40 mc, and was made possible by grants from the National Research Council of Canada and the National Cancer Institute of Canada.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF BRITISH COLUMBIA
VANCOUVER, CANADA

C. Reid

RECEIVED MAY 1, 1956

## 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.<sup>1-3</sup> Thus primary—secondary

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

TABLE I
REDUCTION OF EPOXIDES WITH LITHIUM ALUMINUM HYDRIDE

						Products			
Entry compound	$R_1$	$R_2$	$R_3$	LAH	$A1X_3$	Yield, %	% II	% III	Ref.
Propylene oxide	Me	H	$\mathbf{H}$	0.3	0	60	100	0	a
Propylene oxide	Me	$\mathbf{H}$	$\mathbf{H}$	.25	$1^b$	ca.~42	ca. 80	ca. 20	a
1,2-Epoxydecane	Oct	$_{\mathrm{H}}$	H	.25	0	90	100	0	$^2$
Styrene oxide	Ph	H	H	.25 +	0	94	100	0	3
Styrene oxide	Ph	H	H	. 3	0	82	90-95	5-10	a
Styrene oxide	Ph	$_{\mathrm{H}}$	$\mathbf{H}$	.25	$1^b$	87	2-10	90-98	a
Styrene oxide	Ph	$_{\mathrm{H}}$	$\mathbf{H}$	1.5	c	80	71	28	a
Isobutylene oxide	Me	Me	H	0.3	0	26	95-98	2-5	a
Isobutylene oxide	Me	Me	$_{\mathrm{H}}$	. 25	$1^b$	55	5-7	93-95	a
1,1-Diphenylethylene oxide	Ph	Ph	$\mathbf{H}$	. 4	0	97	100	0	a
1,1-Diphenylethylene oxide	Ph	Ph	H	2.4	С	85	14	86	a
1,1,2-Triphenylethylene oxide	Ph	Ph	Ph	2.2	0	$11.5^{d}$	100	0	a
1,1,2-Triphenylethylene oxide	$\mathbf{P}\mathbf{h}$	Ph	Ph	2.4	c	91	0	100	a
	Propylene oxide Propylene oxide 1,2-Epoxydecane Styrene oxide Styrene oxide Styrene oxide Styrene oxide Isobutylene oxide Isobutylene oxide 1,1-Diphenylethylene oxide 1,1-Diphenylethylene oxide 1,1,2-Triphenylethylene oxide	Propylene oxide Propylene oxide Me 1,2-Epoxydecane Oct Styrene oxide Ph Styrene oxide Ph Styrene oxide Ph Styrene oxide Ph Isobutylene oxide Isobutylene oxide Me 1,1-Diphenylethylene oxide Ph 1,1-Diphenylethylene oxide Ph 1,1,2-Triphenylethylene oxide Ph	Propylene oxide Propylene oxide Me H 1,2-Epoxydecane Oct H Styrene oxide Ph Styrene oxide Ph H Styrene oxide Ph H Styrene oxide Ph H Isobutylene oxide Me Isobutylene oxide Me I,1-Diphenylethylene oxide Ph I,1-Diphenylethylene oxide Ph I,1,2-Triphenylethylene oxide Ph Ph	Propylene oxide Propylene oxide Me H H  1,2-Epoxydecane Oet H H  Styrene oxide Ph H H  Isobutylene oxide Me Me H  Isobutylene oxide Me Me H  1,1-Diphenylethylene oxide Ph Ph H  1,1-Diphenylethylene oxide Ph Ph H  1,1,2-Triphenylethylene oxide Ph Ph	Entry compound         R1         R2         R3         LAH           Propylene oxide         Me         H         H         0.3           Propylene oxide         Me         H         H         .25           1,2-Epoxydecane         Oct         H         H         .25           Styrene oxide         Ph         H         H         .25+           Styrene oxide         Ph         H         H         .25           Styrene oxide         Ph         H         H         1.5           Isobutylene oxide         Me         Me         H         0.3           Isobutylene oxide         Me         Me         H         .25           1,1-Diphenylethylene oxide         Ph         Ph         H         .4           1,1-Diphenylethylene oxide         Ph         Ph         Ph         Ph           1,1,2-Triphenylethylene oxide         Ph         Ph         Ph         Ph         Ph	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Entry compound         R1         R2         R3         LAH         AlX3         Yield, %           Propylene oxide         Me         H         H         0.3         0         60           Propylene oxide         Me         H         H         .25 $1^b$ ca. 42           1,2-Epoxydecane         Oct         H         H         .25         0         90           Styrene oxide         Ph         H         H         .25         0         94           Styrene oxide         Ph         H         H         .3         0         82           Styrene oxide         Ph         H         H         .25 $1^b$ 87           Styrene oxide         Ph         H         H         1.5         c         80           Isobutylene oxide         Me         Me         H         0.3         0         26           Isobutylene oxide         Me         Me         H         .25 $1^b$ $55$ 1,1-Diphenylethylene oxide         Ph         Ph         H         .4         0         97           1,1-Diphenylethylene oxide         Ph         Ph         Ph         Ph	Entry compound         R1         R2         R3         LAH         AlX4         Yield, %         % II           Propylene oxide         Me         H         H         0.3         0         60         100           Propylene oxide         Me         H         H         .25 $1^b$ $ca.42$ $ca.80$ 1,2-Epoxydecane         Oct         H         H         .25 $0$ 90         100           Styrene oxide         Ph         H         H         .25 $0$ 94         100           Styrene oxide         Ph         H         H         .3 $0$ $82$ $90$ - $95$ Styrene oxide         Ph         H         H         .25 $1^b$ $87$ $2$ - $10$ Styrene oxide         Ph         H         H $1.5$ $c$ $80$ $71$ Isobutylene oxide         Me         Me         H $0.3$ $0$ $26$ $95$ - $98$ Isobutylene oxide         Me         Me         H $0.3$ $0$ $26$ $95$ - $98$ Isobutylene oxide <td< td=""><td>Entry compound         R1         R2         R3         LAH         AlXa         Yield, %         % II         % III           Propylene oxide         Me         H         H         0.3         0         60         100         0           Propylene oxide         Me         H         H         1.25         <math>1^b</math> <math>ca.42</math> <math>ca.80</math> <math>ca.20</math>           1,2-Epoxydecane         Oct         H         H         .25         <math>0</math>         90         100         <math>0</math>           Styrene oxide         Ph         H         H         .25+         <math>0</math>         94         100         <math>0</math>           Styrene oxide         Ph         H         H         .3         <math>0</math>         82         <math>90-95</math> <math>5-10</math>           Styrene oxide         Ph         H         H         .25         <math>1^b</math>         87         <math>2-10</math> <math>90-98</math>           Styrene oxide         Ph         H         H         1.5         <math>c</math>         80         <math>71</math> <math>28</math>           Isobutylene oxide         Me         Me         H         .25         <math>1^b</math> <math>55</math> <math>5-7</math> <math>93-95</math>           1,1-Diphenylethylene oxide         Ph</td></td<>	Entry compound         R1         R2         R3         LAH         AlXa         Yield, %         % II         % III           Propylene oxide         Me         H         H         0.3         0         60         100         0           Propylene oxide         Me         H         H         1.25 $1^b$ $ca.42$ $ca.80$ $ca.20$ 1,2-Epoxydecane         Oct         H         H         .25 $0$ 90         100 $0$ Styrene oxide         Ph         H         H         .25+ $0$ 94         100 $0$ Styrene oxide         Ph         H         H         .3 $0$ 82 $90-95$ $5-10$ Styrene oxide         Ph         H         H         .25 $1^b$ 87 $2-10$ $90-98$ Styrene oxide         Ph         H         H         1.5 $c$ 80 $71$ $28$ Isobutylene oxide         Me         Me         H         .25 $1^b$ $55$ $5-7$ $93-95$ 1,1-Diphenylethylene oxide         Ph

<sup>&</sup>lt;sup>a</sup> This work. <sup>b</sup> Aluminum chloride. <sup>c</sup> Generated in situ from 1 mole of allyl bromide. <sup>d</sup> Also recovered 81% starting material.

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,

$$R_1R_2CHCHOHR_3 \leftarrow \begin{array}{c} R_1 \\ R_2 \end{array} C \xrightarrow{O} C \xrightarrow{R_3}$$
III

 $R_1R_2COHCH_2R_3$ 

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  $(I \rightarrow III)$  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

method to other epoxides, including alicyclic and steroid cases.

This work is supported in part under Atomic Energy Commission contract AT(11-1)-38.

(4) Shell Research Fellow, 1955-1956.

DEPARTMENT OF CHEMISTRY UNIVERSITY OF NOTRE DAME NOTRE DAME, INDIANA

ERNEST L. ELIEL DAVID W. DELMONTE<sup>4</sup>

RECEIVED MAY 21, 1956

## THE RADIATION CHEMISTRY OF WATER VAPOR. THE INDIRECT EFFECT ON DEUTERIUM<sup>1</sup>

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<sup>-3</sup> to 10<sup>-2</sup> 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)

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

<sup>(1)</sup> W. G. Brown in R. Adams, "Organic Reactions," John Wiley and Sons, Inc., New York, Vol. VI, 1951, p. 476; L. W. Trevoy and W. G. Brown, This Journal, 71, 1675 (1949); R. Fuchs and C. A. VanderWerf, ibid., 74, 5917 (1952); E. L. Eliel and J. P. Freeman, ibid., 74, 923 (1952).

<sup>(2)</sup> M. S. Newman, G. Underwood and M. Renoll, ibid., 71, 3362 (1949).

<sup>(3)</sup> R. F. Nystrom and W. G. Brown, ibid., 70, 3738 (1948).