[CONTRIBUTION FROM THE ORGANIC CHEMISTRY LABORATORIES OF THE UNIVERSITY OF FLORIDA]

EPOXY ETHERS AND ETHER AMINO ALCOHOLS[1]

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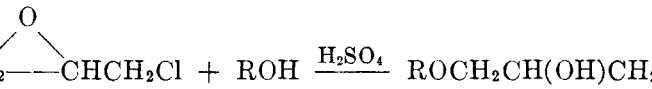
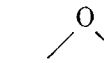
The condensation of epoxyalkanes with alcohols in the presence of sulfuric acid was reported by Fourneau and Ribas (1) and Kharasch and Nudenberg (2). A similar method was used in this laboratory for the condensation of ten aliphatic alcohols (methanol, ethanol, propanol-1, propanol-2, butanol-1, 2-methylpropanol-1, pentanol-1, 2-methylbutanol-1, 3-methylbutanol-1, and hexanol-1) with 1,2-epoxy-3-chloro propane.

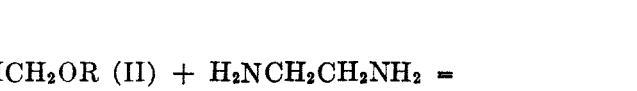


$$CH_2\text{——}CHCH_2Cl + ROH \xrightarrow{H_2SO_4} ROCH_2CH(OH)CH_2Cl \qquad (I)$$

The 1-alkoxy-2-hydroxy-3-chloropropanes (I) obtained were used to synthesize a number of new compounds.

The synthesis of epoxy ethers by the reaction of (I) with NaOH was investigated by Reboul (3), Henry (4), Nef (5), Lespieau (6), Fourneau and Samdahl (7), and Fairbourne, Gibson, and Stephens (8). By suitable modifications, the method was here extended to produce compounds of the type  (II) where R was methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, isobutyl, *n*-pentyl, 2-methyl-*n*-butyl, 3-methyl-*n*-butyl, and *n*-hexyl. The atomic refractions of the constituents (not including the epoxy oxygen) of these epoxy ethers (II) were added and then subtracted from their observed molar refractions. The difference was the refractive equivalent of epoxy oxygen, *i.e.*, 1.890. These data are given in Table II.

Ten new ether amino alcohols of the type $H_2NCH_2CH_2NHCH_2CH(OH)CH_2OR$ were obtained by the monoalkylation of (II) with ethylene diamine.



$$CH_2\text{——}CHCH_2OR \text{ (II)} + H_2NCH_2CH_2NH_2 =$$

$$H_2NCH_2CH_2NHCH_2CH(OH)CH_2OR$$

EXPERIMENTAL

Synthesis of 1-methoxy-2-hydroxy-3-chloropropane. In a 2-l., two-necked, round bottomed flask, fitted with a stirrer and a reflux condenser were placed nine moles (365 cc.) of methanol and 6.7 cc. of H_2SO_4 (*d.* 1.84). Three moles (235 cc.) of 1,2-epoxy-3-chloropropane was added dropwise through the top of the reflux condenser from a dropping-funnel. The mixture was stirred and refluxed for six hours. An excess of $BaCO_3$ (30 g.) was added and stirred at room temperature for several hours. The filtrate was distilled

[1] This paper is abstracted from a portion of a dissertation submitted by H. Flores-Gallardo to the Graduate Council of the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy, July, 1947.

TABLE I

DATA CONCERNING CHLORO-HYDROXY-ETHERS OF THE TYPE $ROCH_2CH(OH)CH_2Cl$

R	MOLAR RATIO OF ALCOHOL TO 1,2-EPOXY-3-CHLOROPROPANE	YIELD PERCENT	B.P. AT 20 MM., °C.	d_4^{25}	n_D^{25}	MOLAR REFRACTION	
						Obs.	Calc'd.
Methyl	3 to 1	68.3	76.5	1.1570	1.4422	28.49	28.70
Ethyl	2 to 1	60.0	80–82	1.0914	1.4370	33.30	33.32
n-Propyl	2 to 1	51.0	97–98	1.0526	1.4378	38.11	37.94
Isopropyl	3 to 1	28.2	87–87.5	1.0530	1.4370	37.96	37.94
n-Butyl	2 to 1	57	110–111	1.0444	1.4420	42.22	42.56
Isobutyl	3 to 1	37.6	100.0–100.2	1.0313	1.4386	42.46	42.56
n-Pentyl	2 to 1	52	120	1.0216	1.4441	46.98	47.17
3-Methyl-*n*-butyl	2 to 1	44.4	118–119	1.0223	1.4436	46.90	47.17
2-Methyl-*n*-butyl[a]	2.3 to 1	45.3	114.8–115.5	1.0638	1.4492	45.56	47.17
n-Hexyl	3 to 1	41.6	133	1.0026	1.4450	51.67	51.79

[a] This compound showed 22.19% Cl on analysis compared to a theoretical of 19.62%. The slight decomposition of the compound on distillation is a possible explanation of the high chlorine value obtained and the low observed molar refraction.

TABLE II

DATA CONCERNING EPOXY ETHERS OF THE TYPE $CH_2\!-\!\overset{O}{\overset{/\backslash}{}}\!-\!CHCH_2OR$

R	YIELD, PERCENT	B.P. °C.	d_4^{25}	n_D^{25}	MOLAR REFR. OBS.	MOLAR REFR., CALC'D (NOT INCL. EPOXY OXYGEN)	REFRACTIVE EQUIVALENT OF EPOXY OXYGEN
Methyl	68	53.5–53.7 at 85 mm.	0.9798	1.4012	21.859	20.115	1.744
Ethyl	75	61.0 at 65 mm.	0.9430	1.4046	26.544	24.733	1.811
n-Propyl	60.2	77.7 at 65 mm.	0.9203	1.4103	31.284	29.351	1.933
Isopropyl	66.6	68.0 at 65 mm.	0.9139	1.4068	31.272	29.351	1.921
n-Butyl	87.5	69.7 at 20 mm.	0.9087	1.4150	35.873	33.969	1.904
Isobutyl	75.2	65.5 at 20 mm.	0.8998	1.4112	35.936	33.969	1.967
n-Pentyl	74.9	86.5–86.7 at 20 mm.	0.9015	1.4201	40.484	38.587	1.897
3-Methyl-*n*-butyl	80.4	80.7 at 20 mm.	0.8982	1.4185	40.501	38.587	1.914
2-Methyl-*n*-butyl	64.4	78.0–78.5 at 20 mm.	0.8997	1.4186	40.443	38.587	1.856
n-Hexyl	86.5	105.0 at 20 mm.	0.8943	1.4242	45.167	43.205	1.962

The atomic refraction of epoxy oxygen given in Table II averages 1.890.

TABLE III

DATA CONCERNING ETHER AMINO ALCOHOLS OF THE TYPE

$H_2NCH_2CH_2NHCH_2CH(OH)CH_2OR$

R	YIELD PERCENT	B.P. °C.	d_4^{25}	n_D^{25}	MOLAR REFRACTION		NITROGEN PERCENT	
					Found	Calc'd	Found	Calc'd
Methyl	82.9	117–119 at 2 mm.	1.0446	1.4748	39.93	40.09	18.77	18.90
Ethyl	78.6	128 at 3 mm.	1.0265	1.4740	44.41	44.71	17.23	17.27
n-Propyl	72.5	130–131 at 2 mm.	0.9987	1.4683	49.08	49.33	15.84	15.89
Isopropyl	76.6	126 at 3 mm.	0.9875	1.4650	49.34	49.33	15.88	15.89
n-Butyl	80.5	134–135 at 2 mm.	0.9775	1.4654	53.85	53.95	14.62	14.72
Isobutyl	76.3	133 at 3 mm.	0.9694	1.4627	53.99	53.95	14.66	14.72
n-Pentyl	83.2	149–150 at 2 mm.	0.9660	1.4645	58.41	58.56	13.65	13.71
3-Methyl-*n*-butyl	84.0	145.7 at 2 mm.	0.9635	1.4641	58.52	58.56	13.66	13.71
2-Methyl-*n*-butyl	77.2	143.7 at 3 mm.	0.9630	1.4648	58.61	58.56	13.56	13.71
n-Hexyl	78.7	158 at 2 mm.	0.9549	1.4650	63.19	63.18	12.74	12.85

first at atmospheric pressure to remove the excess methanol and then at 20 mm.; 1-methoxy-2-hydroxy-3-chloropropane was collected at 76.5°.

In Table I are shown the results obtained when this synthesis was extended to include other alcohols.

Synthesis of 1,2-epoxy-3-methoxypropane. In a 3-l., three-necked, round bottomed flask, provided with an efficient mechanical stirrer and a reflux condenser were placed two liters of ether and two moles (216 cc.) of 1-methoxy-2-hydroxy-3-chloropropane. The flask was surrounded by an ice-water bath, and three moles (120 g.) of finely powdered sodium hydroxide was added in small portions with vigorous stirring. The water-bath was allowed to reach room temperature and the mixture was stirred for eight hours. Then 500 cc. of water was added and the layers formed were separated. The aqueous layer was extracted with ether, the combined ether solutions distilled, and 1,2-epoxy-3-methoxypropane collected at 53.5–53.7° at 85 mm.

The results obtained, when this procedure was used to synthesize other epoxy ethers, are summarized in Table II.

Synthesis of N-(2-hydroxy-3-methoxy propyl)ethylene diamine. To 10 moles of boiling ethylene diamine hydrate contained in a 2-l., three-necked, round bottomed flask, provided with a reflux condenser and a mechanical stirrer, was added dropwise through the top of the condenser one mole (90 cc.) of 1,2-epoxy-3-methoxypropane. The mixture was stirred and refluxed for five hours. It was then distilled and the desired product was collected at 117–119° at 2 mm.

This procedure was followed in the syntheses of other ether amino alcohols; these data are given in Table III.

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