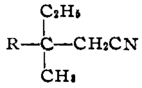
TABLE II

3-ETHYL-3-METHYLALKANENITRILES

 $R-C(C_2H_5)(CH_3)-CH_2CN$	Boiling point, °C.	Mm.	Yield, %	$n^{25}D$	d^{25}	Nitrogen, % Calcd.	Found
n-C_3H_7-	103–104	31	68.6[a]	1.4291	0.8286	10.06	9.84
s-C_3H_7-	103–103	25–24	86.7	1.4363	.8461	10.06	10.06
n-C_4H_9-	112–113	22	76.6	1.4328	.8300	9.14	8.94
n-C_5H_{11}-	127–130	23–25	83.0	1.4358	.8302	8.37	8.33
n-C_6H_{13}-	139–140	20–19	86.0	1.4379	.8314	7.73	7.80

[a] The yield was 81.4% of nitrile when the acid nitrile was worked up (see nitrile preparation).

TABLE III

3-ETHYL-3-METHYLALKANOIC ACIDS, $R-(C_2H_5)(CH_3)C-CH_2COOH$

R-	Boiling point, °C. (15 mm.)	Yield, %	$n^{25}D$	d^{25}	Equiv. wt. Calcd.	Equiv. wt. Found	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
n-C_3H_7-	136–137	95.1	1.4377	0.9205	158.24	159.1	68.31	68.28	11.46	11.73
s-C_3H_7-	138–140	89.6	1.4460	.9409	158.24	159.6	68.31	68.43	11.46	11.65
n-C_4H_9-	147.5–149	96.4	1.4406	.9135	172.26	173.1	69.72	69.60	11.70	11.73
n-C_5H_{11}-	157–160	91.4	1.4426	.9071	186.29	188.3	70.92	70.77	11.91	11.90
n-C_6H_{13}-	169–171	90.5	1.4449	.9030	200.31	202.3	71.95	71.92	12.08	12.02

berg stirrer for 13 hours.[9] (After 2.5 hours the mixture appeared to be homogeneous.) The cooled reaction mixture was diluted with 300 cc. of water and extracted with three portions of ether to remove neutral materials. The aqueous residues were acidified with concentrated hydrochloric acid and extracted three times with ether. The extracts were washed with water and saturated sodium chloride solution and dried with sodium sulfate. After removal of the ether the acid was distilled from a Claisen flask; b.p. 139–140.5° (24–22 mm.), 60.2 g. (95.1%), $n^{25}D$ 1.4375.

The other acids in the series are listed in Table III. The preparation was the same except that the period of heating varied between 12–15 hours. The analytical data refer to values taken on intermediate fractions obtained upon refractionation of these acids.

Direct Hydrolysis of a *t*-Alkylcyanoacetic Ester to Obtain an Acid.—A mixture of 45.1 g. of ethyl 2-cyano-3-ethyl-3-methyloctanoate, 45 g. of potassium hydroxide and 150 cc. of ethylene glycol was heated under reflux for 10 hours. (There were still two phases.) This mixture was separated into acidic and neutral fractions as described above in the preparation of 3-ethyl-3-methylhexane nitrile. The neutral extract was distilled to furnish two fractions: 14 g. (44%, calcd. as nitrile), b.p. 123–130° (20 mm.), $n^{25}D$ 1.4350, and 7.3 g. (21%, calcd. as amide), b.p. 130–190° (20 mm.), $n^{25}D$ 1.4560. The acid fraction was distilled to give 6.4 g. (18%), b.p. 165–167° (23 mm.), $n^{25}D$ 1.4489.

Longer heating would certainly have given a better yield of acid; but this result seemed to indicate that an advantage would be gained by using the two-step method described above.

CHICAGO 14, ILLINOIS

---

[9] Because of the corrosive action of the alkali it is best to use a cheaper, single-necked, round-bottomed flask and to operate the stirrer through a 50-60 mm. condenser in this reaction. Although a mole of water is required for this reaction, no water was added since it was assumed that the reagents were sufficiently wet to supply this need.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Concentration Effects in the Lithium Aluminum Hydride Reduction of 3,4-Epoxy-1-butene

BY RICHARD FUCHS AND CALVIN A. VANDERWERF

RECEIVED AUGUST 1, 1952

In the S_N2 ring opening of 3,4-epoxy-1-butene by lithium aluminum hydride, the percentage of the alcohol resulting from attack at the secondary carbon of the epoxide varied from 30% at high lithium aluminum hydride concentrations to 17% at an epoxide–hydride mole ratio of 1:4, with a corresponding increase in the alcohol resulting from primary attack. The percentage of secondary attack was likewise decreased by partial alcoholysis of the hydride prior to reduction of the epoxide, leaving $[AlH_3OR]^-$ as the predominant ionic species. These results are consistent with two postulations: (1) that the lithium aluminum hydride reduction of epoxides is initiated by attack at the epoxide by the series of ions $[AlH_4]^-$, $[AlH_3OR]^-$, $[AlH_2(OR)_2]^-$ and $[AlH(OR)_3]^-$, which, although electronically similar, increase in steric requirements in the order written; and (2) that steric factors are important in determining the position of attack and hence the direction of ring opening.

The importance of steric *vs.* electronic factors in the direction of S_N2 ring opening in epoxides is still a controversial question which deserves further study. The role played by steric factors can best be demonstrated with an epoxide in which steric and electronic factors act in opposition and with a series of electronically similar bases with different steric requirements.

3,4-Epoxy-1-butene was chosen for study because resonance stabilization in the transition state[1] favors secondary attack, whereas the steric factor favors primary attack. Thus the ratio of the two isomeric alcohols formed by ring opening in any given reaction gives an indication of the relative importance of the two factors. It is known that base-catalyzed ring opening of 3,4-epoxy-1-butene may show a range from essentially 100% secondary

---

[1] P. D. Bartlett and S. D. Ross, THIS JOURNAL, **70**, 926 (1948).

attack by the linear azide ion[2] to 100% primary attack by the bulky malonic ester carbanion.[3]

There is considerable evidence that the reduction of epoxides by lithium aluminum hydride, as well as related reactions of the hydride, proceed by a typical S_N2 mechanism.[4] Trevoy and Brown[3b] have suggested that in the lithium aluminum hydride reduction of epoxides the actual attacking reagent is a series of complex ions beginning with $(AlH_4)^-$ and shifting to $[AlH_2(OR)_2]^-$ and $[AlH(OR)_3]^-$ as the reaction proceeds and as the aluminum ion becomes coördinated successively with alkoxide ions formed by the rupture of the epoxide ring. Electronically these attacking bases are quite similar, but their steric requirements increase markedly with the number of coördinated alkoxide ions.

Inasmuch as the smallest ion of the series, $[AlH_4]^-$, would be least susceptible to steric factors, the percentage of secondary attack in the reduction of 3,4-epoxy-1-butene with lithium aluminum hydride might be expected to increase with an increase in the hydride–epoxide ratio. Conversely, partial alcoholysis of the lithium aluminum hydride prior to its reaction with the epoxide might be expected to decrease the percentage of secondary attack.

Results

As shown in Table I, the percentage of 3-buten-1-ol, the product resulting from attack at the secondary carbon, obtained in the mixture of alcohols resulting from the reduction of 3,4-epoxy-1-butene with lithium aluminum hydride, varied from 30% at a hydride–epoxide mole ratio of approximately 2:1 to 17% at the theoretical mole ratio of 1:4. At approximately molar hydride–epoxide ratios, the percentage of 3-buten-1-ol in the total product of the reaction was reduced to 13% by preliminary partial alcoholysis of the lithium aluminum hydride by addition of somewhat greater than molar quantities of methylisobutylcarbinol. No 2-buten-1-ol, suggestive of an S_N2' reaction, was isolated.

Table I

Run	Epoxide, moles	$LiAlH_4$, moles	$\frac{LiAlH_4}{Epoxide}$	Recovery, %	Total alcohols, %	Rel. % 3-buten-2-ol	Rel. % 3-buten-1-ol	Moles added methylisobutylcarbinol
A	0.50	1.05	2.1	100	100	70	30	..
B	.25	0.52	2.1	76	76	72	28	..
C	.25	.17	0.68	90	90	78	22	..
D	.25	.066	.26	98	72	83	17	..
E	.25	.25	..	75	50	85	15	0.30
F	.25	.19	..	98	62	87	13	.25
G[3b]	.178	.118	.67	..	71	82	18	..

Experimental

Portions of solid lithium aluminum hydride were weighed and added to 250 ml. of anhydrous ether. Each mixture was stirred for one hour, after which no large particles remained. When methylisobutylcarbinol was used (runs E and F), it was added at this point, dissolved in 75 ml. of anhydrous ether. During the entire reaction agitation was maintained by a mercury-sealed tantalum Hershberg stirrer. The third neck of the one-liter flask bore an ammonia condenser.

3,4-Epoxy-1-butene, mixed with an equal volume of ether was then added dropwise. After spontaneous refluxing had subsided, the mixture was heated for one hour, cooled, and 200 ml. of water was added slowly. In order to obviate the possible isomerization of the products no acid was added. The ether layer was separated from the aqueous aluminum hydroxide suspension, and the latter was extracted with 200 ml. of ether. The combined ether extracts were dried over potassium carbonate.

Most of the ether was removed slowly through a 100-cm. bead-packed column. The residue was then fractionated through a 55-cm. tantalum-spiral column of high efficiency. Quantitative recovery was assured by the use of a chaser of di-*n*-butyl ether. For the cases in which methylisobutylcarbinol was added, it served as the chaser. Temperature readings were taken at volume intervals of no more than 0.2 ml. in the critical portions of the distillation curves.

The two butenols are known compounds and their identities were confirmed by the refractive indices and by the preparation of the α-naphthylurethans.

A precision of 2% was attained in duplicate runs. A known mixture of pure epoxybutene, 3-buten-2-ol, 3-buten-1-ol and chaser was fractionated, and gave excellent agreement with the true values.

Lawrence, Kansas

---

(2) C. A. VanderWerf, R. Y. Heisler and W. E. McEwen, unpublished work.

(3) R. Russell and C. A. VanderWerf, This Journal, **69**, 11 (1947). For intermediate values see: (a) ref. 1; (b) L. W. Trevoy and W. G. Brown, *ibid.*, **71**, 1675 (1949); (c) D. Swern, G. N. Billen and H. B. Knight, *ibid.*, **71**, 1152 (1949); and (d) G. D. Zuidema, P. L. Cook and G. Van Zyl, private communication.

(4) See (a) ref. 3(b); (b) E. L. Eliel and J. P. Freeman, *ibid.*, **74**, 923 (1952); (c) E. R. Alexander, *ibid.*, **72**, 3796 (1950); (d) E. L. Eliel, *ibid.*, **71**, 3970 (1949); (e) J. E. Johnson, R. H. Blizzard and H. W. Carhart, *ibid.*, **70**, 3664 (1948).