thienylmagnesium bromide in 200 mg. of absolute ether cooled in an ice-bath, was added 90 g. (0.75 mole) of styrene oxide in an equal volume of ether. The mixture solidified upon standing overnight. The Grignard addition product was decomposed with a saturated solution of ammonium chloride as described above. The ether was removed under reduced pressure and the product I was collected at 169–170° (8 mm.), and fractionated to yield 96.1 g., b.p. 155–160° (4 mm.), yield 63%. *Anal.* Calcd. for $C_{12}H_{12}OS$; C, 71.02; H, 5.92; S, 15.77. Found: C, 71.30; H, 5.86; S, 15.57; phenylurethan, m.p. 106.5–107°. *Anal.* Calcd. for $C_{19}H_{17}O_2NS$: N, 4.33; S, 9.91. Found: N, 4.37; S, 9.71.

1-(2-Thienyl)-3-chloro-2-propanol (VI) from 2-Thienylmagnesium Bromide.—One mole of epichlorohydrin was added to 0.5 mole of 2-thienylmagnesium bromide in 400 ml. of absolute ether at 0–10°. The resulting mixture was hydrolyzed with a saturated solution of ammonium chloride and distilled to give 62.2 g. (0.485 mole) of 1,3-dichloro-2-propanol (b.p. 84° (16 mm.)) which results from the excess of epichlorohydrin. Fifty-three grams of VI was then collected; b.p. 119–122° (8 mm.), yield 60.5%. *Anal.* Calcd. for C_7H_9OSCl: S, 18.15; Cl, 20.07. Found: S, 17.93; Cl, 19.87. The phenylurethan melted at 87°. *Anal.* Calcd. for $C_{14}H_{14}O_2NSCl$: N, 4.74; S, 10.84. Found: N, 4.61; S, 10.94.

1-(2-Thienyl)-3-chloro-2-propanol (VI) from 2-Thienylsodium.—To 0.25 mole of 2-thienylsodium in 125 ml. of benzene was added 0.35 mole of epichlorohydrin with cooling. After stirring overnight the mixture was acidified by passing dry hydrogen chloride into the mixture cautiously while cooling the flask. The benzene was distilled under reduced pressure after the sludge was filtered out and 11.7 g. of 1,3-dichloro-2-propanol was obtained. Fourteen and eight-tenths grams of 1-(2-thienyl)-3-chloro-2-propanol (VI) was obtained; b.p. 120–121° (7 mm.), yield 32.5%. The phenylurethan melted at 86–87° and the melting point was not depressed when mixed with a sample obtained by the Grignard method.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Some Nucleophilic Displacements on 3-Bromo-1,2-epoxybutane and 1-Bromo-2,3-epoxybutane

BY RUSSELL C. WATERS[1] AND CALVIN A. VANDERWERF

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Reaction of 3-bromo-1,2-epoxybutane (I) and of 1-bromo-2,3-epoxybutane (II) with a molar quantity of sodium methoxide in methanol and of sodium ethoxide in ethanol has been shown in each case to yield mainly the corresponding 1-alkoxy-2,3-epoxybutane, indicating that the nucleophilic displacements involved occur preferentially at the primary carbon, without regard for the nature of the substituent at the primary position. The only other and minor product in every case was the corresponding 1,2-dialkoxy-3-butanol, probably formed by further reaction of the major product with alkoxide. Reduction of the 1-alkoxy-2,3-epoxybutanes with lithium aluminum hydride yielded the corresponding 1-alkoxy-2-butanols. With the quantity of lithium aluminum hydride theoretically required to reduce only one of the two functional groups, I gave a mixture of *threo*-3-bromo-2-butanol and 2-butanol and II only 2-butanol and recovered II. Heated with 50% sulfuric acid, 1,2-dimethoxy-3-butanol (IV) was converted to 1-methoxy-2-butanone (VII). The theoretical implications of these results are discussed.

Surprisingly little is known about the relative reactivities toward nucleophilic agents of the halogen-bearing *vs.* the epoxide-ring carbon atoms in α-halogenated epoxides. Many nucleophilic displacements on epichlorohydrin, under typical SN2 conditions, in which the nature of the products clearly indicates preferential attack at the primary carbon of the epoxide ring, are, of course, reported.[2] Trevoy and Brown[3] have commented specifically on the fact that in the reaction of epichlorohydrin with lithium aluminum hydride, the replacement of chlorine by hydrogen proceeds at a slower rate than the reduction of the epoxide ring. Gilman, *et al.*,[4] likewise accept the interpretation[5] that the first step in the synthesis of 1-diethylamino-2,3-epoxypropane from epichlorohydrin and diethylamine is fission of the epoxide ring. In fact all of the reactions of epichlorohydrin which ostensibly consist merely of a displacement of the chlorine by a nucleophilic agent under typical SN2 conditions may possibly proceed *via* initial attack with ring opening at the primary carbon atom of the epoxide-ring to form an intermediate chlorine-containing alkoxide ion, followed by intramolecular displacement of the chloride ion by the alkoxide oxygen with epoxide ring formation in the new position.

Haynes and co-workers[6] have quite recently reported an interesting reaction between epichlorohydrin and sodium acetylide in which pent-2-en-4-yn-1-ol, HC≡C—CH=CH—CH$_2$OH, is the major product. The conclusion of these workers that the first step in the reaction is the substitution of the chlorine atom of epichlorohydrin was based in part upon analogy with the reaction between 1-bromo-2,3-epoxybutane (II) and sodium acetylide, wherein hex-3-en-5-yn-2-ol, HC≡C—CH=CH—CH(OH)—CH$_3$, was the principal product. The two cases are not entirely comparable, however, inasmuch as the change from chlorine to bromine and from an epoxide in which one of the ring carbon atoms is primary to an epoxide in which both are secondary would definitely tend to favor an increase in attack at the halogen-bearing carbon.

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[1] H. P. Cady Fellow, 1950–1952.

[2] See, for example, W. Traube and E. Lehrman, *Ber.*, **34**, 1941 (1901).

[3] L. W. Trevoy and W. G. Brown, THIS JOURNAL, **71**, 1675 (1949).

[4] H. Gilman, C. S. Sherman, C. C. Price, R. C. Elderfield, J. T. Maynard, R. H. Reitsema, L. Tolman, S. P. Massie, Jr., F. J. Marshall and L. Goldman, *ibid.*, **68**, 1291 (1946).

[5] N. S. Droszdov and O. M. Cherntzov, *J. Gen. Chem.* (*U.S.S.R.*), **4**, 969 (1934); see also N. S. Droszdov and O. M. Cherntzov, *ibid.*, 1305 (1934).

[6] L. J. Haynes, I. Heilbron, E. R. H. Jones and P. Sondheimer, *J. Chem. Soc.*, 1583 (1947).

Culvenor and co-workers[7] have reported similar reactions of epichlorohydrin with sodium toluene-*p*-sulfinate and with sodium cyanide forming 3-*p*-tolylsulfonylprop-2-en-1-ol, *p*-CH_3—C_6H_4—SO_2—CH=CH—CH_2OH, and γ-hydroxycrotononitrile, CN—CH=CH—CH_2OH, respectively; they hold that the initial step in these reactions is nucleophilic attack on the ethylene oxide ring.[8]

We have undertaken a study of the mechanism of nucleophilic displacements on a pair of isomeric epoxides, 3-bromo-1,2-epoxybutane (I) and 1-bromo-2,3-epoxybutane (II) which will yield different products, depending upon the mechanism of displacement. The present paper reports the investigation of the reactions of these epoxides with sodium methoxide in methanol, with sodium ethoxide in ethanol and with lithium aluminum hydride in ether.

Results

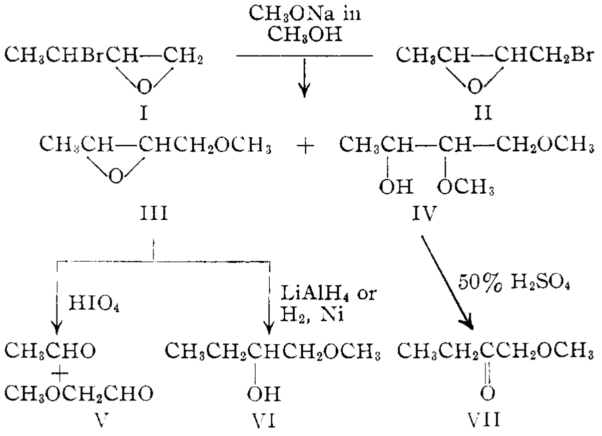
Reaction of 3-bromo-1,2-epoxybutane (I) with a molar quantity of sodium methoxide in absolute methanol afforded a mixture of 1-methoxy-2,3-epoxybutane (III) (42% of the theoretical) and 1,2-dimethoxy-3-butanol (IV) (34% of the theoretical). Similar treatment of 1-bromo-2,3-epoxybutane (II) gave a mixture of III (68%) and IV (16%). IV was obtained in 80% yield by treatment of III with a molar amount of sodium methoxide.

The structure of III was proved by the following: (a) quantitative results in estimation of oxirane oxygen by two methods[9]; oxidation of III with periodic acid[9b] to acetaldehyde and methoxyacetaldehyde (V); reduction, both catalytically and with lithium aluminum hydride, to 1-methoxy-2-butanol (VI) and independent synthesis of III by dehydrohalogenation of the chlorohydrin obtained by addition of hypochlorous acid to methyl crotyl ether.

The structure of IV was established by means of these facts: IV was shown by a Zeisel determination to contain two methoxyl groups; IV gave a positive iodoform test; heated with 50% sulfuric acid, IV was converted into 1-methoxy-2-butanone (VII).

The reactions of I and II with a molar quantity of sodium ethoxide in ethanol paralleled those with sodium methoxide in methanol. I yielded 83% of 1-ethoxy-2,3-epoxybutane and 4% of 1,2-diethoxy-3-butanol. II gave 78% of 1-ethoxy-2,3-epoxybutane and 6% of 1,2-diethoxy-3-butanol. Proof of structure of the products was analogous to that used for the corresponding methoxy homologs, III and IV.

Upon reduction with the quantity of lithium aluminum hydride theoretically required to reduce only one of the two functional groups, I yielded a mixture of *threo*-3-bromo-2-butanol (51%) and 2-butanol (24%). II, on the other hand, gave only 2-butanol (46%) and recovered starting material (42%).



Experimental[10]

Reactions of 3-Bromo-1,2-epoxybutane (I) and of 1-Bromo-2,3-epoxybutane (II) with Sodium Methoxide.—To a stirred solution of 50 g. (0.33 mole) of I,[11] b.p. 146°[12] at 741 mm., in 100 ml. of absolute methanol, a solution of 7.7 g. (0.33 mole) of sodium methoxide was added dropwise with stirring over a 3-hr. period. Stirring and refluxing were continued for 12 hr. during which the theoretical amount of sodium bromide precipitated. The methanol was then removed by distillation, the remaining liquid was extracted three times with 30-ml. portions of absolute ether, and the ether was removed from the combined extracts. Distillation of the residue afforded 14 g. (42%) of 1-methoxy-2,3-epoxybutane (III), b.p. 53° at 50 mm., 124° at 745 mm., $n^{13}D$ 1.4107, $n^{21}D$ 1.4081 and 15 g. (34%) of 1,2-dimethoxy-3-butanol (IV), b.p. 94° at 50 mm., 169–170° at 730 mm., $n^{24}D$ 1.4214. Similarly treated, II,[10] b.p. 144.0–146.2°, gave, in addition to 7% of recovered II, 67.6% of III, b.p. 53.5–54.5° at 55 mm., 121–122° at 730 mm., $n^{10}D$ 1.4096, $n^{21}D$ 1.4045, d^{21}_4 0.9410, and 16.4% of IV, b.p. 93.5–94.2° at 55 mm., 168–170° at 730 mm., $n^{13}D$ 1.4248, $n^{24}D$ 1.4204, d^{21}_4 0.9849.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.8; H, 9.9. Found: C, 58.7; H, 9.7. Calcd. for $C_6H_{14}O_3$: C, 53.7; H, 10.4. Found: C, 53.7; H, 10.4.

Determination of the oxirane oxygen[9] in III and IV gave 99.4% and 98.7%, respectively, of the theoretical values. IV showed a positive iodoform test, and a typical Zeisel determination[13] gave the calculated values for two methoxyl groups.

Reaction of 1-Methoxy-2,3-epoxybutane (III) with Sodium Methoxide.—Sodium (4.6 g., 0.2 mole) was dissolved in 100 ml. of absolute methanol, and to the resulting solution 20.0 g. (0.196 mole) of III was added. The mixture was refluxed for 4 hr. and allowed to stand without heating for an additional 18 hr. Water (15 ml.) was added and the mixture was extracted five times with 50-ml. portions of ether. Distillation of the residue, after removal of the ether from the combined extracts, gave 21 g. (80%) of 1,2-dimethoxy-3-butanol (IV), b.p. 49° at 55 mm., $n^{24}D$ 1.4213.

Reaction of 1-Methoxy-2,3-epoxybutane (III) with Periodic Acid.—Two ml. of III was added to a solution of 5 g. of periodic acid (H_5IO_6) in 10 ml. of water containing 0.2 ml. of concentrated sulfuric acid. An exothermic reaction ensued, and external cooling was required to keep the temperature at 30°. The vapors which distilled were allowed to pass into a solution of 2,4-dinitrophenylhydrazine.[14] The yellow 2,4-dinitrophenylhydrazone which precipitated

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(7) C. C. J. Culvenor, W. Davies and W. E. Savige, *ibid.*, 2198 (1949); C. C. J. Culvenor, W. Davies and F. G. Haley, *ibid.*, 3123 (1950).

(8) C. C. J. Culvenor, private communication.

(9) (a) D. Swern, T. W. Findley, G. N. Billen and J. T. Scanlan, *Anal. Chem.*, **19**, 414 (1947); (b) R. Fuchs, R. C. Waters and C. A. VanderWerf, *ibid.*, **24**, 1514 (1952).

(10) All melting points are corrected, boiling points uncorrected.

(11) Prepared by the method of A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 713 (1941).

(12) In repeated attempts, neither could we obtain significant amounts of a diastereoisomer reported by Petrov,[11] nor, upon very careful fractionation, did we observe the wide distillation range for I upon which he specifically commented.

(13) S. Siggia, "Quantitative Organic Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 27.

(14) Prepared according to R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

melted at 165.5–166.8° after recrystallization from ethanol and did not depress the m.p. of an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone. When spontaneous distillation had ceased, additional acetaldehyde was removed at 35° under 40 mm. pressure. Silver nitrate solution (5 g. in 5 ml. of water) was then added to the residue and the precipitated silver salts were removed by filtration. Excess silver ion was removed from solution by addition of 1 g. of sodium chloride, the precipitated silver chloride being filtered. The filtrate was then mixed with 2,4-dinitrophenylhydrazine solution and the resulting precipitate recrystallized from 75% ethanol. The yellow, needle-like crystals of the 2,4-dinitrophenylhydrazone of methoxyacetaldehyde (V) melted at 123.1–125.0° and did not depress the m.p. of the 2,4-dinitrophenylhydrazone prepared from an authentic sample of methoxyacetaldehyde, obtained by oxidation of methyl cellosolve with chromic anhydride.[15]

Reduction of III.—A solution of 30.0 g. (0.294 mole) of III in 50 ml. of anhydrous ether was added dropwise to a solution of 4.00 g. (0.105 mole) of lithium aluminum hydride in 50 ml. of ether contained in a 250-ml. erlenmeyer flask fitted with a magnetic stirrer, a reflux condenser and a dropping funnel. The solution refluxed vigorously during the addition (30 minutes) and was maintained at the boiling point with stirring for 3 hr. longer. Then 20 ml. of water was added, and the pasty solid which settled was removed by filtration and washed three times with 15 ml. of ether. The combined ether extracts were dried over magnesium sulfate, the ether removed and the residue distilled yielding as the only product 25.0 g. (81.6%) of 1-methoxy-2-butanol (VI), b.p. 135° at 740 mm., n^{25}_{D} 1.4115.[16]

Anal. Calcd. for $C_5H_{12}O_2$: C, 57.7; H, 11.6. Found: C, 57.8; H, 11.5.

The 3,5-dinitrobenzoate, m.p. 90.0–91.2° (reported[16] 91°), did not depress the m.p. of the 3,5-dinitrobenzoate of an authentic sample of 1-methoxy-2-butanol prepared by reaction of 1,2-epoxybutane with sodium methoxide.

Anal. Calcd. for $C_{12}H_{14}N_2O_7$: C, 48.3; H, 4.7; N, 9.4. Found: C, 48.5; H, 4.5; N, 9.2.

A sample of 1-methoxy-2-butanol was also oxidized, by means of sodium dichromate in sulfuric acid, to 1-methoxy-2-butanone, b.p. of azeotrope with water 90° (reported[17] 90°), m.p. of 2,4-dinitrophenylhydrazone 197.2–198.3° (reported[18] 198.0–198.5°).

Hydrogenation of III with Raney nickel catalyst at 130° and 75 atm. afforded VI in 61.4% yield.

Synthesis of III from Crotyl Alcohol.—According to the general method of Hiers and Hager,[19] 72.0 g. (1 mole) of crotyl alcohol was mixed with a cold solution of 80.0 g. (2 moles) of sodium hydroxide in 200 ml. of water, and 189 g. (1.5 mole) of dimethyl sulfate was added to this heterogeneous mixture at 15–25° over the course of 2 hr. with vigorous stirring. Cooling and stirring were continued for 4 additional hr. The upper layer was then separated and dried over potassium carbonate. Distillation afforded 20.0 g. of recovered crotyl alcohol and 32.0 g. (51.7% based on crotyl alcohol not recovered) of methyl crotyl ether, b.p. 79° at 741 mm. (reported[18] 79°). The ether was then treated with hypochlorous acid according to the general method of Donahoe and VanderWerf[20] and the crude product mixture was added dropwise with stirring to a solution of 188 g. of potassium hydroxide in 50 ml. of water at 140–160°. The material which distilled during the operation was collected and dried over potassium carbonate. Distillation afforded, in addition to 30.0 g. of recovered methyl crotyl ether, 6.5 g. of 1-methoxy-2,3-epoxybutane (III), b.p. 53° at 50 mm., which gave all the tests and reactions already described for III.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.8; H, 9.9. Found: C, 58.5; H, 9.6.

Conversion of 1,2-Dimethoxy-3-butanol (IV) to 1-Methoxy-2-butanone (VII).—A mixture of 10.0 g. of IV and 10 ml. of 50% sulfuric acid was heated to the boiling point and 10 ml. of distillate collected. The distillate was dried over potassium carbonate and redistilled yielding 1.9 g. of methanol and 2.5 g. of an azeotropic mixture of water and 1-methoxy-2-butanone (VII), b.p. 88–90°. The 2,4-dinitrophenylhydrazone melted at 197.5–198.5° and did not depress the m.p. of the corresponding derivative of the ketone obtained by oxidation of 1-methoxy-2-butanol.

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.8; H, 5.0; N, 19.9. Found: C, 46.7; H, 5.1; N, 19.5.

Reactions of I and of II with Sodium Ethoxide.—I, treated with sodium ethoxide exactly as described for sodium methoxide, gave 83.3% of 1-ethoxy-2,3-epoxybutane, b.p. 76° at 80 mm., 138° at 731 mm., n^{25}_{D} 1.4100, and 4.0% of a liquid, b.p. 194–195° at 727 mm., n^{20}_{D} 1.4302, believed by analogy with the sodium methoxide case, to be 1,2-diethoxy-3-butanol. Similarly treated, II afforded 1-ethoxy-2,3-epoxybutane, b.p. 137.0–138.5° at 747 mm., n^{23}_{D} 1.4073, in 77.7% yield and 1,2-diethoxy-3-butanol, b.p. 194–197° at 747 mm., n^{24}_{D} 1.4248, in 6.2% yield. 1-Ethoxy-2,3-epoxybutane was readily converted to 1,2-diethoxy-3-butanol by further treatment with sodium ethoxide in ethanol.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.0; H, 10.4. Found: C, 61.7; H, 10.2. Calcd. for $C_8H_{18}O_3$: C, 59.2; H, 11.2. Found: C, 59.0; H, 11.0.

Determination of oxirane oxygen in the 1-ethoxy-2,3-epoxybutane gave 98.8% of the theoretical value. Periodic acid oxidation of 1-ethoxy-2,3-epoxybutane afforded a mixture of acetaldehyde and ethoxyacetaldehyde, m.p. of 2,4-dinitrophenylhydrazone 116.1–117.2°,[21] undepressed by admixture with an authentic sample of the 2,4-dinitrophenylhydrazone of ethoxyacetaldehyde, prepared by oxidation of ethyl cellosolve.[15]

Anal. Calcd. for $C_{10}H_{12}N_4O_5$: C, 44.8; H, 4.5; N, 20.9. Found: C, 44.9; H, 4.4; N, 21.2.

Reduction of 1-ethoxy-2,3-epoxybutane with lithium aluminum hydride gave 1-ethoxy-2-butanol, b.p. 145–147° at 740 mm., n^{20}_{D} 1.4135, in 59% yield. Catalytic hydrogenation afforded the same product in 54% yield. The physical constants of 1-ethoxy-2-butanol were identical with those of an authentic sample prepared by reaction of 1,2-epoxybutane with sodium ethoxide. Oxidation of the alcohol with chromic anhydride yielded 1-ethoxy-2-butanone, b.p. 145–147°,[22] m.p. of 2,4-dinitrophenylhydrazone **145.1–146.2**.[23]

Anal. Calcd. for $C_{12}H_{16}N_4O_5$: C, 48.6; H, 5.4; N, 18.9. Found: C, 48.8; H, 5.3; N, 19.1.

A Zeisel determination of 1,2-diethoxy-3-butanol indicated the presence of two ethoxyl groups. The compound also gave a positive iodoform test.

Reactions of I and of II with Lithium Aluminum Hydride.—To a solution of 3.0 g. (0.078 mole) of lithium aluminum hydride in 30 ml. of ether, a solution of 42 g. (0.28 mole) of I in 50 ml. of anhydrous ether was added dropwise with vigorous stirring over the course of 0.5 hr. The mixture was refluxed for 2 additional hr. and then cooled in an ice-bath while 30 ml. of water was added. The upper ether layer was removed by decantation and the remaining pasty mass was extracted with three 25-ml. portions of ether. The combined extracts were dried over magnesium sulfate and the ether removed. Distillation of the residue yielded 5.0 g. (24%) of 2-butanol, identified by means of physical constants and as the 3,5-dinitrobenzoate, and 22.0 g. (51.4%) of *threo*-3-bromo-2-butanol, b.p. 50–51° at 14 mm., n^{26}_{D} 1.4750 (reported[24] values, b.p. 50.5° at 13 mm., n^{25}_{D} 1.4756). The 3,5-dinitrobenzoate melted at 108.1–109.2° (reported[24] m.p. for 3,5-dinitrobenzoate of *threo*-3-bromo-2-butanol 109°).

Anal. Calcd. for $C_{11}H_{11}BrN_2O_6$: C, 38.1; H, 3.2; N, 8.1; Br, 23.0. Found: C, 38.3; H, 3.3; N, 8.0; Br, 22.8.

Reduction of II under the same conditions gave, in addition to 41.7% of recovered II, a 45.5% yield of 2-butanol.

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(15) R. Ghosh, *J. Indian Chem. Soc.*, **13**, 323 (1936).

(16) Reported values [P. D. Bartlett and S. D. Ross, THIS JOURNAL, **70**, 926 (1948)]: b.p. 133.0–133.6°, n^{25}_{D} 1.4106.

(17) G. Bernard and J. Colonge, *Bull. soc. chim.*, **12**, 356 (1945).

(18) E. Charon, *Ann. chim.*, [7] **17**, 255 (1899).

(19) H. Gilman and A. H. Blatt, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, pp. 58–59.

(20) A. C. Cope, *ibid.*, Vol. 30, 1950, pp. 24–25.

(21) N. L. Drake, H. M. Duvall, T. L. Jacobs, H. T. Thompson and H. M. Sonnichsen, THIS JOURNAL, **60**, 73 (1938), reported 116–117°.

(22) N. E. Rigler and H. R. Henze, *ibid.*, **58**, 474 (1936), reported 146–147°.

(23) A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **16**, 1625 (1946), reported 146°.

(24) S. Winstein and H. J. Lucas, THIS JOURNAL, **61**, 1576 (1939).

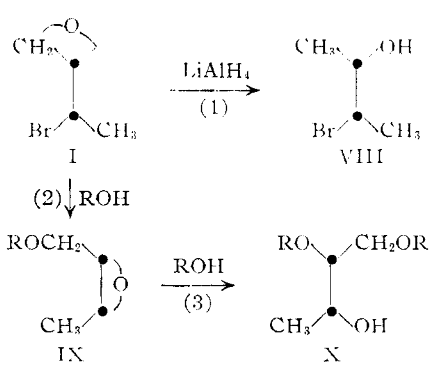
Discussion of Results

Formation of the corresponding 1-alkoxy-2,3-epoxybutanes as the major products in the typical SN2 reactions of I and of II with sodium methoxide and with sodium ethoxide clearly indicates that in every case the initial attack of alkoxide ion was at the terminal carbon atom. Thus, any inherent differences in the reactivity of the bromine-bearing *vs.* the epoxide-ring carbon atoms are completely overshadowed by the apparently more important tendency for attack to occur at the primary position This fact is difficult to rationalize on the basis of electronic effects and appears to be attributable simply to steric factors.

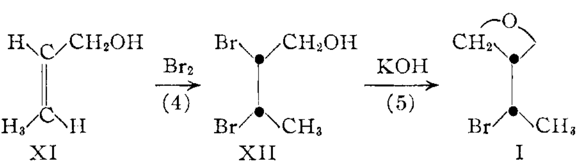
Ready reaction of III with sodium methoxide to form IV suggests that the 1-alkoxy-2,3-epoxybutanes are intermediates in the formation of the 1,2-dialkoxy-3-butanols in the reactions of I and of II with sodium alkoxides. The relatively minor contribution of the second of the two steps in the case of sodium ethoxide suggests that there is greater hindrance to secondary attack for ethoxide than for methoxide ion.

Despite repeated purifications, the physical properties of the 1-methoxy-2,3-epoxybutane, the 1,2-dimethoxy-3-butanol, the 1-ethoxy-2,3-epoxybutane and the 1,2-diethoxy-3-butanol prepared from I differed slightly from those of the presumably identical compounds obtained from II. This suggests, as may well be the case, that the corresponding compounds obtained from the isomeric bromoepoxides are not identical stereochemically. II was synthesized by addition of bromine to *d,l*-methylvinylcarbinol, $CH_3—CH(OH)—CH{=}CH_2$, followed by a dehydrohalogenation of the resulting 3,4-dibromo-2-butanol, $CH_3—CH(OH)—CHBr—CH_2Br$, to the epoxide.[11] From this method of preparation, it must be deduced that II, and therefore the alkoxy derivatives obtained from II, was a mixture of two pairs of racemates. If this is, indeed, the case, the pairs of isomeric racemic mixtures were not, however, separable by fractional distillation.

Formation of essentially pure *threo*-3-bromo-2-butanol, VIII, by reduction of I, with lithium aluminum hydride, reaction 1, in which no bonds are broken at either of the two asymmetric sites in I, indicates that I likewise possessed the *threo* configuration. If this is the case, then the 1-alkoxy-2,3-epoxybutanes (IX) formed from I, in reaction 2, which is thought to proceed with inversion at the bottom (as shown) asymmetric carbon, were presumably the *erythro* compounds. On the other hand, the 1,2-dialkoxy-3-butanols (X) formed from the corresponding *erythro*-1-alkoxy-2,3-epoxybutanes (IX) in a type of reaction, 3, involving an inversion at the top asymmetric carbon, were then the *threo* compounds.



The fact that I has the *threo* configuration in itself carries an interesting implication. I was obtained by dehydrohalogenation, 5, of the 2,3-dibromo-1-butanol (XII) obtained by addition, 4, of bromine to crotyl alcohol (XI). Inasmuch as step 5 proceeds with inversion at the top asymmetric carbon, XII must belong to the *erythro* family. But if that is the case and if addition 4 of bromine to crotyl alcohol is *trans*, then the crotyl alcohol used must also have been the *trans* compound. This conclusion is in agreement with Raman spectra[25] which indicate that ordinary crotyl alcohol is at least 95% the *trans* isomer.



The fact that attack by alkoxide ion on the 1-alkoxy-2,3-epoxybutanes (IX) in step 3 occurred at the 2-carbon may be ascribed to the substituent effect of the electron-withdrawing alkoxy groups. The opposite orientation observed for the reaction of IX with lithium aluminum hydride may perhaps be attributed to the preëminent importance of steric factors in determining the direction of attack,[26] or to a reversal of the substituent effect of the alkoxy groups, brought about by the fact that in the transition state for the reaction, bond breaking has proceeded to a greater extent than bond making.[27]

That opening of the epoxide ring in I by lithium aluminum hydride in step 1 is not followed by displacement of the bromine by the alkoxide oxygen is not surprising. On the basis of the postulation[3] that the alkoxide ion formed by the opening of the ring is immediately coördinated to the aluminum through formation of ions of the type AlH_3OR^-, the alkoxide oxygen is obviously not available for displacement of bromide ion.

Isolation of 2-butanol as the sole product of the reaction between II and lithium aluminum hydride indicates that in this reaction the primary halide and the secondary epoxide are approximately equally reactive or that the reactivity of the second function is increased by reduction of the first. The relative enhancement, compared to the alkoxide reactions, of the reactivity of the secondary epoxide grouping, may perhaps result from acid catalysis of the epoxide ring opening by lithium ion.[27]

Conversion of IV to VII by means of sulfuric acid may proceed either by initial dehydration of IV to

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(25) B. Gredy and L. Piaux, *Compt. rend.*, **198**, 1235 (1934).

(26) The steric influence of the methoxy group on determining the direction of epoxide ring opening by lithium aluminum hydride in certain sugars is apparent in the work of D. A. Prins, THIS JOURNAL, **70**, 3955 (1948).

(27) See A. Feldstein and C. A. VanderWerf, *ibid.*, in press.

form 1,2-dimethoxy-2-butene[28] or *via* hydrogen migration in the carbonium ion formed from IV by loss of OH^-.[29] Reaction through an olefin intermediate finds an analogy in the report[30] that 1,3-dimethoxy-2-butene rapidly rearranges to 4-methoxy-2-butanone in the presence of dilute sulfuric acid.

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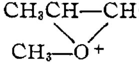
[28] This olefin might actually arise from either IV or 1,3-dimethoxy-2-butanol; in fact, in acid solution the two ethers may perhaps exist in equilibrium through a possible common intermediate



$$CH_3\underset{\diagdown\ \diagup}{CH—CH}CH_2OCH_3 \quad CH_3—O^+$$

which might be formed from either ether through loss of OH with the bonding pair of electrons. Hence, VII might perhaps be formed by treatment of either IV or 1,3-dimethoxy-2-butanol with acid, and the assignment of the position of the methoxy groups in IV is based, not on this reaction, but on the iodoform test. The behavior of 1,3-dimethoxy-2-butanol toward acids is now under investigation in this Laboratory.

[29] See C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 475–476.

[30] R. O. Norris, J. J. Verbanc and G. F. Hennion, THIS JOURNAL, **60**, 1159 (1938).

LAWRENCE, KANSAS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds. V. Propargyl Derivatives[1]

BY GEORGE B. BUTLER AND ROGER A. JOHNSON

RECEIVED AUGUST 31, 1953

In order to determine whether or not quaternary ammonium compounds having the propargyl group as one or more of the substituents would undergo a free radical catalyzed polymerization in a manner similar to the corresponding allyl derivatives, a number of compounds containing this group were prepared and characterized. This series consisted of compounds containing, as the only unsaturated groups, one propargyl group, one propargyl and one allyl group, one propargyl and two allyl groups, one propargyl and three allyl groups, and two propargyl and one allyl groups. As intermediates for these compounds, four unsaturated tertiary amines were prepared and characterized. Polymerization studies showed that only those compounds containing two or more allyl groups produced polymers, and that the propargyl groups did not enter into the polymerization.

Previous work[2,3] has shown that unsaturated quaternary ammonium salts containing two or more allyl or chloroallyl groups undergo polymerization by a free radical catalyzed mechanism. More recent work[4] has shown that even though vinyl ethers will copolymerize with a variety of olefinic compounds by a free radical catalyzed mechanism, such groups, when present in quaternary ammonium salts, do not polymerize or copolymerize with any allyl groups which may be present.

Although data are as yet insufficient to permit wide generalizations with regard to polymerization and copolymerization of acetylenic compounds, many compounds of this type have been found to undergo these reactions. Vinylacetylene under pressure, with or without the usual catalysts such as benzoyl peroxide or sodium borate, is readily polymerized by heat to form viscous drying oils and finally hard resinous solids. Jacobs and Whitcher[5] have shown that phenoxyacetylene undergoes polymerization, quite often violently. Propargyl acetate has been shown by Ladd[6] to undergo a free radical initiated reaction with bromotrichloromethane in presence of free radical forming catalysts to give 2-bromo-4,4,4-trichloro-2-butenyl acetate. Bruson and Butler[7] have shown that 2-nitro-2-methylpropyl propargyl maleate polymerizes on heating with benzoyl peroxide.

The potential use of unsaturated quaternary ammonium salts as intermediates for strongly basic ion-exchange resins indicates the desirability of compounds of lowest possible equivalent weights. The introduction of groups containing acetylenic linkages offers the possibility of a tetrafunctional group toward polymerization or copolymerization reactions. Previous work[2,3] has shown that of the compounds studied, two allyl or chloroallyl groups are necessary for polymerization, and at least three of these groups must be present in a single molecule to cause cross-linking to occur. Because of the possibility of one propargyl group serving the purpose of two allyl groups, thus allowing a decrease in the equivalent weight, this work was undertaken. The results are recorded below in the experimental section and in the accompanying tables.

Experimental

Materials.—Allyl bromide was obtained from Dow Chemical Company and was used as received. 2,3-Dibromopropene was prepared from 1,2,3-tribromopropane,[8] and it in turn was prepared from allyl bromide.[9]

Diallylcyanamide, which was used to prepare diallylamine,[10] was obtained from American Cyanamid Company. Butylamine and diethylamine were obtained from Carbide and Carbon Chemicals Corporation and were used as received. The *t*-butyl hydroperoxide was obtained as a 60% solution from Lucidol Division, Novadel–Agene Corporation.

Preparation of 2-Bromoallylamines.—The following preparation of 2-bromoallyldiallylamine will illustrate the method used for preparation of this compound, bis-(2-bromoallyl)-butylamine, and 2-bromoallyldiethylamine: A mixture of 56.3 g. of $NaHCO_3$ with enough water to form a thin sus-

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[1] The work described in this manuscript was presented in part before the Southeastern Regional Meeting of the American Chemical Society, Wilson Dam, Alabama, October, 1951, and was abstracted from a thesis presented by Roger A. Johnson to the Graduate School of the University of Florida in partial fulfillment of the requirements for the degree Master of Science, February, 1952.

[2] G. B. Butler and R. L. Bunch, THIS JOURNAL, **71**, 3120 (1949).

[3] G. B. Butler and F. L. Ingley, *ibid.*, **73**, 895 (1951).

[4] G. B. Butler and R. L. Goette, *ibid.*, **74**, 1939 (1952).

[5] T. L. Jacobs and W. J. Whitcher, *ibid.*, **64**, 2635 (1942).

[6] E. C. Ladd, U. S. Patent 2,554,533 (to U. S. Rubber Co.).

[7] H. A. Bruson and G. B. Butler, U. S. Patent 2,404,688 (to Rohm & Haas Co.).

[8] "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 209.

[9] *Ibid.*, p. 521.

[10] *Ibid.*, p. 201.