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DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER, CANADA
C. REID

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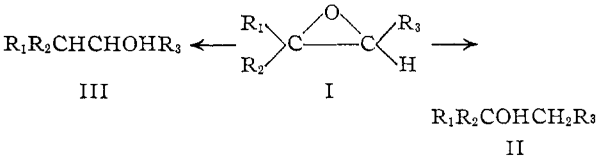
ANOMALOUS REDUCTION OF EPOXIDES WITH LITHIUM ALUMINUM HYDRIDE

Sir:

Lithium aluminum hydride attacks unsymmetrically substituted epoxides predominantly at the least substituted carbon atom to give the more highly substituted alcohol.[1-3] Thus primary–secondary epoxides (I, R_1 = alkyl, $R_2 = R_3$ = H) give secondary alcohols (II, same), and primary–tertiary or secondary–tertiary epoxides (I, R_1, R_2 = alkyl, R_3 = H or alkyl) give tertiary alcohols (II, same). Representative examples from the literature and from our own work are listed in the table (entries 1, 3, 4, 5, 8, 10, 12).



In contrast, we have now found that *reversal* of the direction of ring opening occurs (I → III) when the reduction is carried out in the presence of aluminum chloride or bromide. Substantially complete reversal is achieved in phenyl-substituted epoxides (entries 6, 11, 13) and in isobutylene oxide (entry 9). With propylene oxide (entry 2) only partial reversal occurred and the crude reaction product contained halohydrins. No aliphatic secondary–tertiary epoxide has as yet been studied.

The reductions were carried out in the customary way.[1] Water-soluble products were isolated by continuous ether extraction. Mixtures of solid products (entries 10–13) were analyzed by chromatographic separation. Liquid mixtures (entries 1, 2, 5–9) were analyzed by mass spectrometry; in most cases the analyses were checked by infrared comparison with synthetic mixtures. The reduction mixture for experiments 2, 6, 7, 9, 11 and 13 was obtained by adding standardized ethereal lithium aluminum hydride to cold ethereal aluminum chloride, or by adding allyl bromide in ether to the standardized hydride solution prior to addition of the epoxide.

We are presently studying the mechanism of the abnormal ring opening as well as extensions of the method to other epoxides, including alicyclic and steroid cases.

TABLE I

REDUCTION OF EPOXIDES WITH LITHIUM ALUMINUM HYDRIDE

	Entry compound	R_1	R_2	R_3	Moles LAH	Moles AlX_3	Yield, %	Products % II	% III	Ref.
1	Propylene oxide	Me	H	H	0.3	0	60	100	0	*a*
2	Propylene oxide	Me	H	H	.25	1[b]	*ca.* 42	*ca.* 80	*ca.* 20	*a*
3	1,2-Epoxydecane	Oct	H	H	.25	0	90	100	0	2
4	Styrene oxide	Ph	H	H	.25+	0	94	100	0	3
5	Styrene oxide	Ph	H	H	.3	0	82	90–95	5–10	*a*
6	Styrene oxide	Ph	H	H	.25	1[b]	87	2–10	90–98	*a*
7	Styrene oxide	Ph	H	H	1.5	*c*	80	71	28	*a*
8	Isobutylene oxide	Me	Me	H	0.3	0	26	95–98	2–5	*a*
9	Isobutylene oxide	Me	Me	H	.25	1[b]	55	5–7	93–95	*a*
10	1,1-Diphenylethylene oxide	Ph	Ph	H	.4	0	97	100	0	*a*
11	1,1-Diphenylethylene oxide	Ph	Ph	H	2.4	*c*	85	14	86	*a*
12	1,1,2-Triphenylethylene oxide	Ph	Ph	Ph	2.2	0	11.5[d]	100	0	*a*
13	1,1,2-Triphenylethylene oxide	Ph	Ph	Ph	2.4	*c*	91	0	100	*a*

[a] This work. [b] Aluminum chloride. [c] Generated *in situ* from 1 mole of allyl bromide. [d] Also recovered 81% starting material.

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(3) R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

(4) Shell Research Fellow, 1955–1956.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA
ERNEST L. ELIEL
DAVID W. DELMONTE[4]

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THE RADIATION CHEMISTRY OF WATER VAPOR. THE INDIRECT EFFECT ON DEUTERIUM[1]

Sir:

The rate of formation of hydrogen deuteride in gaseous mixtures of tritium–water (0.284 hydrogen-atom % tritium) and deuterium is a direct measure of the rate of formation of hydrogen atoms. Samples containing 0.185 g. of tritium–water vapor and deuterium gas at mole fractions in the range 10^{-3} to 10^{-2} were heated in sealed Pyrex tubes (238 ml., 47 mm. i.d.) at temperatures from 120 to 165° and total pressures of 1000 millimeters. Evolution of foreign gases from the tube walls was kept negligibly small by heating and pumping on the tubes for at least 12 hours at 510° followed by 12 hours at 440° before admission of the reactants. Isotopic analysis of the hydrogen was performed on a mass spectrometer. No exchange was observed in the absence of tritium–water. G(HD)

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.