

SYNTHESIS OF OLIGO(ETHYLENE GLYCOL) DERIVATIVES

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Oligo(ethylene glycol) derivatives were obtained by the reaction of oligo(ethylene glycol) chlorohydrins with epichlorohydrin using H_2SO_4 catalyst and subsequent treatment with NaOH in ether solution. The structure of the obtained products was characterized by ^{13}C NMR and IR spectra.

Kharash and Nudenberg¹ reported that the polyfunctional 1-chloro-3-(2-hydroxyethoxy)-2-propanol can be synthesized by treating ethylene glycol with epichlorohydrin (ECH) in the presence of H_2SO_4 . Werner and Farenhorst² prepared aromatic bisglycidyl ethers from ECH and dihydric phenols in basic media. In the following years, the condensation of some hydroxyalkyl ethers with phenol and 1- and 2-naphthol without acid catalyst was studied by Petrov and Stephenson³. In their study, the addition to epoxide ring was achieved by thermal treatment. The base-catalyzed reaction of ECH with catechol and monohydric phenols was made by Stephenson⁴. The reaction of glycol chlorohydrins, instead of glycols, with ECH in the presence of H_2SO_4 was studied by Kawai⁵. Some polyglycols were prepared by Erk et al.⁶⁻⁸ to be further used in the synthesis of polyoxalactones and macrocyclic ethers. Furthermore, the reaction of oligo(ethylene glycols) with some aromatic and aliphatic asymmetric epoxides in the presence of HClO_4 was studied by Erk^{9,10}.

In recent years, many epoxides and diepoxides such as oligo(ethylene glycol) diglycidyl ethers, 2-substituted 2-(chloromethoxy)oxiranes^{11,12} and 1,2-bis(2,3-epoxypropoxy)benzene¹³ were prepared for the synthesis of macrocyclic ethers.

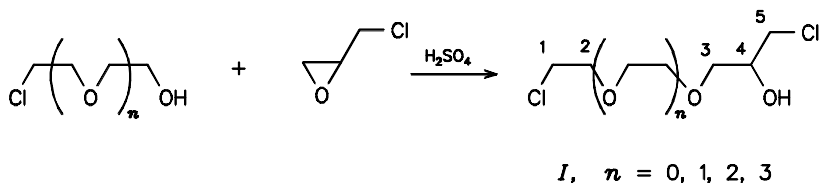
In this study, some oligo(ethylene glycol) derivatives were prepared as intermediates for the synthesis of crown ethers bearing alcohol groups.

EXPERIMENTAL

^{13}C NMR spectra of *I* and *II* were recorded in CDCl_3 with proton noise decoupling using a Bruker AC 50.33 MHz FT spectrometer. Internal field frequency stabilization was provided by lock signal from TMS dissolved in the solvent. IR spectra were recorded in CHCl_3 solutions using Perkin-Elmer 782 model IR spectrophotometer.

Oligo(ethylene Glycol) Derivatives *I*

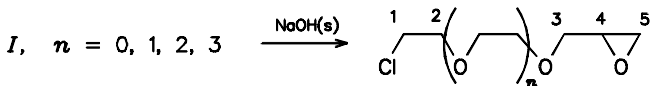
ECH (1 mol) was added to oligo(ethylene glycol) chlorohydrin (2 mol) with catalytic amount of H_2SO_4 (98%) and refluxed at 140 – 170 °C for 10 h (Scheme 1). After cooling the reaction mixture was neutralized with NaHCO_3 and distilled under reduced pressure.



SCHEME 1

Oxiranes *II*

I (0.3 mol) was dissolved in 200 ml of ether and cooled to 0 °C. Powdered NaOH (0.36 mol) was added portionwise into the solution during 2 h while stirring (Scheme 2). The reaction mixture was further stirred at 0 °C for 2 h and at room temperature for 2 h. The ether phase was washed with water several times to remove the unreacted NaOH and dried over Na_2SO_4 . Ether was evaporated and the products were distilled under reduced pressure.



SCHEME 2

RESULTS AND DISCUSSION

In this study new oligo(ethylene glycol) derivatives *I* and *II* were synthesized. In addition, the compounds were characterized by ^{13}C NMR and IR spectroscopic measurements. Some properties of the products are given in Table I.

In the ^{13}C NMR spectra of both *I* ($n = 0$) and *II* ($n = 0$), 5 peaks related to 5 different C atoms were observed. However, in the other *I* and *II*, only two and one signals, respectively, were observed for the carbons of the repeating units (Tables II and III).

In the IR spectra of *II*, the most characteristic asymmetrical C–O–C stretching band and the symmetrical stretching band of epoxy ring appeared at 1 125 cm^{-1} and 1 250 cm^{-1} , respectively. An additional evidence for the formation of epoxy ring was the disappearance of OH band (3 500 cm^{-1}), which was present in the starting *I*.

TABLE I
Characteristics of oligo(ethylene glycol) derivatives *I* and *II*

Compound	B.p. °C/kPa	n_D^{25}	Yield %	Formula (M. w.)	Calculated/Found	
					% C	% H
<i>I</i> , $n = 0$	140 – 144/2.7	1.4750	40	C ₅ H ₁₀ Cl ₂ O ₂ (173.0)	34.68	5.78
					34.79	5.80
<i>I</i> , $n = 1$	126 – 128/0.2	1.4741	55	C ₇ H ₁₄ Cl ₂ O ₃ (217.1)	38.71	6.45
					38.83	6.44
<i>I</i> , $n = 2$	148 – 153/0.2	1.4691	50	C ₉ H ₁₈ Cl ₂ O ₄ (261.1)	41.38	6.90
					41.45	6.92
<i>I</i> , $n = 3$	176 – 184/0.2	1.4727	34	C ₁₁ H ₂₂ Cl ₂ O ₅ (305.2)	43.28	7.21
					43.34	7.20
<i>II</i> , $n = 0$	96 – 100/2.7	1.4497	51	C ₅ H ₉ ClO ₂ (136.6)	43.96	6.59
					43.86	6.57
<i>II</i> , $n = 1$	96 – 100/0.2	1.4558	41	C ₇ H ₁₃ ClO ₃ (180.6)	46.54	7.20
					46.63	7.22
<i>II</i> , $n = 2$	128 – 130/0.2	1.4594	42	C ₉ H ₁₇ ClO ₄ (224.7)	48.11	7.57
					48.00	7.56
<i>II</i> , $n = 3$	162 – 166/0.2	1.4610	56	C ₁₁ H ₂₁ ClO ₅ (268.6)	49.16	7.82
					49.25	7.84

TABLE II
50.33 MHz decoupled ¹³C NMR chemical shifts (ppm) of *I* in CDCl₃

Carbon	$n = 0$	$n = 1$	$n = 2$	$n = 3$
1	42.58	45.53	42.29	42.25
2	71.45	71.84	71.65	71.57
3	71.02	70.99	70.74	70.63
4	69.75	69.95	69.66	69.54
5	45.58	45.63	45.46	45.41
in repeating unit	–	70.45	69.97	69.87
	–	70.21	70.23	70.12

TABLE III
50.33 MHz decoupled ^{13}C NMR chemical shifts (ppm) of *II* in CDCl_3

Carbon	$n = 0$	$n = 1$	$n = 2$	$n = 3$
1	42.49	42.28	42.09	42.33
2	70.86	70.67	70.36	70.82
3	71.38	71.39	71.09	71.49
4	50.23	50.11	49.77	50.28
5	43.46	43.39	43.00	43.64
in repeating unit	–	69.94	69.63	70.10

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