vents used did not form peroxides, as determined iodometrically, under experimental conditions.

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Reaction of 1-Bromo-2,3-epoxybutane with Phenol in the Presence of Boron Trifluoride

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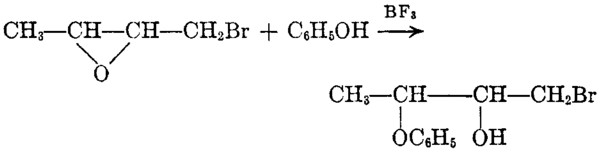
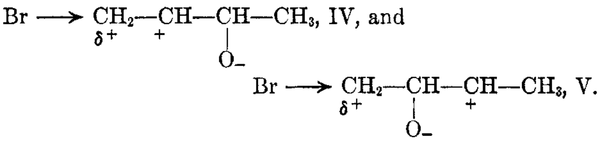
The reaction between 1-bromo-2,3-epoxybutane, I, and phenol in basic solution has been reported[1] to yield 3-phenoxy-1,2-epoxybutane.

In the present work phenol was allowed to react with I in the presence of boron trifluoride to find whether the direction of epoxide ring opening was the same as that reported for the reaction conducted in basic medium. The product of the acid-catalyzed reaction was found to consist chiefly of 1-bromo-3-phenoxy-2-butanol, II.



Dehydrobromination[2] of II at room temperature produced 3-phenoxy-1,2-epoxybutane, III. Upon treatment with silver oxide, III was oxidized to 2-phenoxypropionic acid.

The acid-catalyzed opening[3] of the epoxide ring of I may proceed in either direction, giving two possible carbonium ions:



$$\mathrm{Br} \longrightarrow \underset{\delta+}{\mathrm{CH_2}}-\overset{}{\underset{+}{\mathrm{CH}}}-\underset{\mathrm{O}^-}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_3},\ \text{IV, and}$$

$$\mathrm{Br} \longrightarrow \underset{\delta+}{\mathrm{CH_2}}-\underset{\mathrm{O}^-}{\underset{|}{\mathrm{CH}}}-\underset{+}{\mathrm{CH}}-\mathrm{CH_3},\ \text{V.}$$

Species IV would be predicted to be the less stable ion because of the presence of two positive charges (one real, one partial) on adjacent carbon atoms. Since V leads to the formation of II, the adjacent charge rule[3a,4] may be used to explain the predominant formation of that isomer. Such an interpretation is successful in accounting for the exclusive formation of 3-phenoxy-1-chloro-2-propanol[5] during the reaction of epichlorohydrin with phenol in the presence of boron trifluoride.

EXPERIMENTAL

Boiling points and melting points are uncorrected. 1-Bromo-2,3-epoxybutane, b.p. 143–145°, was prepared by the method of Petrov.[6]

Reaction of 1-bromo-2,3-epoxybutane, I, *with phenol.* In a 1-l., three-necked flask was placed a solution of 94 g. (1 mole) phenol and 1 g. boron trifluoride dissolved in 500 ml. benzene. While the temperature was maintained in the range −2° to +2°, 37.7 g. (0.25 mole) of I were added dropwise and with vigorous agitation. The addition required about 30 min. After the addition of I was complete, the solution was stirred for an additional 30 min. Water was then added to destroy the catalyst. The water was removed and the benzene was distilled at reduced pressure. At 15 mm. pressure phenol was removed by distillation in the range 78–90°. The product was 36.7 g. (60% yield) of clear, colorless oil, b.p. 100–105° at 0.3 mm., $n_{\mathrm{D}}^{22^\circ}$ 1.5500, which was found to be 1-bromo-3-phenoxy-2-butanol, II. An attempt to oxidize this compound with sodium hypoiodite was not successful.

Anal. Calcd. for $C_{10}H_{13}O_2Br$: C, 49.10; H, 5.35; Br, 32.60. Found: C, 49.78; H, 5.56; Br, 32.52.

Dehydrobromination of 1-bromo-3-phenoxy-2-butanol, II. A mixture of 35.2 g. of II, 200 ml. ethanol, and 50 ml. of 6*N* sodium hydroxide was shaken vigorously at room temperature for 1 hr. One liter of water was then added, and the product was removed by three extractions with diethyl ether. Analysis of the aqueous phase by the Mohr method indicated 96% removal of the bromine. The ether solution of epoxide was washed with water until neutral and dried over anhydrous calcium sulfate. The residue after removal of the ether was fractionated through a short Vigreux column to give 18.8 g. (80% yield) of 3-phenoxy-1,2-epoxybutane, III, b.p. 74–77° at 0.3 mm., $n_{\mathrm{D}}^{21^\circ}$ 1.5188. The residue was 3 g. of yellowish oil which gave a positive qualitative test for bromine.

Oxidation of 3-phenoxy-1,2-epoxybutane, III. Oxidation of III was carried out by stirring 3 g. of III with 17 g. silver oxide and 50 ml. of 10% sodium hydroxide solution for 18 hr. on the steam bath. The metallic silver was removed by filtration, and the solution was acidified with dilute hydrochloric acid. Several ether extractions yielded 3 g. of crude crystals upon evaporation of the ether. Recrystallization from hot water produced 2.4 g. (79% yield) of 2-phenoxypropionic acid, m.p. 115–116°. The amide and anilide were prepared and found to melt at 131° and 117–118°, respectively. These values are in good agreement with the literature values for 2-phenoxypropionic acid and derivatives.

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[1] R. L. Rowton and R. R. Russell, *J. Org. Chem.*, 23, 1057 (1958).

[2] The presence of 1-bromo-2-phenoxy-3-butanol was neither proved nor disproved. A small quantity of bromine-containing material remained after treatment of II with sodium hydroxide, but no attempt was made to identify it.

[3] Unimolecular ring opening of the oxonium complex is often accepted as the mechanism of such reactions in acid media. (a) A. A. Petrov, *Chem. Tech.* (*Berlin*), 6, 639 (1954). (b) S. Winstein and R. B. Henderson, *Heterocyclic Compounds*, R. C. Elderfield, Ed., John Wiley & Sons, New York, N. Y., 1950, Vol. 1, p. 37.

[4] A. E. Remick, *Electronic Interpretations of Organic Chemistry*, 2nd Ed., John Wiley & Sons, New York, N. Y., 1950, p. 150.

[5] E. Levas, *Ann. chim.*, [12], 3, 145 (1948).

[6] A. A. Petrov, *J. Gen. Chem.* (*U.S.S.R.*), 11, 713 (1941).