crystallizations of the nitration mixture from ethanol. In subsequent attempts to obtain this compound, we were unable to remove small amounts of the 2,5-dinitro isomer (about 5% from the nmr spectrum).

2,5-Dinitro-1,4-di-*t*-butylbenzene, mp 191.5–192.5° (lit.[3] 191°), was obtained by successive recrystallizations of the nitration mixture from isopropyl alcohol.

The work was carried out during the tenure (by M. J. N.) of a Scientific Research Council Advanced Course Studentship.

Registry No.—I (R = Me), 89-58-7; I (R = Et), 10482-00-5; I (R = *i*-Pr), 10472-64-7; I (R = *t*-Bu), 3463-35-2; II (R = Me), 711-41-1; II (R = Et), 10472-67-0; III (R = Me), 712-32-3; III (R = Et), 10472-69-2; III (R = *t*-Bu), 10472-70-5; IV (R = Me), 609-92-7; IV (R = Et), 10472-72-7; IV (R = *t*-Bu), 10472-73-8.

The Reaction of Epihalohydrins with *n*-Butyl- and Allyllithium

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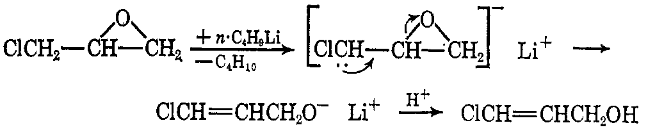
In connection with a search for new epoxides, it was of interest to examine the reaction of certain organolithium compounds with epihalohydrins.

Reactions of alkali metal organic compounds with chloroepoxypropane have been reported in the literature.[1–3] Although Gilman, *et al.*,[3] obtained the expected ring-opening product, 1-aryl-3-chloropropanol-2, from reaction of aryllithium with epichlorohydrin in ether at −78°, it was found in our laboratory that the more strongly basic *n*-butyllithium reacts in an anomalous manner.

When *n*-butyllithium in *n*-heptane was treated at −50° with the stoichiometric amount of *dl*-epichlorohydrin in dry diethyl ether, a mixture of *cis*- and *trans*-β-chloroallyl alcohols was isolated in 75% yield. The isomers could be separated by vapor phase chromatography,[4] and identified by comparison of their infrared spectra[5] with authentic samples prepared by hydrolysis of the corresponding 1,3-dichloropropenes.[6] In addition, a small amount (*ca.* 15%) of propargyl alcohol was found in the reaction mixture.

None of the seven-carbon compounds, heptene 1,2-epoxide, 1-chloro-2-hydroxyheptane, or hepten-2-ol-1 (from base-catalyzed rearrangement of the intermediate heptene epoxide[7]) were detected in the reaction mixture.

Formation of β-chloroallyl alcohol involves proton abstraction from the chlorine-bearing carbon atom followed by rearrangement of the carbanion.



The simultaneous formation of *n*-butane was verified by vapor phase chromatography.

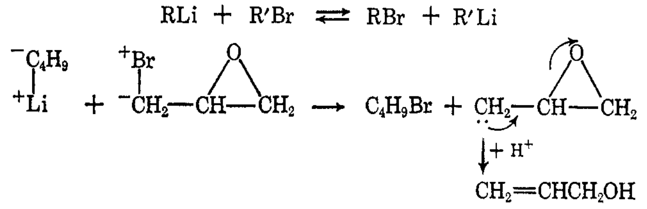
Proton abstraction appears to be restricted to the chlorine-bearing carbon since none of the two isomeric carbonyl compounds, chloroacetone and 3-chloropropanal, which would be expected from attack on the carbon atoms of the oxirane ring could be detected in a vapor phase chromatogram.

Similar base-catalyzed isomerizations of alkylene oxides have been encountered by Culvenor, *et al.*,[7] in the rearrangement of glycidonitrile and phenylglycidylsulfone to the corresponding allyl alcohols by alkali and by Letsinger, *et al.*,[8] in the rearrangement of cyclohexene oxide to cyclohexen-3-ol in the presence of *n*-butyllithium.

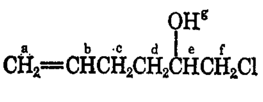
Formation of propargyl alcohol from epihalohydrins in strongly basic medium has been observed by Eglinton, *et al.*,[9] when epichlorohydrin was treated with sodium amide in liquid ammonia.

The reaction of *n*-butyllithium with epibromohydrin takes a different course. Halogen–metal interchange takes place exclusively and 1-bromobutane and allyl alcohol are the sole identifiable reaction products. The exchange reaction which is normally reversible and whose equilibrium position depends strongly on the relative electron-attracting power of the R groups[10] is in this case driven to completion by rearrangement of the initially formed carbanion to the more stable alkoxide ion (Scheme I).

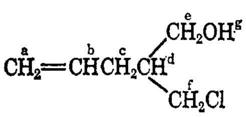
SCHEME I



The less basic allyllithium takes a position between aryllithium[3] and butyllithium in its reactivity toward epichlorohydrin. When treated at −5 to 0° in ether–hexane, 48% of the corresponding ring-opening product was isolated.



I



II

In addition, 43% of a mixture of the geometrical isomers of β-chloroallyl alcohol was obtained.

Opening of the oxirane ring by the allyl anion can give either 1-chloro-2-hydroxy-hexene-5 (I) or its isomer (II).

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(1) G. Volema and J. F. Arens, *Rec. Trav. Chim.*, **78**, 140 (1959).

(2) L. J. Haynes, I. Heilbron, E. R. H. Jones, and F. Sondheimer, *J. Chem. Soc.*, 1583 (1947).

(3) H. Gilman, B. Hofferth, and J. B. Honeycutt, *J. Am. Chem. Soc.*, **74**, 1594 (1952).

(4) All vapor phase chromatograms were obtained on an Aerograph instrument equipped with a 5-ft diethylene succinate-on-firebrick column and thermoconductivity detector at a gas flow of 30 ml of He/min.

(5) Infrared spectra were obtained on a Perkin-Elmer Model 237 grating infrared spectrophotometer.

(6) L. F. Hatch and A. C. Moore, *J. Chem. Soc.*, 2873 (1952).

(7) C. C. J. Culvenor, W. Davies, and W. E. Savage, *ibid.*, 2198 (1949).

(8) R. L. Letsinger, J. G. Traynham, and E. Bobko, *J. Am. Chem. Soc.*, **74**, 399 (1952).

(9) G. Eglinton, E. R. H. Jones, and M. C. Whiting, *J. Chem. Soc.*, 2873 (1952).

(10) See, *e.g.*, R. G. Jones and H. Gilman, *Org. Reactions*, **6**, 339 (1951).

(11) H. Schaltegger, *Helv. Chim. Acta*, **45**, 1368 (1962).

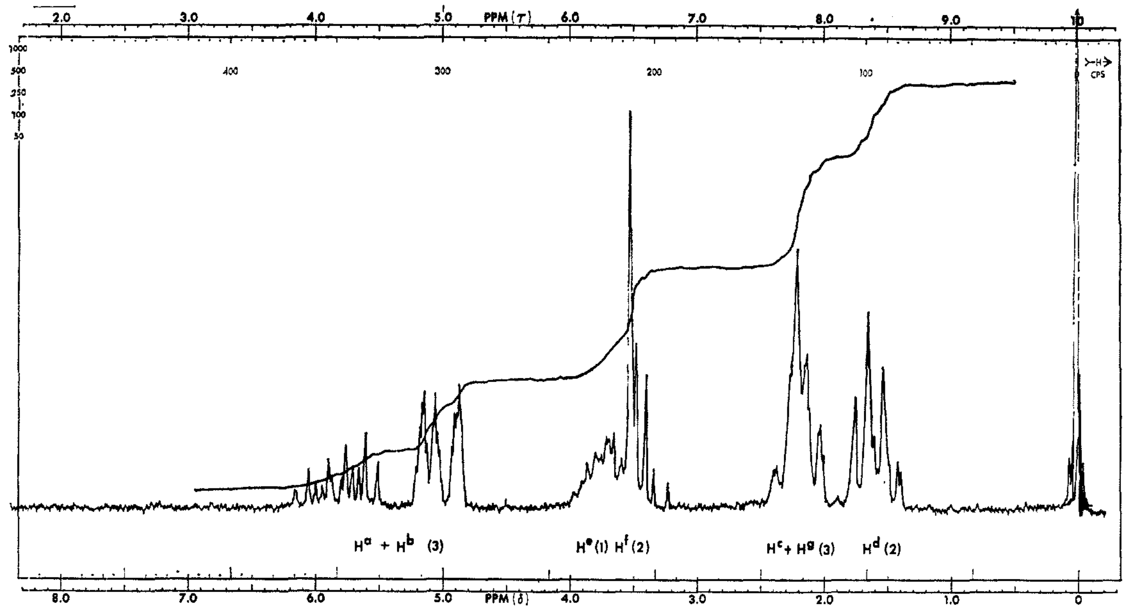

Figure 1.—Nmr spectrum of 1-chloro-2-hydroxy-hexene-5 in CCl_4. Figures in parentheses indicate number of protons.

Although the reaction with bases generally leads to compounds of type I, it was shown recently by Schaltegger[11] in the case of cyclopentadiene anion that attack takes place on the middle C atom.

Confirmation of the structure of the reaction product could be obtained from its nmr spectrum.[12a]

The resonances at $\delta = 4.7$ to 6.2 ppm, by comparison with the spectrum of diallyl ether,[12b] correspond to terminal unsaturation ($CH_2{=}CHC$).

The assignments of the remaining resonances were made as indicated in Figure 1.

The relative numbers of protons in the 1.5- to 2.5-ppm and 3.0- to 4.0-ppm range are 5 and 3 by integration.

This is consistent only with structure I (protons c, d, and g at 1.5 to 2.5 ppm and e and f at 3.0 to 4.0 ppm). The nmr spectrum of the isomeric structure II would be expected to integrate to four protons in each of the two regions corresponding to proton sets c, d, and g and e and f, respectively.

Experimental Section

1. **Reaction of Butyllithium with Epichlorohydrin.**—A 100-ml, three-necked flask was fitted with two adapters, a stirrer, a nitrogen inlet, a low-temperature thermometer, and a drying tube. The remaining opening was sealed with a rubber cap. A solution of epichlorohydrin (4.85 g, 0.052 mole) in 25.0 ml of anhydrous ether was placed into the flask and cooled to −50° in a Dry Ice–acetone bath. By means of a syringe penetrating the rubber cap a solution of 3.45 g (0.052 mole) of *n*-butyllithium in 25 ml of *n*-hexane was added slowly over 1 hr to the vigorously stirred solution. After the mixture was allowed to warm to room temperature it was neutralized with glacial acetic acid and filtered from lithium acetate. The filtrate was distilled on a 10-in. Vigreux column. The fraction boiling between 90 and 120° at normal pressure contained 5% of unreacted epichlorohydrin and 15% propargyl alcohol[13] which were identified by gas chromatography (peak enhancement method) and infrared analysis on samples collected off the gas chromatograph. The portion (3.65 g) boiling from 85 to 90° (60 mm) separated upon gas chromatography into two fractions (retention times at 125°, 5 and 7 min). Samples of each fraction were collected and examined. Fraction 1 (retention time 5 min, 15% yield) has an infrared spectrum identical with *trans*-β-chloroallyl alcohol obtained by hydrolysis of *trans*-1,3-dichloropropene with aqueous Na_2CO_3. Fraction 2 (retention time 7 min, 60% yield) is identical with the chloroallyl alcohol obtained from *cis*-1,3-dichloropropene. Both fractions 1 and 2 were analyzed for chlorine content.

Anal. Calcd for C_3H_5ClO: Cl, 38.3; Found: Cl, 37.92 (fraction 1); 38.16 (fraction 2).

2. **Reaction of Butyllithium with Epibromohydrin.**—In the apparatus and under the conditions of the previous experiment 31.0 g of a solution of *n*-butyllithium in hexane containing 6.4 g of C_4H_9Li with 13.7 g of epibromohydrin in 30 ml of anhydrous ether were allowed to react. After neutralization with acetic acid, filtration and distillation of ether and the main part of hexane on a Vigreux column, the residue (15.0 g) was analyzed by vapor phase chromatography. Allyl alcohol (retention time 1 min at 92°) and *n*-bromobutane (retention time 0.5 min at 92°) were the only reaction products obtained. They were identified by infrared analysis of chromatographically pure samples.

3. **Reaction of Allyllithium with Epichlorohydrin.**—A solution of allyllithium in ether was prepared from allyl phenyl ether following the instructions given by Eisch and Jacobs.[14] Epichlorohydrin (13.8 g, 0.15 mole) in 70 ml of dry *n*-hexane was added dropwise at −5 to 0° to the stirred solution containing 7.25 g (0.15 mole) of allyllithium. The mixture was hydrolyzed by shaking with 200 ml of ice-cold 1 *N* aqueous sulfuric acid, the aqueous phase was extracted with two 100-ml portions of ether, and the combined ether layers were extracted with cold 5% sodium carbonate solution to remove phenol. The residue (20 g) after removal of the ether was distilled at normal pressure. It contained 5.6 g (43% based on epichlorohydrin) of β-chloroallyl alcohols and 9.3 g (48%) of 1-chloro-2-hydroxy-hexene-5, bp 180–184°. An analytical sample was obtained by gas chromatography.

Anal. Calcd for $C_6H_{11}ClO$: C, 53.54; H, 8.24; Cl, 26.44. Found: C, 53.52; H, 8.3; Cl, 26.0.

Infrared absorptions at 2.97 (OH stretching), 3.3 (CH stretching in $C{=}CH_2$), 6.1 ($C{=}C$ stretching), 9.3 (OH deformation), and 10.1 and 10.95 μ (CH out-of-plane deformations in $CH{=}CH_2$), and the nmr spectrum (see discussion section) are in agreement with structure I.

Acknowledgment.—The author wishes to thank Mr. J. A. Rogers for the preparation and discussion of the nmr spectrum of compound I.

Registry No.—Butyllithium, 109-72-8; allyllithium, 3052-45-7; epichlorohydrin, 106-89-8; epibromohydrin, 3132-64-7; 1-chloro-2-hydroxyhexene-5, 10293-98-8.

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[12] (a) The nmr spectrum was determined on a Varian A-60A spectrometer with tetramethylsilane (TMS) as internal standard. (b) "High Resolution NMR Spectra Catalog," Varian Associates, Palo Alto, Calif., 1963.

[13] If not stated otherwise, yields were estimated from the peak areas on vapor phase chromatograms.

[14] J. J. Eisch and A. M. Jacobs, *J. Org. Chem.*, **28**, 2145 (1963).