The calculated entropies of vaporization to the hypothetical perfect gas at 25° and atmospheric pressure are 24.35 e. u. for *o*-xylene, 25.24 e. u. for *m*-xylene, 25.96 e. u. for *p*-xylene and 26.39 e. u. for mesitylene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Isomeric Monoalkyl Ethers of 2-Methyl-1,2-propanediol from 1,2-Epoxy-2-methylpropane[1]

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Introduction

The monoalkyl ethers of 2-methyl-1,2-propanediol, the alkyl group of which is methyl, ethyl or propyl and containing a tertiary alcohol group, have been prepared[2] from the methyl ester of the alkoxyethanoic acid by use of methylmagnesium iodide.

The monoalkyl ethers of 2-methyl-1,2-propanediol, the alkyl group of which is methyl or ethyl and containing a primary alcohol group, have been prepared by Edlund.[3] This method consisted in refluxing 1,2-epoxy-2-methylpropane with the alcohol in the presence of 10% sulfuric acid. Edlund did not report the formation under these conditions of ethers containing the tertiary alcohol groups. This work was confirmed by the authors.

The purpose of this investigation is to show that both of the isomeric monoalkyl ethers of 2-methyl-1,2-propanediol are formed when 1,2-epoxy-2-methylpropane and absolute alcohols are permitted to react under pressure.

Discussion

When 1,2-epoxy-2-methylpropane is heated at 230–270° in an autoclave with absolute methanol, ethanol or 1-propanol, both of the isomeric monoalkyl ethers of 2-methyl-1,2-propanediol are formed. The pressure developed depends on the alcohol used. As the reaction takes place there is a drop in pressure. A mole ratio of three of alcohol to one of 1,2-epoxy-2-methylpropane was used. The excess alcohol was used to decrease the probability of the reaction of the monoalkyl ethers with 1,2-epoxy-2-methylpropane. The fractional distillation of the reaction mixtures indicated that one or more products in addition to the desired ethers were formed.

An examination of Table I reveals that the percentage conversion of 1,2-epoxy-2-methylpropane to the monoalkyl ethers of 2-methyl-1,2-propanediol decreases in the order methyl > ethyl > propyl. The rate of the reaction decreases in the same order as indicated by the fact that the time required was the least with methanol and less with ethanol than with 1-propanol. It is evident that this phenomenon is dependent upon the property of the alcohol used, since identical mole ratios of the reactants were taken.

Experimental

The reactions were carried out in a stainless steel autoclave. The heating was continued until there was a drop in pressure of approximately 300–400 lb. per sq. in. The reaction mixtures were fractionally distilled. The column used was packed with Penn-State spirals[4] and is described in the literature.[5] The unreacted 1,2-epoxy-2-methylpropane and the alcohol were removed at atmospheric pressure. The remaining mixture was fractionally distilled at a suitable pressure. A constant pressure was maintained during the vacuum fractional distillations by means of a regulator similar in principle to that described by Munch.[6] The products were purified by fractional distillation with the above column or by means of a Podbielniak column.

The value of $n^{20}D$ for the compounds was determined by means of a Pulfrich refractometer. The liquid was cooled to 20° with water from an electrically controlled thermostat.

The reaction of 1,2-epoxy-2-methylpropane with absolute 1-propanol is described below. The reaction of 1,2-epoxy-2-methylpropane with absolute methanol and with absolute ethanol was carried out in a similar manner.

Reaction of 1,2-Epoxy-2-methylpropane with Absolute 1-Propanol.—Five runs were made using 144 g. of 1,2-epoxy-2-methylpropane and 360 g. of absolute 1-propanol. The temperature varied from 235 to 260°, the average temperature being about 255°. Approximately twenty

(1) Based upon a portion of a thesis submitted by C. E. Sparks to the Faculty of Purdue University in partial fulfilment of the requirements for the degree of Doctor of Philosophy, June, 1936.

(2) Palomaa, *C. A.*, **13**, 2863 (1919).

(3) U. S. Patent No. 1,968,032, July 31, 1934.

(4) Wilson, Parker and Laughlin, THIS JOURNAL, **55**, 2795 (1932).

(5) Hass, McBee and Weber, *Ind. Eng. Chem.*, **27**, 1195 (1935).

(6) Munch, *J. Chem. Ed.*, **9**, 1275 (1932).

TABLE I

MONOALKYL ETHERS OF 2-METHYL-1,2-PROPANEDIOL

Name	Boiling point, Reported °C.	Mm.	Found °C.	Mm.	$n^{20}D$, Reported[c]	Found	Percentage yield[a]
1-Methoxy-2-methyl-2-propanol	116.6[c]	747	115–115.6	734.6	1.40473	1.4047	36.5
2-Methoxy-2-methylpropanol	142[d]	765	140.8–141.2	742		1.4190	29.6
			140.2–141[b]	745.5		1.4188[b]	54.7[b]
1-Ethoxy-2-methyl-2-propanol	128.2–128.4[c]	759.2	127.9–128.2	738.5	1.40591	1.4060	32.3
2-Ethoxy-2-methylpropanol	147.8[d]		146–146.5	742		1.4193	16.5
			145.6–146.3[b]	747		1.4192[b]	43.4[b]
2-Methyl-1-propoxy-2-propanol	150–151[c]	763	147–147.5	748.6	1.41017	1.4101	14.1
2-Methyl-2-propoxypropanol			162–163	739.2		1.4219	16.1
			161.6–163[b]	739.2		1.4223[b]	16.7[b]

[a] Based on the amount of 1,2-epoxy-2-methylpropane reacting. [b] Synthesized by the method of Edlund. [c] Ref. 7. [d] U. S. Patent No. 1,968,032, July 31, 1934.

hours of heating were necessary to produce a drop in pressure of about 300 lb. per sq. in. The combined reaction mixtures from the five runs were fractionally distilled. The unreacted 1,2-epoxy-2-methylpropane and 1-propanol were removed at atmospheric pressure. The following fractions were obtained at reduced pressure: 45–61° at 50 mm. (122 g.), 61–67° at 50 mm. (8 g.), 67–78° at 50 mm. (134 g.), 78–83° at 50 mm. (14 g.), 72–83° at 30 mm. (153 g.), 75–84° at 20 mm. (11 g.), 71–85° at 10 mm. (25 g.), residue (65 g.).

2-Methyl-1-propoxy-2-propanol.—The fraction (134 g.) boiling at 67–78° at 50 mm. was fractionally distilled at 50 mm. The compound possessed a b. p. of 147.2–147.6° at 742 mm. The b. p. of 2-methyl-1-propoxy-2-propanol is reported[7] as 150–151° at 763 mm. The compound was fractionally distilled at 50 mm. by means of a Podbielniak column and the boiling point was not raised. The compound was heated at 100–110° with a small amount of phthalic anhydride in order to esterify any traces of the isomer which might have been present. The resulting mixture was fractionally distilled at 50 mm. with a Podbielniak column. The fraction 73.8–74° at 50 mm. was the pure compound: b. p. 147–147.5° at 748.6 mm., $n^{20}D$ found 1.4101, reported[7] 1.41017.

Anal. Calcd. for $C_7H_{16}O_2$: C, 63.58; H, 12.24. Found: (I) C, 63.59; H, 12.18. (II) C, 63.47; H, 12.26.

It is concluded that the boiling point previously reported[7] in the literature for 2-methyl-1-propoxy-2-propanol is incorrect.

2-Methyl-2-propoxypropanol.—The fraction (153 g.) boiling at 72–83° at 30 mm. was fractionally distilled at 30 mm. Three fractions were obtained. The second and third fractions were combined and fractionally distilled at 30 mm. with a Podbielniak column. The fraction 76–76.5° at 30 mm. was the pure compound: b. p. 162–163° at 739.2 mm.; $n^{20}D$ 1.4219; d_{20} 0.894 g. per cc.

Anal. Calcd. for $C_7H_{16}O_2$: C, 63.58; H, 12.24. Found (I) C, 63.62; H, 12.28; (II) C, 63.58; H, 12.08.

This compound was also prepared by the Edlund[8] method. It was purified by fractional distillation at 30 mm. with a Podbielniak column. The fraction 76–76.5° at 30 mm. had a b. p. of 161.6–163° at 739.2 mm.; $n^{20}D$ 1.4223.

The molecular refractivity, R_L,[8] was calculated using the value of $n^{20}D$ as 1.4221 (the average of 1.4219 and 1.4223): R_L (calculated by Lorentz and Lorenz formula) 37.56, R_L (from sum of atomic refractivities) 37.69.

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Summary

When 1,2-epoxy-2-methylpropane is heated at 230–270° in an autoclave with absolute methanol, ethanol or 1-propanol, both of the isomeric monoalkyl ethers of 2-methyl-1,2-propanediol are formed.

Methanol shows a higher conversion to the monoalkyl ethers than does ethanol. The latter shows a better conversion than 1-propanol.

2-Methyl-2-propoxypropanol was prepared and identified.

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(7) Karvonen, *C. A.*, **18**, 1978 (1924).

(8) Findlay, "Practical Physical Chemistry," Longmans, Green and Co., New York, 1923, p. 91.