

A very similar mechanism has been proposed by Conover and Tarbell⁴ for the hydrogenolysis of some amino- and alkoxy-substituted aromatic acids and carbonyl compounds by lithium aluminum hydride. The reaction was only observed with those compounds which are capable of forming a carbonium ion highly stabilized by resonance.

In agreement with this hypothesis, the reaction of *p*-dimethylaminobenzophenone with a large excess of methylmagnesium bromide in boiling benzene did not afford a detectable quantity of anomalous product corresponding to III.

EXPERIMENTAL

Reaction of Michler's ketone with methylmagnesium bromide.

A suspension of 2.0 moles of methylmagnesium bromide in 500 ml. of benzene under nitrogen was treated with 128 g. (0.48 mole) of Michler's ketone, m.p. 173–176°, dissolved in 1.5 liters of hot benzene. After heating under reflux for 3 hr., the mixture was chilled and treated with saturated ammonium chloride solution. The crude product (119 g.), m.p. 60–110°, was fractionally crystallized from ethanol to give 59 g. (46.5%) of II, R=H, m.p. 122–124° (lit. m.p. 124°). The balance of the material was obtained as crude III, R=H, m.p. 60–75°. Repeated recrystallization of the latter from aqueous alcohol afforded material melting at 78.5–81°.

Anal. Calcd. for C₁₉H₂₆N₂: C, 80.80; H, 9.28; N, 9.92. Found: C, 80.49; 80.60; H, 9.58, 9.62; N, 10.06, 9.90.

An authentic sample of III, R=H, m.p. 80–83.5°, mixed m.p. 78.5–82°, was prepared by the reaction of dimethylaniline hydrochloride with acetone.⁵ The infrared spectra of the two samples were identical.

Reaction of Michler's ketone with benzylmagnesium chloride. A suspension of 0.8 mole of benzylmagnesium chloride⁶ in 150 ml. of benzene under nitrogen was treated with 52.5 g. (0.20 mole) of Michler's ketone dissolved in 400 ml. of boiling benzene. The mixture was heated under reflux for 5 hr., then chilled and treated with saturated ammonium chloride. The crude product was washed twice with warm ethanol to give 70 g. (80.5%) of white solid, m.p. 165–173°. This dissolved readily in dilute hydrochloric acid to give a colorless solution, showing the absence of II (R=C₆H₅) or the corresponding carbinol. Both of these compounds would give intense blue or green colors with dilute acids. An analytical sample, m.p. 169–173°, was prepared by recrystallization from ligroin (Skellysolve B).

Anal. Calcd. for C₃₁H₃₄N₂: C, 85.67; H, 7.89; N, 6.45. Found: C, 85.73, 85.97; H, 8.03, 7.92; N, 6.83, 6.72.

(4) L. H. Conover and D. S. Tarbell, *J. Am. Chem. Soc.*, **72**, 3586 (1950).

(5) J. von Braun, *Ann.*, **472**, 1 (1929).

(6) H. Gilman and W. E. Catlin, *Org. Syntheses*, **Coll. Vol. I**, 471 (1941).

Heating of the material at 60° for several days caused a progressive lowering of the melting point, apparently due to rearrangement since the composition was unchanged. The reaction product of benzylmagnesium chloride with 1,2,3,4-tetraphenylfulvene undergoes a similar depression of the melting point on standing.⁷

An attempt to prepare III (R=C₆H₅) by the reaction of dimethylaniline hydrochloride with dibenzyl ketone at 170° resulted in nearly complete recovery of starting materials.

RESEARCH DEPARTMENT
RESEARCH AND ENGINEERING DIVISION
MONSANTO CHEMICAL CO.
DAYTON, OHIO

(7) A. G. Bonagura, M. B. Meyers, J. J. Storer, and E. I. Becker, *J. Am. Chem. Soc.*, **76**, 6122 (1954).

Reaction of 1-Bromo-2,3-epoxybutane and 3-Bromo-1,2-epoxybutane with Phenol¹

RICHARD L. ROWTON AND ROBERT R. RUSSELL

Received December 20, 1957

The reaction between epichlorohydrin and phenol in basic solution has been reported by Boyd and Marle² as producing 3-phenoxy-1,2-epoxypropane. This result leads to some interesting speculations as to the mechanism of the reaction. Because of the structure of the epichlorohydrin, it is impossible to state beyond peradventure whether the phenoxide ion reacted by a simple replacement of the chloride ion from the epichlorohydrin, or whether the phenoxide ion first attacked the terminal epoxide carbon to form an intermediate secondary alkoxide ion which became stabilized by loss of the chloride ion and formation of a new oxirane ring. The final product in either case would be the same. An interesting point of conjecture is the lack of reaction between the phenoxide ion and the central carbon of the epichlorohydrin. From considerations of the electronic structure of the molecule one would expect this central carbon atom to be the most highly electrophilic,³ hence in the absence of other influences predominate reaction should be at this carbon.

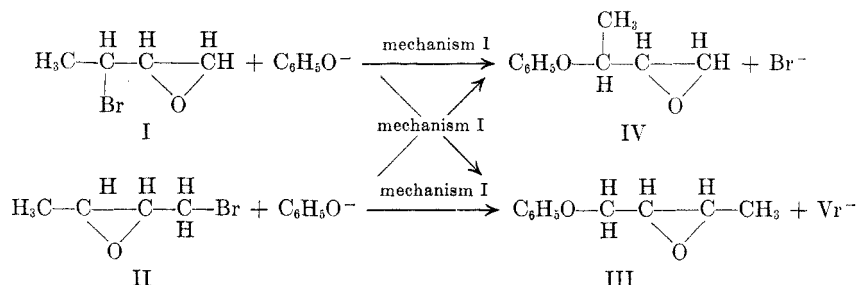
To obviate the difficulty inherent in the structure of epichlorohydrin in studying this reaction mechanism, two isomeric haloepoxides were used which are similar in structure to epichlorohydrin. These compounds were 3-bromo-1,2-epoxybutane, I, and

(1) This paper was presented before the Organic Division of the American Chemical Society at its 125th meeting in Kansas City, Mo., March 23 to April 1, 1954.

(2) D. R. Boyd and E. R. Marle, *J. Chem. Soc.*, **93**, 838 (1908).

(3) The chloromethyl group tends to withdraw electrons in one direction from this carbon and the oxygen atom in the other. See A. E. Remick, *Electronic Interpretations of Organic Chemistry*, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 59.

1-bromo-2,3-epoxybutane, II.⁴ If direct replacement of bromine in each compound is designated as *mechanism one* and initial attack of the phenoxide ion on the epoxide carbon farthest from the halogen bearing carbon is designated *mechanism two*, the two possibilities can be represented by the following reactions.



In the reactions representing mechanism two it is understood that a secondary alkoxide ion is formed as an intermediate⁵ which becomes stabilized by loss of a bromide ion.

Identification of the products of reaction was accomplished by oxidation of the phenoxy substituted epoxides with silver oxide in the presence of 10% sodium hydroxide solution. The products of oxidation thus produced were acids which were identified by melting points and melting points of their derivatives.

The products of reaction here reported indicate that in both cases the phenoxide ion reacted with the bromoepoxides by initial attack on the epoxide carbon atom remote from the halogen bearing carbon atom and that reaction thus occurred *via* mechanism II. It is interesting to note that in the reaction of the same two epoxides with the methoxide ion in methanol and the ethoxide ion in ethanol, reported by Waters and VanderWerf,⁵¹ a single mechanism does not obtain. In these reactions the terminal epoxide I reacted by mechanism II whereas the internal epoxide II reacted according to what we have termed mechanism I.

EXPERIMENTAL

Reaction of 3-bromo-1,2-epoxybutane, I, with phenol. In a typical reaction, 28 g. (0.185 mole) of I was stirred with 17.4

(4) These compounds were prepared from crotyl bromide by the method of Petrov. A. A. Petrov, *J. Gen. Chem. (U.S.S.R.)*, **11**, 713 (1941). No attempt was made to separate the stereoisomers of II reported by Petrov.

(5) Numerous examples of this behavior of epoxides in basic solution have been reported: (a) S. J. Cristol and R. G. Helmreich, *J. Am. Chem. Soc.*, **74**, 4083 (1952). (b) G. K. Helmkamp and H. J. Lucas, *J. Am. Chem. Soc.*, **74**, 951 (1952). (c) C. O. Guss, *J. Am. Chem. Soc.*, **71**, 3460 (1949). (d) W. Reeve and A. Sadle, *J. Am. Chem. Soc.*, **72**, 1251 (1950). (e) R. M. Adams and C. A. VanderWerf, *J. Am. Chem. Soc.*, **72**, 4368 (1950). (f) R. R. Russell and C. A. VanderWerf, *J. Am. Chem. Soc.*, **69**, 11 (1947). (g) H. E. Chitwood and B. T. Freure, *J. Am. Chem. Soc.*, **68**, 680 (1946). (h) R. G. Kadesch, *J. Am. Chem. Soc.*, **68**, 41 (1946). (i) R. C. Waters and C. A. VanderWerf, *J. Am. Chem. Soc.*, **76**, 709 (1954).

g. (0.185 mole) of phenol and 9.3 g. (0.23 mole) of sodium hydroxide in 110 ml. of water at 25° for 20 hr. The organic layer was then separated and combined with the ether extract of the aqueous layer. After drying over anhydrous sodium sulfate, the ether was removed and the residual material was vacuum distilled to yield 10.5 g. of recovered I, a small intermediate fraction, and 10 g. of 1-phenoxy-2,3-epoxybutane, III, b.p. 111–116° at 5 mm. 53% of the theoretical yield based upon I not recovered.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.14; H, 7.43; oxirane oxygen,⁶ 9.64. Found: C, 72.28; H, 7.17; oxirane oxygen, 9.59.

Reaction of 1-bromo-2,3-epoxybutane, II, with phenol. In an analogous procedure to the above, 0.432 mole of II, 0.432 mole of phenol, 0.54 mole of sodium hydroxide in 260 ml. of water, were stirred for 12 hr. at 25°. The organic layer and the ether extract of the aqueous layer were dried over sodium sulfate as before. The residue after removal of the ether was vacuum distilled to give 7.3 g. of 3-phenoxy-1,2-epoxybutane, IV, b.p. 105–108° at 5 mm., 32% based on II not recovered.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{O}_2$: C, 73.14; H, 7.43; oxirane oxygen, 9.64. Found: C, 73.27; H, 7.27; oxirane oxygen, 9.40.

Oxidation of 1-phenoxy-2,3-epoxybutane, III. Oxidation of III was carried out by stirring 1 g. with 5 g. of silver oxide and 50 ml. of 10% sodium hydroxide solution for 24 hr. on the steam bath. At the end of this time the aqueous layer was separated by filtration, acidified, then extracted with ether, dried, and ether evaporated. The white crystalline residue was recrystallized twice from hot water and 0.15 g. of pure phenoxyacetic acid, m.p. 97–98°, was recovered. The *p*-bromophenacyl ester was prepared and melted at 149–151°. There was no depression in mixed melting points with authentic samples. No other acid was isolated from the reactions.

Oxidation of 3-phenoxy-1,2-epoxybutane, IV. The oxidation of IV was carried out in exactly the same manner as with III. The same quantities of material were used. The material was filtered and the filtrate acidified with dilute hydrochloric acid to precipitate a white crystalline solid. This solid was separated and recrystallized from hot water to yield 0.6 g. of 2-phenoxypropionic acid, m.p. 114.5–116°. A small additional quantity was obtained from ether extraction of the aqueous mother liquor. No other acid was found, however. The amide and the *p*-toluide were prepared and found to melt at 129–130° and 114–115°, respectively. These values are in good agreement with the literature values for 2-phenoxypropionic acid and derivatives.

DEPARTMENT OF CHEMICAL ENGINEERING
MISSOURI SCHOOL OF MINES AND METALLURGY
ROLLA, MO.

(6) The method of Swern *et al.* was used to determine oxirane oxygen. Daniel Swern, T. W. Finley, G. H. Billen, and J. T. Scanlan, *Ind. Eng. Chem., Anal. Ed.*, **19**, 414 (1947).