[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Chemistry of Epoxy Compounds. VIII.[2] Reaction of Allyl Alcohol with Unsymmetrical Oxirane Compounds. An Electronic Interpretation[2a]

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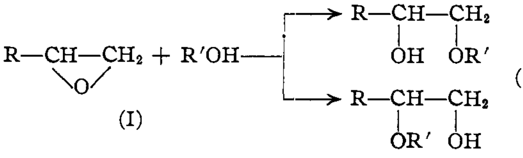
When an unsymmetrical oxirane compound (I) reacts with an alcohol (equation I), two isomeric hydroxy ethers can form, depending on which carbon–oxygen bond of the oxirane group is cleaved. The literature on such reactions is voluminous, yet only two cases[3,4] have come to our attention in which the reaction mixture has been carefully fractionated and the structure of the resulting products established. Furthermore, the effects of acidic or alkaline catalysts, and the electronic effect of substituent groups, on the direction of ring opening have been explored only to a limited extent,[3,4,5a,6,7] and in the case of extremely reactive oxirane compounds, notably 3,4-epoxy-1-butene, reaction conditions producing high yields (above 75%) of hydroxy ethers have not been reported, the usual yield being 20 to 68%.[4,5a,8] We have studied the reaction of allyl alcohol with propylene oxide, glycidol, epichlorohydrin, 3,4-epoxy-1-butene and styrene oxide [R-(I) = CH_3–, HO–CH_2–, Cl–CH_2–CH_2═CH–, and C_6H_5–] in the presence of acidic and alkaline catalysts, and the results of these experiments are described in this paper (Table I). A literature survey on ring opening reactions of this type (equation I) revealed no publications reporting the use of allyl alcohol. After our work was almost complete, however, the preparation of 2-alloxy-1-phenylethanol in 31% yield by the phosphoric acid-catalyzed reaction of allyl alcohol with styrene oxide was reported,[9] although proof of structure was not given.



(Eq. I)

The procedure which we followed in studying this reaction (equation I) consisted of four steps: (a) Determination of reaction conditions which gave high yields of hydroxy ethers in the presence of alkaline and acidic catalysts (alkaline catalysts could not be employed with epichlorohydrin). The yield was usually determined by distillation of the neutralized reaction mixture through a low hold-up fractionating column of the Vigreux type, which was capable of cleanly separating unreacted allyl alcohol from hydroxy ether and also of separating the latter from di- and polyethers. (b) Redistillation of the hydroxy ether fraction through a low hold-up, highly efficient fractionating column (more than one hundred theoretical plates) in an attempt to separate isomeric hydroxy ethers which might have formed; (c) determination of the identity and purity of the products by well-known means (iodine absorption, per cent. hydroxyl, carbon analysis, etc.); (d) determination of the position of the hydroxyl group, introduced as a result of the ring opening reaction, by one or more chemical diagnostic tests. For example, by oxidation with periodic acid,[10] the α-glycol group was determined in the reaction prod-

TABLE I

CHARACTERISTICS OF HYDROXY ETHERS OBTAINED BY THE REACTION OF ALLYL ALCOHOL WITH UNSYMMETRICAL OXIRANE COMPOUNDS

Hydroxy ether	B. p. °C.	B. p. Mm.	Carbon, %[a] Calcd.	Carbon, %[a] Found	Hydroxyl, %[b] Calcd.	Hydroxyl, %[b] Found	Iodine No.[c] Calcd.	Iodine No.[c] Found	$n^{30}D$ (Abbe)	d^{30}_4	Molecular refraction Calcd.	Molecular refraction Found
1-Alloxy-2-propanol (II)	71–71.5	31	62.0	61.9	14.6	14.2	218	215	1.4258	0.9112	32.61	32.65
2-Alloxy-1-propanol (III)	77–78	30	62.0	61.8	14.6	14.4	218	216	1.4298	0.9215	32.61	32.55
1-Alloxy-3-chloro-2-propanol (IV)	107–108	31	47.8	47.7	11.3	11.0	168	167	1.4582	1.102	37.48	37.32
1-Alloxy-2,3-propanediol (VI) + 2-Alloxy-1,3-propanediol (VII)[d]	107–109	4.3–4.5	54.5	54.5–54.7	25.7	24.9–25.2	192	189	1.4583–1.4589	1.061	34.13	34.01–34.05
2-Alloxy-2-phenylethanol (VIII)	118–119	4.5	74.1	74.0	9.54	9.80	142	142	1.5167	1.031	52.10	52.27
2-Alloxy-1-phenylethanol (IX)	114–114.5	4.6–4.8	74.1	73.6	9.54	9.67	142	142	1.5159	1.030	52.10	52.25
3-Alloxy-4-hydroxy-1-butene (X)	86–87	30–31	65.6	65.5	13.3	13.0	396	393	1.4450	0.9297	36.76	36.72

[a] Wet combustion method of Van Slyke and Folch [*J. Biol. Chem.*, **136**, 509 (1940)]. [b] Method of Ogg, Porter and Willits [*Ind. Eng. Chem., Anal. Ed.*, 17, 394 (1945)]. [c] One-hour Wijs method. [d] 70:30 mixture.

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] For paper VII, see THIS JOURNAL, **70**, 1235 (1948).

[2a] This paper was presented at the 114th meeting of the American Chemical Society held in Washington, D. C., August 30–September 3, 1948. Article not copyrighted.

[3] Chitwood and Freure, THIS JOURNAL, **68**, 680 (1946).

[4] Bartlett and Ross, *ibid.*, **70**, 926 (1948).

[5] (a) Kadesch, *ibid.*, **68**, 41 (1946); (b) Bissinger, *et al.*, *ibid.*, **69**, 2955 (1947).

[6] Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **14**, 1038 (1944).

[7] Petrov, *ibid.*, **16**, 1206 (1946).

[8] Petrov, *Acta Univ. Voronegiensis*, **8**, No. 2, 71 (1935); *J. Gen. Chem.* (*U.S.S.R.*), **8**, 131 (1938).

[9] Newman, Magerlein and Wheatley, THIS JOURNAL, **68**, 2112 (1946).

[10] Pohle, Mehlenbacher and Cook, *Oil and Soap*, **22**, 115 (1945).

ucts of allyl alcohol with glycidol. The degree of reaction of benzoyl chloride with the hydroxy ethers obtained from allyl alcohol and epichlorohydrin, styrene oxide and 3,4-epoxy-1-butene was determined under controlled conditions,[5a,11] and the values so obtained were compared with those for related primary and secondary alcohols of known structure. In addition, with the exception of the reaction products of allyl alcohol with epichlorohydrin and glycidol, the time required to dissolve 0.05 g. of metallic sodium in a large molar excess of hydroxy ether was determined. When isomers could be cleanly separated by distillation, the last two tests permitted unequivocal identification of the primary and secondary alcohol (secondary and primary ether, respectively) since the degree of reaction with benzoyl chloride was significantly higher and the time required to dissolve the sodium was significantly lower in the case of the primary alcohol (secondary ether) (Tables II and III). Furthermore, in every instance in which we were able to separate the isomers, and in the few cases reported in the literature, the primary alcohol (secondary ether) had a higher boiling point, density and index of refraction than the secondary alcohol (primary ether).

TABLE II

SOLUTION TIME OF SODIUM[a] IN VARIOUS HYDROXY COMPOUNDS

Compound	OH	Max. temp. attained during reaction, °C.	Sol. time, minutes
1-Alloxy-2-propanol (II)	Sec.	35	69
2-Alloxy-1-propanol (III)	Prim.	39	38
2-Alloxy-2-phenylethanol (VII)	Prim.	25	240
2-Alloxy-1-phenylethanol (IX)	Sec.	25	>450
3-Alloxy-4-hydroxy-1-butene (X)	Prim.	33–38	14 to 20
1-Propanol	Prim.	56	4
2-Propanol	Sec.	25	>480
2-Propen-1-ol (allyl alcohol)	Prim.	62	1
n-Butanol	Prim.	30	11
2-Buten-1-ol (crotyl alcohol)	Prim.	46	2.3
2-Methyl-2-propen-1-ol (methallyl alcohol)	Prim.	49	1.6
3-Buten-2-ol (methyl vinyl carbinol)	Sec.	25	35

[a] 0.05 g. (0.00217 mole) of sodium added to 0.0434 mole of hydroxy compound.

TABLE III

DEGREE OF REACTION OF BENZOYL CHLORIDE WITH VARIOUS HYDROXY COMPOUNDS[5a,11]

Compound	OH	Degree of reaction (expressed as %)
1-Alloxy-3-chloro-2-propanol (IV)	Sec.	11
2-Alloxy-2-phenylethanol (VIII)	Prim.	91
2-Alloxy-1-phenylethanol (IX)	Sec.	19
3-Alloxy-4-hydroxy-1-butene (X)	Prim.	85–94
X + 4-Alloxy-3-hydroxy-1-butene (XI)	[a]	64–75
3-Methoxy-4-hydroxy-1-butene[5a]	Prim.	61–78
4-Methoxy-3-hydroxy-1-butene[5a]	Sec.	8–22
2-Buten-1-ol (crotyl alcohol)	Prim.	97
3-Buten-2-ol (methylvinylcarbinol)	Sec.	17

[a] Primary and Secondary. Prepared by the acid-catalyzed reaction of allyl alcohol with 3,4-epoxy-1-butene.

Experimental[11a]

Materials.—Allyl alcohol, propylene oxide, 3,4-epoxy-1-butene, epichlorohydrin and styrene oxide were the purest commercial products obtainable, and they were distilled (styrene oxide under vacuum) through efficient fractionating columns immediately before use. Glycidol was prepared by the dehydrohalogenation of freshly distilled glycerol α-monochlorohydrin in isopropyl alcohol, substantially as reported by Marple and Evans.[12] A twice-distilled product, b. p. 40° at 2.5 mm., and n^{25}D 1.4292, was employed in the reactions. Oxirane oxygen,[13] calcd., 21.6; found, 21.2.

Propylene Oxide and Allyl Alcohol. (a) **Preparation of 1-Alloxy-2-propanol (II).**—To a stirred solution of 3.2 g. of freshly cut sodium in 290 g. (5 moles) of allyl alcohol in a 500-ml. round-bottom distilling flask at 25°, 29.1 g. (0.5 mole) of propylene oxide was added dropwise. No rise in temperature was observed. The resulting solution was refluxed for one hour, and most of the unreacted allyl alcohol was then separated by distillation at atmospheric pressure (maximum pot temperature, 120°) through a short helix-packed column. Sufficient 6 *N* aqueous sulfuric acid was added to the residual solution at room temperature to neutralize the sodium alloxide, and distillation was continued at about 30 mm. through a Vigreux column 2 feet long and 1/2 inch in diameter. After recovery of an additional quantity of allyl alcohol, 51 g. (88% yield) of a colorless liquid, b. p. 72–73° at 30–31 mm., n^{30}D 1.4258–1.4264, which was identified as alloxypropanol, was obtained. This was redistilled through a Podbielniak column 90 cm. long and 13 mm. in diameter; 90% of the product boiled at 71–71.5° at 31 mm., n^{30}D 1.4258. The remainder consisted of allyl alcohol and distillation residue. Comparison of the physical properties of the main fraction with those of the products obtained in (b) below indicated that it was 1-alloxy-2-propanol. This was confirmed by the sodium solution test (Table II).

(b) **Preparation of 2-Alloxy-1-propanol (III) and II.**—To a stirred solution of 58.1 g. (1.0 mole) of propylene oxide and 581 g. (10 moles) of allyl alcohol at 25°, 0.58 g. of 95% sulfuric acid was added dropwise. The temperature rose spontaneously from 25 to 30°, and the solution was then refluxed for one hour. (Elimination of the refluxing step caused a considerable reduction in yield.) Sufficient sodium hydroxide was then added to the solution, after it was cooled to room temperature, to neutralize the sulfuric acid, and the solution was distilled through a short helix-packed column. After distillation of the unreacted allyl alcohol at atmospheric pressure, the distillation was completed at 30 mm., yielding 97 g. (84% yield) of a colorless liquid, b. p. 72–75° at 30 mm., n^{30}D 1.4288, which was identified as alloxypropanol. Redistillation through the Podbielniak column gave two distinct fractions, b. p. 71–73° at 30 mm., n^{30}D 1.4258 (II), and b. p. 77–78° at 30 mm., n^{30}D 1.4298 (III). The relative proportions of these fractions (based on hydroxy ether employed as distillation charge) were about 60% of III and 40% of II. The results are summarized in Tables I and II.

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

[11a] All reactions and distillations were conducted in an atmosphere of nitrogen.

[12] Marple and Evans, U. S. Patent 2,248,635 (1941).

[13] Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 414 (1947).

Epichlorohydrin and Allyl Alcohol. Preparation of 1-Alloxy-3-chloro-2-propanol (IV).—To a stirred solution of 581 g. (10 moles) of allyl alcohol containing 0.92 g. of 95% sulfuric acid at 25°, 92.4 g. (1.0 mole) of epichlorohydrin was added dropwise in five minutes. No rise in temperature was obtained. The solution was refluxed for three hours (a one-hour reflux time caused a considerable reduction in yield) and was then worked up as described under alloxypropanol. Eighty-nine grams (59% yield) of a colorless liquid, b. p. 106–107.5° at 29 to 30 mm., n^{30}_{D} 1.458–1.459, which was identified as alloxychloropropanol, was obtained. Redistillation through the Podbielniak column yielded 1-alloxy-3-chloro-2-propanol (IV), b. p. 107–108° at 31 mm., n^{30}_{D} 1.4582. None of the isomeric 2-alloxy-3-chloro-1-propanol (V) appeared to be present. The results are summarized in Tables I and III.

Alkaline catalysts could not be employed in this system because of the ease with which the chlorine atom in epichlorohydrin was detached. The following alkaline catalysts were tried: potassium hydroxide, sodium hydroxide, sodium, benzyltrimethylammonium hydroxide, trimethylamine and pyridine.

Glycidol and Allyl Alcohol. Preparation of 1-Alloxy-2,3-propanediol (VI) and 2-Alloxy-1,3-propanediol (VII).—To a stirred solution of 5.3 g. of sodium in 470 g. (8.1 moles) of allyl alcohol at 25°, 60 g. (0.81 mole) of glycidol was added dropwise. No rise in temperature was observed. The solution was refluxed for three hours, and then worked up as described under alloxypropanol. Seventy-five grams (71% yield) of a colorless liquid, b. p. 104–107° at 3.1 mm., which was identified as alloxypropanediol, was obtained. It was redistilled through the Podbielniak column, b. p. 107–109° at 4.3 to 4.5 mm., n^{30}_{D} 1.4589, but no separation of isomers could be effected. Periodic acid oxidation[10] indicated that the mixed hydroxy ethers consisted of 70 to 75% of VI and 25 to 30% of VII.

Almost identical results (74% yield) were obtained in a similar experiment in which 5.3 g. of 95% sulfuric acid was substituted for the sodium employed above. The catalyst was neutralized with sodium hydroxide. The results are summarized in Table I.

Styrene Oxide and Allyl Alcohol. (a) **Preparation of 2-Alloxy-2-phenylethanol** (VIII).—To a stirred solution of 2.8 g. of sodium in 232 g. (4.0 moles) of allyl alcohol at 25°, 48 g. (0.4 mole) of styrene oxide was added dropwise in five minutes. No rise in temperature was observed over a one-hour period, after which the solution was refluxed for one hour and then worked up as previously described. Fifty-eight g. (81% yield) of a colorless liquid, b. p. 113–117° at 4.5 to 5.0 mm., which was identified as alloxyphenylethanol, was obtained. Redistillation through the Podbielniak column yielded two distinct fractions, b. p. 114° at 4.7 mm., n^{30}_{D} 1.5158, and b. p. 118–119° at 4.5 mm., n^{30}_{D} 1.5167, which were identified as 2-alloxy-1-phenylethanol (IX) and 2-alloxy-2-phenylethanol (VIII), respectively. The latter represented about 90% of the material redistilled.

(b) **Preparation of 2-Alloxy-1-phenylethanol** (IX).—To a stirred solution of 1.2 g. of 95% sulfuric acid and 581 g. (10 moles) of allyl alcohol at 25°, 120 g. (1.0 mole) of styrene oxide was added dropwise in twenty minutes, the temperature being maintained between 25 and 30° by means of an ice–water-bath. The reaction was strongly exothermic. When the exothermic reaction was complete, the solution was refluxed for one hour, and then worked up as described earlier. One hundred and forty-eight grams (83% yield) of a colorless liquid, b. p. 116–118° at 4.8 mm., which was identified as alloxyphenylethanol, was obtained. Redistillation through the Podbielniak column indicated that the product consisted solely of 2-alloxy-1-phenylethanol (IX), b. p. 114–114.5° at 4.6 to 4.8 mm., n^{30}_{D} 1.5159. The results are summarized in Tables I, II and III.

3,4-Epoxy-1-butene and Allyl Alcohol. Preparation of 3-Alloxy-4-hydroxy-1-butene (X).—To a stirred solution of 6.5 g. of sodium in 581 g. (10 moles) of allyl alcohol at 25°, 70.1 g. (1.0 mole) of 3,4-epoxy-1-butene was added dropwise in twenty minutes. No rise in temperature was observed. The reaction mixture was allowed to stand for about thirty hours, and then worked up as described earlier. Eighty-five grams (66% yield) of a colorless liquid, b. p. 86–90° at 30 to 32 mm., n^{30}_{D} 1.444, was obtained. This was identified as alloxyhydroxybutene. Redistillation through the Podbielniak column yielded 3-alloxy-4-hydroxy-1-butene (X), b. p. 86–87° at 30 to 31 mm., n^{30}_{D} 1.4449–1.4452.

A similar experiment was conducted in which the 3,4-epoxy-1-butene was added dropwise to allyl alcohol containing 0.70 g. of 95% sulfuric acid as the catalyst. The reaction was extremely exothermic, and the reaction flask had to be kept in an ice-bath to maintain the temperature between 25 and 30° during the addition. After the exothermic reaction was complete, the reaction mixture was stirred at 25 to 30° for one hour (refluxing for one hour resulted in only a 60% yield of hydroxy ether), and then worked up as described earlier. One hundred and one grams (79% yield) of a colorless liquid, b. p. 83–87° at 25 mm., n^{30}_{D} 1.445, which was identified as alloxyhydroxybutene, was obtained. Redistillation through the Podbielniak column gave a main fraction which appeared to be identical (b. p., d^{30}_{4}, n^{30}_{D}, etc.) with the product (X) obtained from the alkali-catalyzed experiment, but the benzoyl chloride test suggested that the product from the acid-catalyzed reaction contained some of the secondary alcohol (primary ether) (XI). The results are summarized in Tables I, II and III.

In a smaller scale run, the sulfuric acid catalyst was added dropwise to an uncooled but stirred solution of allyl alcohol and 3,4-epoxy-1-butene. The reaction was vigorously exothermic, and only a 30% yield of hydroxy ether was obtained.

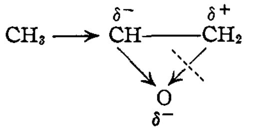
Sodium Solution Test.—A freshly cut piece of sodium (0.05 g., 0.00217 mole) was added at 25° to 0.0434 mole of hydroxy compound contained in a test-tube. The test-tube was immediately stoppered with a loosely fitting cork supporting a thermometer which reached to the bottom. The maximum temperature attained during the solution of the sodium, as well as the time required for complete solution, was observed. Solution times could be duplicated within 10 to 20%. The results obtained with some of the hydroxy ethers prepared during this investigation and also with some simple primary and secondary alcohols are shown in Table II.

Degree of Reaction with Benzoyl Chloride.—The benzoylation procedure of Kadesch[5a] and Norris and Haines[11] was employed. The results obtained with some of the hydroxy ethers prepared during this investigation and also with some primary and secondary alcohols of known structure are shown in Table III.

3,5-Dinitrobenzoates.—Attempts to prepare the 3,5-dinitrobenzoates of the hydroxy ethers by reaction with 3,5-dinitrobenzoyl chloride in pyridine solution yielded oils which could not be induced to crystallize.

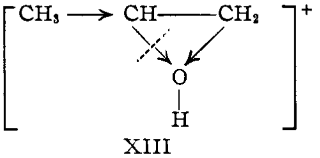
Discussion

In propylene oxide (XII), the well-known mild electron-releasing effect of the methyl group should increase the electron density of the carbon atom to which it is attached. Since nucleophilic attack by an alkoxide ion (RO^-) would be expected to take place preferentially at the carbon atom of lower electron density, namely, at the terminal carbon atom, a secondary alcohol (primary ether) should be obtained. Confirmation of

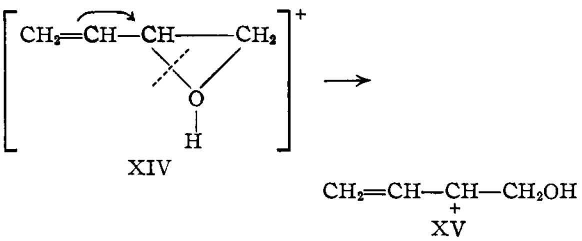


XII

this hypothesis is afforded both by our study of the alkali-catalyzed reaction of allyl alcohol with propylene oxide, in which II is obtained exclusively, and by the work of Chitwood and Freure[3] and Reeve and Sadle,[14] who obtained the secondary alcohol (primary ether) almost exclusively from the alkali-catalyzed reaction of propylene oxide with methanol, ethanol, isopropyl alcohol, *n*-butanol and 2-ethylhexanol. When an acidic catalyst is employed, both carbon–oxygen bonds of the oxirane ring are weakened,[3,15] but because of the higher electron density of the carbon atom to which the methyl group is attached, coupled with the repelling effect exerted on the (negative) oxygen atom, this carbon–oxygen bond should be weaker than the other. Cleavage, therefore, should occur as shown in XIII, and a primary alcohol (secondary ether) (III) should be obtained. The hydroxy ethers obtained in the acid-catalyzed reaction of allyl alcohol with propylene oxide consisted mainly of III, as the theory indicates, although II was also obtained in fair yield. The formation of II was not unexpected, since both carbon–oxygen bonds are weakened and the methyl group does not exert a sufficiently powerful electron-releasing effect to cause one carbon–oxygen bond to be so much weaker than the other that preferential cleavage occurs exclusively. As the quantity of acid catalyst is decreased,[3] smaller proportions of primary alcohol (secondary ether) and larger proportions of secondary alcohol (primary ether) form, since the bond-weakening effect diminishes and the electron-releasing effect of the methyl group becomes the major determining factor in influencing the direction of ring opening.

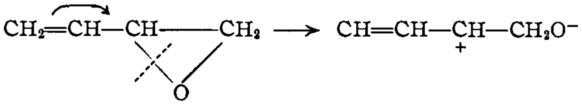

XIII

In 3,4-epoxy-1-butene, however, the nature of the catalyst exerted a relatively small effect, the acid-catalyzed reaction yielding a mixture consisting predominantly of the primary alcohol (secondary ether) (X) and the alkali-catalyzed reaction apparently yielding X exclusively. The results of the acid-catalyzed reaction are in agreement with the results previously reported by Kadesch[5a] and by Bartlett and Ross[4] on the acid-catalyzed reaction of 3,4-epoxy-1-butene with methanol. The formation of X in the acid-catalyzed reaction can be explained by assuming the presence of an intermediate carbonium ion, XV,[5a] which should form readily from 3,4-epoxy-1-butene (XIV), since the bond-weakening effect of the strongly electron-releasing vinyl group and the bond-weakening effect of the oxonium ion operate in the same direction. Such an ion should be stabilized as a result of resonance.


XIV

XV

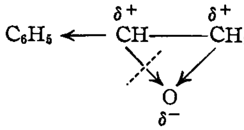
The alkali-catalyzed reaction of 3,4-epoxy-1-butene with methanol, however, yields a secondary alcohol (primary ether) predominantly.[4,5a] Since the only difference between our work and that previously reported is the employment by us of allyl alcohol, it can be concluded, perhaps, that allyl alcohol or sodium alloxide enhances the electron-release effect of the vinyl group to such an extent at the precise moment of attack that a considerable bond-weakening effect occurs between the non-terminal carbon atom and the oxirane oxygen atom, yielding an ion as an intermediate (XVI → XVII).


XVI XVII

Nucleophilic attack would occur, of course, at the positive carbon atom, and a primary alcohol would again be obtained.

The ease with which 3,4-epoxy-1-butene and analogous compounds form aldehydes during acid-catalyzed hydration[5,16,17] supports the formulation XIV → XV.

Since the phenyl group can exert either a mild electron-releasing or electron-attracting effect,[18,19,20] the products obtained in the reaction of allyl alcohol with styrene oxide will depend on which effect is taking place. The product obtained in the alkali-catalyzed reaction consisted almost exclusively of primary alcohol (secondary ether) (VIII). The phenyl group, therefore, must exert an electron-attracting effect (XVIII), since formation of the primary alcohol occurs as a result of nucleophilic attack by alkoxide ion on the car-


XVIII

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[14] Reeve and Sadle, paper presented at the 113th meeting of the American Chemical Society held in Chicago, Illinois, April, 1948.

[15] Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, p. 301.

[16] Pummerer and Reindel, *Ber.*, **66**, 335 (1933).

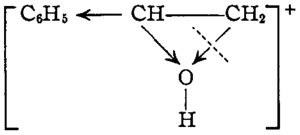
[17] Petrov, *J. Gen. Chem.* (*U.S.S.R.*), **13**, 481 (1943).

[18] Day, "Electronic Mechanisms of Organic Reactions," Stephenson Bros., Philadelphia, Pa., 1947, p. 46.

[19] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 61.

[20] Swern, THIS JOURNAL, **69**, 1692 (1947).

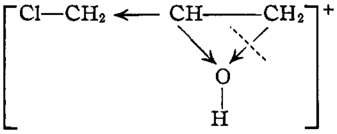
bon atom with the lower electron density, the non-terminal carbon atom in this case. When an acidic catalyst is employed, the lower electron density on the non-terminal carbon atom makes this carbon–oxygen bond stronger than the other because of the increased attraction of the non-terminal carbon atom for the oxygen atom (XIX).



XIX

Since the terminal carbon–oxygen bond is the weaker of the two, the secondary alcohol (primary ether) (IX) should, and does, form in good yield.

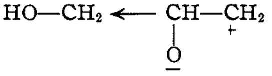
The chloromethyl group in epichlorohydrin (XX) must also exert an electron-attracting effect, since the product obtained when it was treated with allyl alcohol in the presence of sulfuric acid was the secondary alcohol (primary ether) (IV).



XX

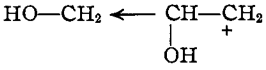
The failure to obtain the isomeric primary alcohol (secondary ether) (V) was somewhat surprising, since the chloromethyl group should exert a less powerful electron-attracting effect than the phenyl group.

In the reaction of glycidol with allyl alcohol, the nature of the catalyst was without effect in determining the direction of ring opening. Since the hydroxymethyl group is a strong electron-attracting group, it may be assumed that the ions XXI and XXII exist in alkaline and acidic media, respectively.



$\mathrm{HO{-}CH_2 \leftarrow \underset{\underset{O^-}{|}}{CH}{-}\overset{}{CH_2^{+}}}$

XXI



$\mathrm{HO{-}CH_2 \leftarrow \underset{\underset{OH}{|}}{CH}{-}CH_2^{+}}$

XXII

This formulation is analogous to that proposed earlier for 3,4-epoxy-1-butene, except that in glycidol there should be a powerful bond-strengthening effect between the non-terminal carbon atom and the oxirane oxygen atom caused by the strongly electron-attracting hydroxymethyl group, which would favor formation of XXI and XXII.[21] On the basis of this formulation, only α-glycol (VI) should be obtained regardless of the alkalinity or acidity of the systems. The fact that α-glycol formation predominated appears to substantiate the premise, in the main, but the formation of considerable and identical quantities of VII is still without explanation.

Acknowledgment.—We are indebted to Frances Cooper and Mary Jane Welsh for the carbon analyses, to R. E. Koos for some of the iodine number and per cent. hydroxyl determinations, and to M. E. Coy for determining the degree of reaction of the hydroxy compounds with benzoyl chloride.

Summary

The reaction of allyl alcohol with the unsymmetrical oxirane compounds propylene oxide, glycidol, 3,4-epoxy-1-butene, epichlorohydrin and styrene oxide, in the presence of acidic and alkaline catalysts, has been studied. Reaction conditions are described for obtaining good yields (60 to 90%) of hydroxy ethers.

A technique is reported for determining the structure of the hydroxy ethers. This consists in efficient fractional distillation of the reaction products and analysis of the main fractions, followed by the application of one or more chemical diagnostic tests. These include periodic acid oxidation, measurement of the time required to dissolve a known weight of sodium in a large molar excess of hydroxy ether, and determination of the degree of reaction of benzoyl chloride with the hydroxy ether under controlled conditions. When employed under the proper conditions and with suitable substrates, the benzoyl chloride test should be generally applicable in determining whether a hydroxyl group is primary or secondary.

Electronic mechanisms for the reactions have been suggested.

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[21] After completion of the manuscript, the paper by Vladimirova and Petrov [*J. Gen. Chem.* (*U. S. S. R.*), **17**, 51 (1947); *C. A.*, **42**, 118i] in which an ion similar to XXI was proposed, came to our attention.