The kinetics[6] of epoxide ring opening and the occurrence of inversion indicate that these reactions are bimolecular nucleophilic displacements on carbon.[2b,7] Walden inversion has been demonstrated for a wide variety of epoxide ring opening reactions including the acid-catalyzed reaction with water[7b,8] and alcohols.[7b,9] The directive influences in ring opening are generally consistent with this mechanism. The nucleophilic reagent attacks the least substituted carbon atom, that of lowest electron density. This mode of reaction will henceforth be referred to as the "normal" reaction.

There are a few notable exceptions to the normal mode of addition. One of these is 3,4-epoxy-1-butene which reacts abnormally with hydrogen chloride and hydrogen bromide to give 2-halo-3-buten-1-ols[10] although it reacts normally with alcohols in the presence of sodium to give 1-alkoxy-3-buten-2-ols.[2a]

It was the purpose of the present work to study the ring opening of 3,4-epoxy-1-butene, not with a variety of reagents but with one reagent under different conditions in an effort to determine the factors governing the direction of ring opening. The reagent selected was methanol. Actually it was found that reaction proceeded either normally or abnormally depending on the catalyst. This appears to be the first reported example of the reversal of the direction of ring opening of an epoxide with a given reagent by varying the conditions.

Results and Discussion

The reaction of 3,4-epoxy-1-butene (I) with methanol in the presence of 0.5% of sulfuric acid gave 2-methoxy-3-buten-1-ol (III) instead of the normal product II. The formation of III was demonstrated by its oxidation with dichromate to methoxymalonic acid (IV) which was identified as its amide by melting point and saponification equivalent. The 3,5-dinitrobenzoate of III melted at 107–109°. When I was refluxed with methanol containing 1.0–1.5% of sodium a monomethyl ether was obtained whose 3,5-dinitrobenzoate melted at 72°. This indicated that ring opening occurred in the normal manner to give 1-methoxy-3-buten-2-ol (II) in agreement with the observation of Petrôv.[2a] In both the sodium and sulfuric acid-catalyzed reactions the temperature and manner of mixing the reactants were varied as described in the Experimental part. With a given catalyst there were no appreciable differences in the properties of the products which are listed in Table I. The boiling point and refractive index are about the same for II and III. Close correspondence in physical properties has also been observed for a similar pair of isomers, VII and VIII, previously[10] and in the present work.

Monoether II was converted to the corresponding chloride, VI, by decomposing its chloroformate with pyridine. The allyl chloride type of structure was indicated for VI by its reactive chlorine atom. Its solution (0.04 *M*) in 25% aqueous ethanol was 50% hydrolyzed after seventy minutes at 70°. The chloride, V, was derived from III through the chloroformate as before. Heating in the same way at 70° for seventy minutes resulted in the hydrolysis of

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[1] A few examples of the many known instances are given in Ellis, "The Chemistry of Petroleum Derivatives," Reinhold Publishing Corp., New York, N. Y., 1934, pp. 542–543, 557–558, vol. II, 1937, pp. 586–589.

[2] (a) Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 131 (1938); *C. A.*, **32**, 4524, 5369 (1938); (b) Peat, *Ann. Reports*, **36**, 262–266 (1939); (c) Kharasch and Nudenberg, *J. Org. Chem.*, **8**, 189 (1943).

[3] (a) Fourneau and Ribas, *Bull. soc. chim.*, **39**, 1584 (1926); **41**, 1046 (1927); (b) Evans, Marple and Shokal, U. S. Patent 2,314,039; (c) Petrov, *J. Gen. Chem.* (U. S. S. R.), **10**, 981 (1940); (d) Grummitt and Hall, THIS JOURNAL, **66**, 1229 (1944).

[4] (a) Fairbourne, Gibson and Stephens, *J. Chem. Soc.*, 1965 (1932); (b) Brenaus, *Bull. soc. chim.*, **13**, 525 (1913).

[5] Lindemann, *Ber.*, **24**, 2145 (1891); Fourneau, German Patent 228,205.

[6] Brönsted, Kilpatrick and Kilpatrick, THIS JOURNAL, **51**, 428 (1929).

[7] (a) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 301–303; (b) Winstein and Lucas, THIS JOURNAL, **61**, 576 (1939); (c) Grigsby, Hind, Chanley and Westheimer, *ibid.*, **64**, 2606 (1942).

[8] Wilson and Lucas, *ibid.*, **58**, 2396 (1936), and earlier references given there.

[9] (a) Winstein and Henderson, *ibid.*, **65**, 2196 (1943); (b) Nicolet and Poulter, *ibid.*, **52**, 1186 (1930).

[10] Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **11**, 991 (1941).

TABLE I

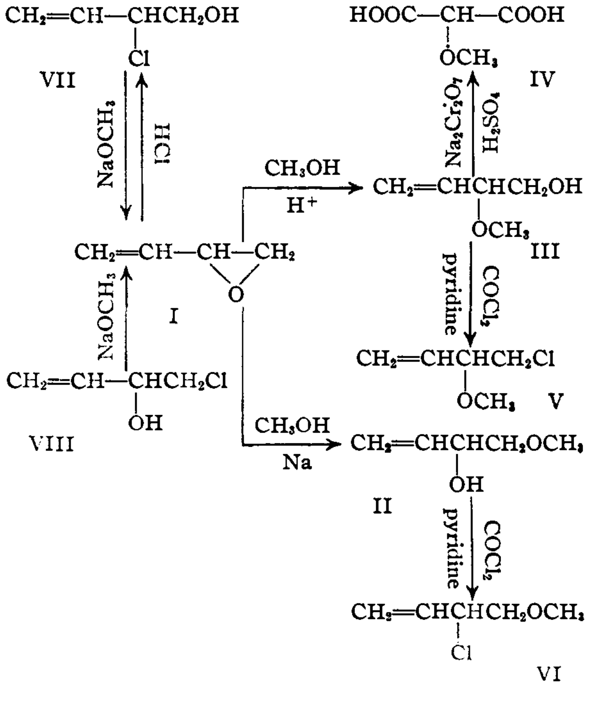
ERYTHROL MONOMETHYL ETHER

Method of preparation	Prep. no.	Proc.	% Yield	B. p., °C.	B. p., Mm.	$n^{20}D$	Unsat. equiv.[a]	% OH[b]	% Reaction with BzCl
I + CH_3OH (H_2SO_4)	1	[c]	43[h]	69–72	46–57	1.430	...	..	..
	2	[d]	63[i]	70–72	50	1.4288	109	16.8	78
	3	[d]	50	69–79	46–52	1.4280	...	16.7	61
	4	[e]	40	70–71	44–49	1.4280	114	..	66
I + CH_3OH (Na)	5	[c]	40[k]	60–61	55	1.4319	...	..	..
	6	[d]	65	71–75	49–58	1.4299	...	..	22
	7	[g]	68[j]	69–71	49	1.4300	106	16.9	8
	8	[d]	44	71–73	49	1.4288	...	..	7
	9	[f]	45	69–71	49	1.4275	...	..	17
VII + $NaOCH_3$	...	...	52	70	50	1.4290	105	16.6	42
VIII + $NaOCH_3$	...	...	51	69–71	49	1.4297	106	16.6	41

[a] Determined by the bromide–bromate method. The theoretical equivalent for $C_5H_{10}O_2$ is 102.1. [b] Determined by the acetyl chloride–pyridine method. The calculated hydroxyl content for $C_5H_{10}O_2$ is 16.7%. [c] The reactants were combined quickly and refluxed for about five hours. [d] To the refluxing methanol containing the catalyst was added I during about one hour. Refluxing was continued for several hours. [e] I was added to methanol and catalyst with stirring during 1.2 hours at 15–25°. Stirring was continued one and one-half hours at 20–30°. [f] Procedure same as in ref. e followed by refluxing for forty minutes. The reactants were combined quickly, allowed to stand one hour at room temperature and refluxed for two and one-half hours. [h] The 3,5-dinitrobenzoate obtained as light tan plates from aqueous ethanol, m. p. 107–109°. [i] *Anal.* Calcd. for $C_5H_{10}O_2$: C, 58.81; H, 9.87. Found: C, 58.47; H, 9.64. [j] *Anal.* Calcd. for $C_5H_{10}O_2$: C, 58.81; H, 9.87. Found: C, 58.25; H, 9.39. This microanalysis and the one previous by Dr. T. S. Ma, University of Chicago. [k] The 3,5-dinitrobenzoate obtained as white needles from aqueous ethanol, m. p. 70–72°.

only 9% of V, thus further indicating that the addition of methanol to I in the presence of sulfuric acid occurred abnormally to yield III.

Further confirmation of the structure of II and III was obtained by determining their reactivity toward benzoyl chloride. A standard method was adopted in which the various erythrol monomethyl ether samples were heated with benzoyl chloride in dimethylaniline for ninety minutes at 50°. The results are given in the last column of Table I and show that III had the greater reactivity expected of a primary alcohol, reacting about three to five times more rapidly than II. Under the same conditions the analogous isomeric pair, VII and VIII, reacted to the extent of 43 and 12%, respectively.



The evidence presented indicates only that II and III are the predominating products from I and methanol in the presence of sodium and sulfuric acid, respectively. The presence of a small amount of the alternate product in each case is not precluded.

It was desired to synthesize II and III by an independent method as a further check on the structures assigned. Accordingly, VIII was added to an equivalent amount of sodium methoxide in refluxing methanol to give the desired II as shown by the m. p. of 70° for its 3,5-dinitrobenzoate (mixed m. p. of 70–71° with the 3,5-dinitrobenzoate of II from I). However, VII and sodium methoxide did not yield the replacement product, III, but also gave II since its 3,5-dinitrobenzoate melted at 68–71°. The two erythrol monoethers from VII and VIII also showed the same reactivity toward benzoyl chloride. Therefore, the conversion of VII to II by sodium methoxide must have involved I as an intermediate. The conversion of VII (and VIII) to I by sodium hydroxide is known to be extremely rapid.[11] The conversion would be expected to be even more rapid by the stronger base, sodium methoxide and more rapid than the competing direct displacement reaction.[12] The formation of II from I and methanol in the presence of catalytic amounts of sodium methoxide has already

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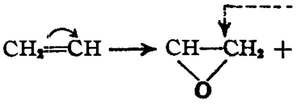
(11) Kadesch, THIS JOURNAL, **67**, 46 (1945).

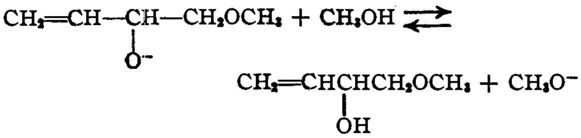
(12) Young and Andrews, *ibid.*, **66**, 421 (1944); Tamele, Ott, Marple and Hearne. *Ind. Eng. Chem.*, **33**, 115 (1941),

been demonstrated. That I was also the intermediate in the conversion of VIII to II by sodium methoxide was shown by carrying out the reaction at room temperature for a limited time (thirty-five minutes). Analysis of the distillate from the reaction mixture indicated the presence of 55% of I. Several cases of the conversion of α-chlorohydrins to epoxides by alcoholates have been reported.[13]

Mechanism of the Reaction of 3,4-Epoxy-1-butene with Methanol.—The normal reaction which occurs with methanol in the presence of a little sodium is due to a bimolecular nucleophilic displacement by methoxide ion

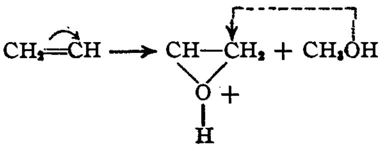


which is regenerated.

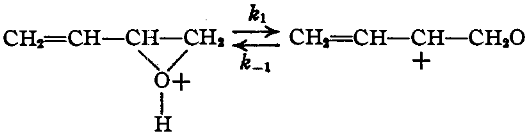


$$CH_2{=}CH{-}\underset{\displaystyle O^-}{\underset{|}{CH}}{-}CH_2OCH_3 + CH_3OH \rightleftarrows CH_2{=}CH\underset{\displaystyle OH}{\underset{|}{CH}}CH_2OCH_3 + CH_3O^-$$

This type of S_N2 mechanism might be expected to lead to the normal product in the acid-catalyzed reaction also.



If, instead, a unimolecular ring opening[14] occurs in the acid-catalyzed reaction, the formation of the abnormal product may be accounted for.



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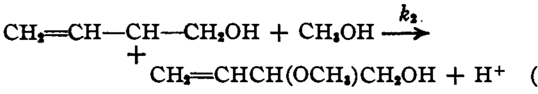

$$CH_2{=}CH{-}\underset{+}{CH}{-}CH_2OH + CH_3OH \xrightarrow{k_2} CH_2{=}CHCH(OCH_3)CH_2OH + H^+ \quad (2)$$

The unimolecular ring opening[15] is assisted by the resonance stabilization of the intermediate carbonium ion ($CH_2{=}CH{-}{}^+CH{-}CH_2OH \longleftrightarrow {}^+CH_2{-}CH{=}CH{-}CH_2OH$). It was found that the rate of the reaction depends upon the methanol concentration. This is consistent with the unimolecular mechanism provided that $k_{-1} \gg k_2$.

One might expect the resonating carbonium ion intermediate to also give rise to $CH_3OCH_2CH{=}CHCH_2OH$, derived from the resonance structure ${}^+CH_2CH{=}CHCH_2OH$. Such a result would be a new type of terminal addition occurring at the ends of the conjugated double bond-epoxide ring system. A small amount of higher boiling material corresponding closely in properties to 4-methoxy-2-buten-1-ol was actually obtained but attempts at positive identification were unsuccessful. However, from the addition of hydrochloric acid to 3,4-epoxy-1-butene there was isolated a small higher boiling fraction in about 2% yield which was identified as 1-chloro-2-buten-4-ol. The identification consisted of preparing the α-naphthylurethan and demonstrating its identity with the α-naphthylurethan of an authentic specimen by melting point and mixed melting point.

On the basis of the present results it becomes significant that the few examples of abnormal addition to unsymmetrical epoxides, described in the literature, involve acid catalysis. 1-Bromo-3,4-epoxy-1-butene[16] reacts abnormally with hydrogen bromide as does 2-chloro-3,4-epoxy-1-butene[17] with hydrogen chloride. Styrene oxide reacts abnormally with hydrogen iodide to give $C_6H_5CHICH_2OH$.[18] Unimolecular ring opening of the oxonium intermediate and resonance stabilization of the resulting carbonium ion intermediate are undoubtedly also involved in these reactions with hydrogen halides. The intermediate carbonium ion from styrene oxide, $C_6H_5{-}{}^+CHCH_2OH$, is stabilized by resonance with three quinoid structures. Isobutylene oxide is abnormal in its acid-catalyzed reaction with alcohols to give $(CH_3)_2C(OR)CH_2OH$,[19] which appears to involve S_N1 ring opening. The latter two epoxides are known to react normally with ammonia and amines.[1,20]

In contradiction to these considerations is the report of Emerson[21] that styrene oxide reacts with alcohols in the presence of sulfuric or phosphoric acid to give the normal product, $C_6H_5{-}CH(OH)CH_2OR$. However, no proof of structure was given.[22] The present theory would call for

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(13) Späth, *Monatsh.*, **36**, 1 (1915); Rider and Hill, THIS JOURNAL, **52**, 1521 (1930).

(14) The possibility of unimolecular (S_N1) ring opening in "onium" rings of this type has been pointed out, Winstein and Buckles, THIS JOURNAL, **64**, 2780 (1942), footnote 25.

(15) Step 1 also accounts for the side reaction of aldehyde formation during the acid-catalyzed hydration of 3,4-epoxy-1-butene and its analogs, Pummerer and Reindel, *Ber.*, **66B**, 335 (1933); Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **13**, 481 (1943). Support for this interpretation comes from the observation of aldehyde formation (1) as a side reaction in the hydrolysis of 2-chloro-3-buten-1-ol or 1-chloro-2-buten-4-ol by water and in (2) the treatment of erythrol with aqueous sulfuric acid, reactions which undoubtedly involve the ion, $CH_2{=}CH{-}{}^+CH{-}CH_2OH \longleftrightarrow + CH_2{-}CH{=}CH{-}CH_2OH$ (unpublished findings from this Laboratory).

(16) Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 1887 (1940).

(17) Petrov, *ibid.*, **9**, 2232 (1939).

(18) Tiffeneau, *Ann. chim.*, [8] **10**, 342 (1907); Golumbic and Cottle, THIS JOURNAL, **61**, 996 (1939).

(19) Sparks and Nelson, *ibid.*, **58**, 671 (1936); Edlund, U. S. Patent 1,968,032; Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **10**, 981 (1940).

(20) Tiffeneau and Fourneau, *Compt. rend.*, **146**, 697 (1908); Kitchen and Pollard, *J. Org. Chem.*, **8**, 342 (1943); Emerson, THIS JOURNAL, **67**, 516 (1945).

(21) Ref. 20; see also Thomas and Hochwalt, U. S. Patent 2,372,615.

(22) Emerson merely indicated a correspondence in physical properties with the monoether prepared from $C_6H_5CH(OH)CH_2Cl$, ROH and aqueous alkali. The close similarity in physical properties between the similar pair, II and III, makes this evidence of doubtful value.

the structure, $C_6H_5CH(OR)CH_2OH$, for Emerson's products as would the known abnormal addition of hydroiodic acid to styrene oxide.[18]

Experimental[23]

1-Chloro-3-buten-2-ol (VIII).—In a typical preparation a mixture of butadiene and carbon dioxide (6:1) was passed into a stirred 3.5% calcium hypochlorite solution (0.845 mole) at 0–3°. The reaction was complete after 1.8 hours as observed by the disappearance of oxidizing power toward potassium iodide. The mixture was filtered to remove calcium carbonate, saturated with sodium chloride and extracted four times with one-sixth its volume of ether. The combined ether extracts were distilled through a short Vigreux column. 1-Chloro-3-buten-2-ol[24] was collected at 65–68° (35 mm.), n^{20}_{D} 1.4650, 52% yield. Higher boiling material containing considerable dichlorohydrin was obtained.

Distillation of a portion of the chlorohydrin through a 1.7 × 75-cm. Fenske column packed with glass helices gave a material of b. p. 64.0–64.8° (30 mm.), n^{20}_{D} 1.4660, d^{20}_{4} 1.111.

The 3,5-dinitrobenzoate was obtained as white plates from aqueous ethanol, m. p. 61.5–63.5°.

3,4-Epoxy-1-butene (I).—In a typical preparation 106.5 g. (one mole) of 1-chloro-3-buten-2-ol was added to 1.5 moles of 50% sodium hydroxide at 115–135° with agitation during one hour. The 3,4-epoxy-1-butene was continuously removed as it was formed, the vapor temperature being 60–68°. When the rate of evolution decreased an additional 0.5 mole of 50% sodium hydroxide was added dropwise giving rise to an additional amount of epoxide. The distillate consisted of two phases (3,4-epoxy-1-butene is only 6% soluble in water) to which sodium chloride was added. The upper organic layer was separated, dried over calcium chloride and distilled from a modified Claisen flask to give 58.9 g. (84% yield) of 3,4-epoxy-1-butene[24,25] at 65–72°, n^{20}_{D} 1.4162.

A portion was distilled through a 1.1 × 45-cm. Fenske column packed with glass helices to give a material of b. p. 65.0–65.8° (739 mm.), n^{20}_{D} 1.4170, d^{20}_{4} 0.875.

2-Chloro-3-buten-1-ol (VII).—To two moles of concentrated hydrochloric acid a solution of 70 g. (1.0 mole) of 3,4-epoxy-1-butene in 100 cc. of ether was added with stirring during seventy minutes below 5°. Stirring was continued for one hour and the excess hydrochloric acid neutralized with solid sodium carbonate. The aqueous layer was saturated with ammonium sulfate, separated and extracted with ether. The combined ether solutions were washed with ammonium sulfate solution, dried over sodium sulfate and distilled through a 25-cm. wire spiral packed column. The product had b. p. 65–67° at 28 mm.,[10] n^{20}_{D} 1.4655, yield 61%.

Anal. Calcd. for C_4H_7OCl: Cl, 33.3. Found: Cl, 32.8.

In another preparation two moles of 3,4-epoxy-1-butene was added to three moles of concentrated hydrochloric acid below 10°. The yield was 57%.

Some 2-chloro-3-buten-1-ol was carefully purified by distillation (performed by Mr. R. H. Fredenburg) through a 1.7 × 75-cm. Fenske column packed with glass helices, b. p. 69.5–70.0° at 30 mm., n^{20}_{D} 1.4665.

The 3,5-dinitrobenzoate, m. p. 65.5° from aqueous ethanol, showed a mixed m. p. of 48–55° with the 3,5-dinitrobenzoate of 1-chloro-3-buten-2-ol.

Reaction of 3,4-Epoxy-1-butene with Methanol

(A) Sulfuric Acid Catalyst.—Several reactions were carried out in the presence of 0.5% of sulfuric acid using three equivalents of methanol. Certain variations in reaction conditions were made and are indicated in Table I. The product was obtained after shaking the mixture with a little solid potassium carbonate and distilling from a modified Claisen flask. In preparation one there was collected, in addition to the main product, some material with b. p. 87–98° (6 mm.), n^{20}_{D} 1.453, Hanus iodine number 276 (calculated for $C_9H_{16}O_3$, 298), which was probably the secondary product from the alcohol initially formed and more epoxide.

(B) Sodium Catalyst.—Also several reactions were carried out using three equivalents of methanol to which 1% (of total reactants) of sodium was added. The variations in reaction conditions employed are given in Table I. The reaction mixture was distilled directly from a modified Claisen flask except in preparations 8 and 9 in which the mixture was first neutralized with sulfuric acid (some gelatinous precipitate formed at this point) and filtered.

Effect of Methanol Concentration on the Rate of the Acid-Catalyzed Reaction of 3,4-Epoxy-1-butene with Methanol.—The rate of reaction of 0.1 *M* 3,4-epoxy-1-butene in dry ether containing 0.002 *M* sulfuric acid was observed at 20° by determining[9b] the unreacted epoxide. After seventeen and one-half hours 0.43% of the epoxide had reacted when 0.1 *M* methanol was used and 2.41% had reacted when 0.5 *M* methanol was present.

Oxidation of 2-Methoxy-3-buten-1-ol (III).—Some 2-methoxy-3-buten-1-ol (preparation 1) was heated for two hours with sodium dichromate in 60% sulfuric acid. An oil was isolated which was refluxed with thionyl chloride for thirty-five minutes and poured into concentrated ammonium hydroxide. The solid amide obtained was crystallized twice from water and dried. It sublimed in a closed tube at 200–210°[26] but did not melt.

Saponification equivalent for methoxymalonamide was 66.0 (calcd.); 64.4 (found).

The possibility of the amide being methoxyacetamide was eliminated since it has m. p. 96.5°[27] and its saponification equivalent is 89 (calcd.).

1(2)-Chloro-2(1)-methoxy-3-butene (V, VI).—Phosgene was passed into some 1-methoxy-3-buten-2-ol (II, preparation 6) at room temperature. Two drops of pyridine were added to the crude chloroformate, decomposition[28] being achieved by heating gently on the steam-bath for sixty-five minutes when carbon dioxide evolution was essentially complete. The product was distilled, boiling point about 78° at 70 mm. This product had a sharp, penetrating odor and showed a negative test for chloroformate chlorine (no carbon dioxide evolution on treatment with 20% aqueous pyridine). The determination of the chloride ion liberated showed that a 0.044 molar solution of the chloride in 25% aqueous ethanol hydrolyzed at 70° to the extent of 50% after seventy minutes and 71% after seven hours.

Some 2-methoxy-3-buten-1-ol (III, preparation 2) was converted to its chloroformate by the method above. In this case satisfactory decomposition was achieved in the presence of pyridine only by heating in a bath at 120–134° for one and one-half hours. The mixture, giving a negative test for chloroformate chlorine, was filtered and the filtrate distilled through a short column. A 0.036 molar solution of the chloride in 25% aqueous ethanol hydrolyzed at 70° to the extent of 9% after seventy minutes and 28% after seven hours.

Benzoylation of Erythrol Monomethyl Ether (II, III).—The procedure used to determine the relative ease of benzoylation of various erythrol monomethyl ether samples was as follows: In a 3-cc. test-tube were placed 22 drops (0.0029 mole) of Eastman Kodak Co. benzoyl chloride, freshly redistilled, twelve drops (0.0017 mole) of the sample and 0.7 cc. of diethylaniline. The tube was stoppered, shaken thoroughly and placed in a thermostat at 50° for ninety minutes. The amount of reaction occur-

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(23) All melting points are uncorrected.

(24) Petrov, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 131 (1938); **11**, 991 (1941).

(25) (a) Petrov, *ibid.*, **8**, 142 (1938); *C. A.*, **32**, 6616 (1938); (b) Pariselle, *Compt. rend.*, **150**, 1343 (1910); *Ann. chim.*, **24**, 315 (1911); (c) Pummerer and Reindel, *Ber.*, **66B**, 335 (1933).

(26) Methoxymalondiamide has been reported to have m. p. 203–204° (slight dec.), Pryde and Williams, *J. Chem. Soc.*, 1627 (1933).

(27) Kilpi, *Z. physik. Chem.*, **80**, 182 (1912).

(28) Houssa and Phillips, *J. Chem. Soc.*, 2510 (1929).

ring was determined by titrating the hydrogen chloride liberated.[29] The results in terms of the per cent. of sample reacting are contained in Table I.

Authentic samples of 1-chloro-3-buten-2-ol and 2-chloro-3-buten-1-ol (structurally analogous to the two isomeric erythrol monomethyl ethers) reacted to the extent of 12 and 43%, respectively, by this method. In this case 0.0019 mole of sample was used.

Reaction of 2-Chloro-3-buten-1-ol (VII) with Sodium Methoxide.—To 0.35 mole of sodium methoxide in 110 cc. of methanol there was added 37.3 g. (0.35 mole) of 2-chloro-3-buten-1-ol with stirring during thirty-five minutes at 40–50°. The separation of sodium chloride began immediately. The mixture was refluxed for thirty minutes, filtered and distilled through a 25-cm. column packed with a wire spiral (see Table I). The yield of methoxybutenol was 52%. Its 3,5-dinitrobenzoate was prepared and crystallized three times from aqueous ethanol, m. p. 68–71°.

Reaction of 1-Chloro-3-buten-2-ol (VIII) with Sodium Methoxide

(A) To Give Methoxybutenol.—The reaction was carried out as was the one with 2-chloro-3-butene-1-ol above except that refluxing was for three hours (see Table I). The yield of methoxybutenol was 51%. Its 3,5-dinitrobenzoate was crystallized from aqueous ethanol, m. p. 70°. The mixed melting point between this and the 3,5-dinitrobenzoate from preparation 5 was 70–71°.

(B) To Give 3,4-Epoxy-1-butene.—To 0.15 mole of sodium methoxide in 40 cc. of methanol was added 15.9 g. (0.15 mole) of 1-chloro-3-buten-2-ol at one time. The separation of sodium chloride began immediately. The mixture was allowed to remain at room temperature with frequent shaking for thirty-five minutes. The mixture was distilled at 16–20 mm. pressure (vapor temperature 24–25°) almost to complete dryness. Titration of an aliquot of the distillate for the presence of the epoxide ring using ethereal hydrogen chloride[9b] indicated a 55% yield of 3,4-epoxy-1-butene.

Identification of 1-Chloro-2-buten-4-ol as a Product of the Reaction of Hydrochloric Acid with 3,4-Epoxy-1-butene.—From a preparation of 2-chloro-3-buten-1-ol from 3,4-epoxy-1-butene (one mole), carried out as above, there was collected, in addition to the main product (40.2 g., 54% yield) at 65–66° (24–29 mm.), 8.1 g. of higher boiling material at 56–62° (3–4 mm.). This was redistilled from a small flask to give (1) b. p. 34° (5 mm.) to 53° (2 mm.), $n^{20.5}_D$ 1.4735, (2) b. p. 54–55° (2 mm.), $n^{20.5}_D$ 1.4792, and a residue. The α-naphthylurethan of fraction 2 was needles from ligroin, m. p. 88–90°. The α-naphthylurethan of an authentic sample of 1-chloro-2-buten-4-ol, prepared from butadiene and hypochlorous acid,[11] melted at 88–89°. A mixed melting point on the two urethans showed no depression. The yield of 1-chloro-2-buten-4-ol based on 3,4-epoxy-1-butene was about 2%.

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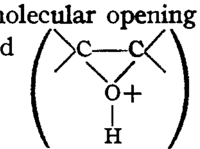
Summary

1. The addition of methanol to 3,4-epoxy-1-butene in the presence of sodium produced, at least predominantly, 1-methoxy-3-buten-2-ol. However, in the presence of sulfuric acid the addition was reversed giving 2-methoxy-3-buten-1-ol. In this case the direction of ring opening was opposite to that usually experienced with epoxides and has been termed "abnormal."

2. It has been suggested that the abnormal reaction involves an unimolecular opening of the ring in the conjugate acid  of the epoxide rather than the usual bimolecular opening in one step with Walden inversion. This forms a resonating carbonium ion intermediate ($CH_2{=}CH{-}{}^+CH{-}CH_2OH \longleftrightarrow {}^+CH_2{-}CH{=}CH{-}CH_2OH$). This intermediate also accounts for the formation of small amounts of 1-chloro-2-buten-4-ol in the addition of hydrochloric acid to 3,4-epoxy-1-butene and for aldehyde formation during the acid-catalyzed hydration of the latter.

3. The addition reactions of 1,2-epoxides have been discussed briefly. The suggestion was made that a few other acid-catalyzed ring openings of styrene oxide, isobutylene oxide and 3,4-epoxy-1-butene derivatives which proceed abnormally also involve unimolecular opening and a carbonium ion intermediate.

4. The reaction of both 1-chloro-3-buten-2-ol and 2-chloro-3-buten-1-ol with sodium methoxide gave 1-methoxy-3-buten-2-ol. The epoxide was the intermediate in each case.

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[29] Norris and Haines, THIS JOURNAL, 57, 1425 (1935).