Fig. 4), the viscosity of the quenched material changed continuously from a glass at C to a liquid with the approximate consistency of SAE 20 lubricating oil.

Table II is a summary of analyses of the two phases, together with the original composition. The composition of the two immiscible liquids cannot be determined with great accuracy without elaborate equipment for sampling under the pressure–temperature conditions encountered. However, the heavy phase quenches readily to a glass which, with some caution, can be sampled with little or no contamination from the light phase, but the latter cannot be sampled nearly so accurately because of contamination from the condensed vapor phase and solution of some of the heavy phase.

TABLE II

Temp., °C.	Initial composition, %			Composition of light phase, %			Composition of heavy phase, %		
	SiO_2	Na_2O	H_2O	SiO_2	Na_2O	H_2O	SiO_2	Na_2O	H_2O
250	33.9	13.0	53.1	21.8	9.0	69.2	45.5	17.5	37.0
300	35.1	12.9	52.0	17.2	6.7	76.1	51.0	18.0	31.0
350	36.1	12.6	51.3	12.1	4.5	83.4	55.4	20.1	24.5

The analysis of the heavy phase was used in locating the boundary of the immiscible area on the high silica end of the region. The boundary of the immiscible area in the low silica region was defined by allowing the bombs to remain inverted in the furnace a few minutes prior to removal, and quenching in the inverted position for forty-five seconds, after which the bombs were turned right side up and opened. The heavy phase collects on the silver washer, and amounts as small as 0.05 g. of the glass can easily be detected.

The Immiscible Region.—In the three-dimensional temperature–composition prism the region of liquid immiscibility in a ternary system in which there is no solubility gap in the liquid phases of the binary systems has the shape of a spheroid when it is not intersected by the stability field of a crystalline phase. Theoretically, this spheroid may be cut off by the stability fields of crystalline phases in almost any manner. In most examples the lower portion of the spheroid is intersected by one or more stability fields of crystalline phases. The present system is unusual in that the upper portion of the spheroid is apparently cut off by stability fields of $Na_2Si_2O_5$ and quartz. Immiscibility has not been found in several runs at 200°, hence the lower consolute point on the immiscibility spheroid is probably between 200 and 250°. The upper extent of the immiscible region has not been reached.

Acknowledgment.—This work was undertaken on the basis of preliminary experiments done at the Geophysical Laboratory by Dr. G. W. Morey and O. F. Tuttle.

Summary

A portion of the system Na_2O–SiO_2–H_2O was investigated. Equilibrium relations were determined at 250, 300 and 350°. The system possesses liquid immiscibility with a lower consolute temperature between 200 and 250°. The immiscible region is intersected at 250° by the quartz stability field, and at 300 and 350° by the stability fields of quartz and $Na_2Si_2O_5$.

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Methanolysis of 3,4-Epoxy-1-butene

BY PAUL D. BARTLETT AND SIDNEY D. ROSS[1]

Introduction

Kadesch[2] reported that the allylic epoxide, 3,4-epoxy-1-butene, was attacked by methanol at the primary position in the presence of sodium methoxide and at the secondary position in the presence of sulfuric acid. In an attempt to prepare the resulting isomeric ether–alcohols we repeatedly obtained products from both acid and alkaline treatments yielding the same 3,5-dinitrobenzoate (m. p. 75.5–76°). Furthermore, the yield of this derivative was highest in the case of the acid-catalyzed methanolysis from which Kadesch reported only a 3,5-dinitrobenzoate melting at 107–109°. As a result of these discrepancies we have made a more careful study of the reaction than was at first intended, with the following conclusions: The product of the acid-catalyzed methanolysis is the primary alcohol 2-methoxy-3-buten-1-ol (II) as reported by Kadesch, although its 3,5-dinitrobenzoate melts at 75.5–76° and not at 107–109°. The alcohol is accompanied by a small amount of crotonaldehyde and by a larger amount of a dimolecular product, probably the 2-erythryl ether of 2-methoxy-3-buten-1-ol (VIII). The low-boiling product of the base-catalyzed methanolysis is a mixture of II and 1-methoxy-3-buten-2-ol (I) which could not be separated and from which only the 3,5-dinitrobenzoate of II could be crystallized. We obtained neither the dinitrobenzoate of I nor any compound resembling the dinitrobenzoate of Kadesch melting at 107–109°. Our results and their relation to the results of Kadesch are summarized in the flow sheet and in Table I.

Discussion of Results

Kadesch[2] has given an able discussion of the

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[1] Pittsburgh Plate Glass Fellow, 1945–1946.

[2] Kadesch, THIS JOURNAL, 68, 41 (1946).

TABLE I

COMPARISON OF PRESENT RESULTS (B. & R.) WITH THOSE OF KADESCH (K.) ON METHANOLYSIS OF 3,4-EPOXY-1-BUTENE

Reagent	Mole % and investigator	Structure assigned to product	M. p. of 3,5-dinitrobenzoate, °C.	Method of structure proof
H_2SO_4 in CH_3OH	0.16 (K.)	II	107–109	Oxidation to $CH_3OCH(COOH)_2$
	1–5 (B. & R.)	II	75.5–76	Hydrogenation to
		VIII		$\mathrm{III} \xrightarrow{\text{ox.}} \mathrm{V} \begin{smallmatrix} \nearrow \mathrm{VI} \\ \searrow \mathrm{VII} \end{smallmatrix}$
		$CH_3CH{=}CHCHO$		
$NaOCH_3$ in CH_3OH	1.4–2.1 (K.)	I	72	Comparison with results of Petrov.[2a]
	2.3 (B. & R.)	II	75.5–76	
		I	.....	Hydrogenation to $\mathrm{IX} \xrightarrow{\text{ox.}} \mathrm{X}$

mechanisms of the opening of the epoxide ring which might be expected under acidic and basic conditions. This author points out that the S_N1 mechanism, favored by acidic conditions, should involve cleavage of the allylic, secondary C-O bond rather than that of the non-allylic, primary C-O bond. Our results are in entire accord with this interpretation of the acidic mechanism although we, like Kadesch, have not carried out kinetic or quantitative studies of the reaction. With regard to the alkaline methanolysis, Kadesch cites previous reasons for believing that the mechanism of this reaction is of the S_N2 type, in view of which it was not surprising to find apparently exclusive opening of the expoxide ring at the primary position. The recent results of Chitwood and Freure[3] on the alcoholysis of propylene oxide provide further examples of the occurrence of attack by alkoxide ion exclusively at the primary position in a saturated epoxide. Our observation that the alkaline methanolysis of 3,4-epoxy-1-butene leads to a mixture of the primary and secondary methyl ethers raises the question: is the attack at the secondary position due to the appearance of the S_N1 mechanism even in alkaline solution, or does the allylic character of the secondary position make it susceptible to S_N2 attack in competition with the primary position?

An experiment for which we are indebted to Dr. Harry F. Herbrandson seems to settle this question in favor of the S_N2 mechanism in the case of both products of the alkaline cleavage. Methanolysis of the oxide by a concentration of sodium methoxide more than seven times that used previously by us led to essentially the same proportion of the isomers in the product. Had the attack on the primary position involved direct participation of the methoxide ion and the attack on the secondary position not, this experiment should have given seven times the ratio of I to II previously observed. It is, of course, well recognized that allylic character can enhance the reactivity of halides in direct bimolecular displacement reactions as well as in reactions of the S_N1 type.[4] This can be regarded as a lowering of the energy of the transition state through allylic resonance.

A factor limiting the interpretation of the relative amounts in which isomers are isolated in this reaction should perhaps be pointed out.[5] If our interpretation of the higher-boiling material is correct, the primary alcohol II is much more likely to be converted into such material than is the secondary alcohol I, and the ratio of (II)/(I) isolated will be smaller than the ratio of reactivities at carbon atoms 3 and 4 whenever higher-boiling products are also present.

Experimental Details

Methanolysis of 3,4-Epoxy-1-butene with 1 mole per cent. Sulfuric Acid.—To methanol (192.2 g. (6 moles) dried over magnesium methoxide, b. p. 64.6°, $n^{25}D$ 1.3279) and sulfuric acid (1.92 g. (0.02 mole) Merck reagent grade; sp. gr. 1.84) in a three-neck flask, fitted with a mechanical stirrer and reflux condenser and heated to reflux, was added over a ninety-minute period 120 g. (2 moles) of 3,4-epoxy-1-butene. This epoxide was obtained from the Columbia Chemical Division of the Pittsburgh Plate Glass Co. and redistilled through a Lecky-Ewell type column rated at sixty theoretical plates. The oxide had b.p. 67°, $n^{23}D$ 1.4151. Boiling was continued for two hours after the addition, ten grams of potassium carbonate was added and the mixture was stirred at room temperature for one-half hour. The total reaction mixture was then distilled through the column used in purifying the 3,4-epoxy-1-butene. The following fractions were obtained:

Fraction	Pressure, mm.	B. p., °C.	Wt., grams	$n^{25}D$
1	760	64.6	131	1.3280
2	55	to 65	1.5	1.3829
3	55	65–69	4.5	1.4250
4	55	69–71	10.5	1.4280
5	55	71	17.5	1.4280
6 (Trap)			6.5	1.3849
7	55	71	11.0	1.4280
8	55	69	42.5	1.4280
9	55	69	7.0	1.4278
Combined higher boiling fractions			59.5	

Fraction 1 above is recovered methanol, fractions 2, 3 and 6 are intermediate fractions and fractions 4, 5, 7, 8 and 9 are 2-methoxy-3-buten-1-ol, II. Fraction 7 was analyzed.

Anal. Calcd. for $C_5H_{10}O_2$: C, 58.68; H, 9.85. Found: C, 59.13; H, 9.99.

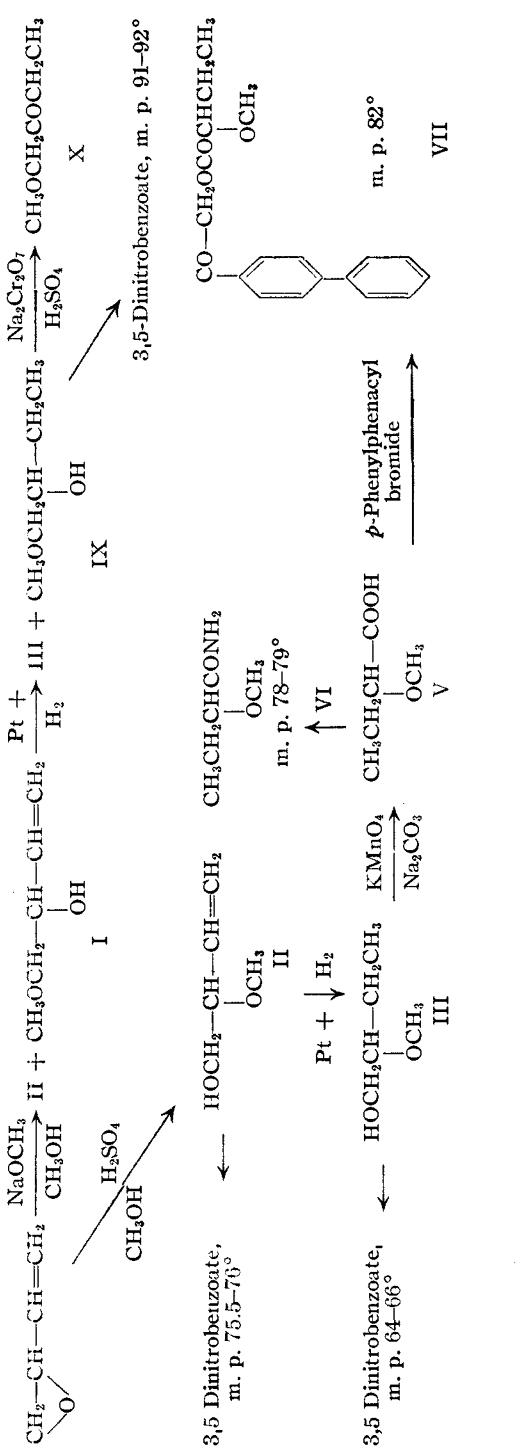
Detection of Crotonaldehyde.—A little of fraction 6 was treated with 2,4-dinitrophenylhydrazine in alcohol. A

[2a] Petrov, *J. Gen. Chem.* (*USSR*), **8**, 131 (1938).

[3] Chitwood and Freure, THIS JOURNAL, **68**, 680 (1946).

[4] For example, in the bimolecular reaction between chlorides and potassium iodide in acetone at 50°, allyl chloride is 79 times as reactive as *n*-butyl chloride (Conant, Kirner and Hussey, THIS JOURNAL, **47**, 488 (1925)).

[5] For this point we are indebted to Dr. X, a colleague of Referee 5.



drop of concentrated hydrochloric acid was added and the mixture was warmed on the steam-bath. On cooling the hydrazone crystallized. The melting point after crystallization from ethanol–acetic acid was 188–189°. The melting point of a mixture with an authentic sample of the 2,4-dinitrophenylhydrazone of crotonaldehyde showed no depression.

Preparation of the 3,5-Dinitrobenzoate of II.—Fractions 4, 7 and 9 were converted to the 3,5-dinitrobenzoate by heating 0.92 g. of 3,5-dinitrobenzoyl chloride with 0.31 g. of the alcohol in 10 cc. of benzene containing 0.40 g. of pyridine. All three fractions gave quantitative yields of crude ester. On recrystallization from alcohol–water they gave, respectively, 83.5, 89 and 78% yields of the pure ester melting at 75.5–76°.

Anal. Calcd. for $C_{12}H_{12}O_7N_2$: C, 48.65; H, 4.08. Found: C, 48.82; H, 3.95.

Methanolysis of 3,4-Epoxy-1-butene with 5 mole per cent. Sulfuric Acid.—A procedure similar to that in the 1 mole per cent. acid run gave 113.5 g. of recovered methanol, 22.5 g. of intermediate fraction, 62.5 g. of 2-methoxy-3-buten-1-ol, II and 68 g. of higher boiling material.

The High-Boiling Product, VIII.—Repeated fractionation of the combined higher boiling fractions from the two acid-catalyzed reactions above gave finally 15.0 g. of a viscous, colorless liquid boiling constantly at 112° at 23 mm. and having $n^{25}D$ 1.4520. The product shows one active hydrogen in the Grignard machine and has been assigned structure VIII.

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.76; H, 9.37. Found: C, 63.27, 63.59; H, 9.47, 9.54.

Treatment of 2-methoxy-3-buten-1-ol, II (47 g., 0.46 mole), with 3,4-epoxy-1-butene (18 g., 0.3 mole) in the presence of a small pellet of sodium followed by warming for three and one-half hours on the steam-bath gave on distillation 22 g. of a colorless liquid having b. p. 113° at 21 mm. and $n^{25}D$ 1.4510. This product, too, shows one active hydrogen in the Grignard machine, but analogy with the base-catalyzed methanolysis of the oxide points to its being a mixture of isomers rather than a single substance.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 63.31, 63.46; H, 9.68, 9.46.

Hydrogenation of 2-Methoxy-3-buten-1-ol, II.—2-Methoxy-3-buten-1-ol, II (30.6 g., 0.3 mole), in 100 cc. of absolute ethanol was hydrogenated over 0.2 g. of Adams catalyst. Hydrogen was rapidly taken up while the gage showed a drop in pressure of 25.5 lb. The catalyst was filtered off and the product was distilled giving 27 g. of 2-methoxy-1-butanol, III, which boiled at 60–63° at 25 mm. and had $n^{25}D$ 1.4130. A small portion, redistilled through a one-foot Vigreux column for analysis, had b. p. 147.2° and $n^{25}D$ 1.4138.

Anal. Calcd. for $C_5H_{12}O_2$: C, 57.61; H, 11.62. Found: C, 58.43; H, 11.91.

Preparation of the 3,5-dinitrobenzoate as previously described for II gave a quantitative yield of crude ester and a 66% yield of purified 3,5-dinitrobenzoate, m. p. 64–66°.

Anal. Calcd. for $C_{12}H_{14}O_7N_2$: C, 48.32; H, 4.73. Found: C, 48.66; H, 4.81.

Oxidation of 2-Methoxy-1-butanol, III.—2-Methoxy-1-butanol III (10 g., 0.96 mole), in 30 cc. of water containing 3 g. of sodium carbonate was placed in a three-neck flask fitted with a mechanical stirrer and cooled in an ice-bath. Potassium permanganate (19.8 g., 1.25 mole) in 600 cc. of water was added gradually with stirring. The mixture was stirred an additional six hours with cooling and finally left standing over-night at room temperature. The manganese dioxide was filtered off and the aqueous solution was concentrated *in vacuo* to a volume of 50 cc. It was then extracted continuously with ether. The ether extract was dried over magnesium sulfate and distilled yielding 1.5 g. of crude 2-methoxybutyric acid, V, b. p. 90–107° at 25 mm.

Preparation of 2-Methoxybutyramide, VI.—The acid, V, (0.5 g.) was refluxed with thionyl chloride for thirty minutes, the excess thionyl chloride was removed and 5 cc. of concentrated ammonia was added. The aqueous solution was extracted continuously with ether. The ether extract was dried and the ether was then removed yielding a viscous brown oil. The oil was extracted with boiling water. The aqueous extract was decolorized with Norite and the water was removed *in vacuo*. This gave the crude amide, VI, melting at 69–75°.[6] Several crystallizations from a mixture of benzene, petroleum ether and methanol

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[6] Duvillier, *Ann. chim.*, [5] **17**, 548 (1879).

raised the melting point to 78–79°. On admixture with acetamide (m. p. 81° pure) the melting point was depressed to 40–65°. Mixing with propionamide (m. p. 79–80° pure) resulted in an oil.

Preparation of the *p*-Phenylphenacyl Ester, VII.—The acid V (0.5 g.), in 3 cc. of water was just neutralized with 10% sodium hydroxide. It was then made acid with a few more drops of V. Ethanol (8 cc.) and *p*-phenylphenacyl bromide (0.5 g.) were added, and the mixture was refluxed for one hour. This gave a crude product which after two crystallizations from methanol weighed 0.5 g. and melted at 82° alone and when mixed with a synthetic specimen made from 2-methoxybutyric acid obtained by the methanolysis of 2-bromobutyric acid.

Anal. Calcd. for $C_{19}H_{20}O_4$: C, 73.06; H, 6.45. Found: C, 72.81; H, 6.63.

Base-catalyzed Methanolysis of 3,4-Epoxy-1-butene.—To methanol (192.2 g., 6 moles, dried over magnesium methoxide, b. p. 64.6°, $n^{25}D$ 1.3279) and sodium (3.2 g., 0.14 mole) heated to reflux was added dropwise 3,4-epoxy-1-butene (120 g., 1.7 moles, b. p. 67°, $n^{25}D$ 1.4151). The mixture was heated under reflux for four hours after the addition and then left standing overnight. Seven cc. of acetic acid was added to decompose the sodium methoxide and the total reaction mixture was distilled in a Lecky–Ewell type still rated at sixty theoretical plates. The following fractions were obtained.

Fraction	Pressure, mm.	B. p., °C.	Wt., grams	$n^{25}D$
1	760	64.1	124.5	1.3280
2	55	50–70	6.5	1.4222
3	55	70–71	7.0	1.4261
4	55	70–71	9	1.4281
5	55	70–71	19	1.4290
6	55	71	7.0	1.4290
7	55	71	9.7	1.4291
8	55	71	6.5	1.4283
9	55	71	18.0	1.4265
Combined higher boiling fractions			47.9	

Fraction 1 above is recovered methanol, fractions 2 and 3 are intermediate fractions and fractions 3–8 contain mixtures of 3-methoxy-3-buten-1-ol, II, and 1-methoxy-3-buten-2-ol, I.

Preparation of the 3,5-Dinitrobenzoate of the Base-catalyzed-Product.—3,5-Dinitrobenzoates were prepared from fractions 4 and 8 as previously described for the acid-catalyzed product. Fraction 1 gave only an 11% yield of the ester (m. p. 73–75°) whereas fraction 8 gave a 39% yield of the same derivative. No other solid 3,5-dinitrobenzoate could be isolated from either reaction mixture.

Hydrogenation of the Base-catalyzed Product.—Fractions 3–8 of the base catalyzed product above were combined and 30.6 g. (0.3 mole) was hydrogenated over 0.2 g. of Adams catalyst in 100 cc. of ethanol. The hydrogen pressure dropped by 28 lb. On distillation the following fractions were obtained.

Fraction	Pressure, mm.	B. p., °C.	Wt., grams	$n^{25}D$
1	85	73–75	8.5	1.4106
2	85	75–76	6.0	1.4110
3	30	to 60°	1.5	1.4129
4	30	60–62.5	4.0	1.4135

Fraction 1 above gave a 78% yield of a 3,5-dinitrobenzoate melting at 91.5–92°. This is the 3,5-dinitrobenzoate of 1-methoxy-2-butanol, IX.

Anal. Calcd. for $C_{12}H_{14}O_7N_2$: C, 48.32; H, 4.73. Found: C, 48.39; H, 4.50.

Fraction 4 above gave a 44% yield of the 3,5-dinitrobenzoate of 2-methoxy-1-butanol, III, m. p. 64–66°, showing no depression on mixture with the previously obtained sample.

Oxidation of 1-Methoxy-2-butanol, IX.—To a stirred mixture of sodium dichromate monohydrate (15.8 g., 0.053 mole) and sulfuric acid (12.6 g., 0.129 mole) in 75.5 cc. of water was slowly added 1-methoxy-2-butanol, IX (fraction 1 above, 8 g., 0.077 mole). The reaction mixture was surrounded with an ice-bath and the temperature was not permitted to rise above 50° during the addition. The reaction mixture was permitted to come to room temperature and then steam distilled. The steam distillate was extracted continuously with ether. The ether extract was dried and distilled yielding 3 g. of 1-methoxy-2-butanone, X, b. p. 132–135°, $n^{25}D$ 1.4068 (reported, b. p. 133–133.6°, $n^{20}D$ 1.4063).[7]

The ketone gave a 2,4-dinitrophenylhydrazone which after several crystallizations from acetic acid melted at 193.2–194° (reported, 198–198.5°).[8]

Summary

The addition of methanol to 3,4-epoxy-1-butene in the presence of sulfuric acid produced predominantly 2-methoxy-3-buten-1-ol. Small amounts of crotonaldehyde and a higher boiling product resulting from the attack of 2-methoxy-3-buten-1-ol on 3,4-epoxy-1-butene were also obtained.

With sodium methoxide as catalyst the predominant product was 1-methoxy-3-buten-2-ol, but some 2-methoxy-3-buten-1-ol was also obtained.

The mechanisms of these reactions have been discussed.

CAMBRIDGE, MASSACHUSETTS RECEIVED JULY 24, 1947

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[7] Henze and Rigler, THIS JOURNAL, **56**, 1350 (1934).

[8] Maruyama, *Sci. Papers inst. Phys. Chem. Research* (*Tokyo*), **20**, 53 (1933); *C. A.*, **27**, 1863 (1933).