Russian Journal of Organic Chemistry, Vol. 38, No. 5, 2002, pp. 754–755. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 5, 2002, pp. 790–791.
Original Russian Text Copyright © 2002 by Raskulova, Volkova, Danilevich, Shainyan, Khaliullin.

SHORT COMMUNICATIONS

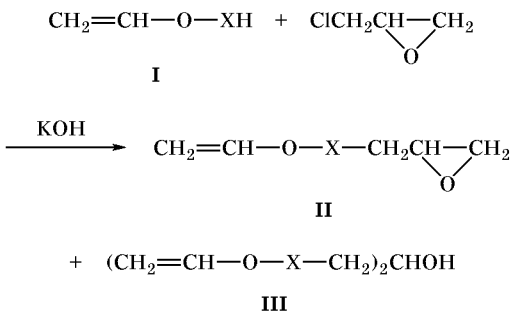
Formation of Diol Divinyl Diethers in the Synthesis of 1,2-Epoxy-3-(vinyloxyalkoxy)propanes

T. V. Raskulova, L. I. Volkova, Yu. S. Danilevich, B. A. Shainyan, and A. K. Khaliullin

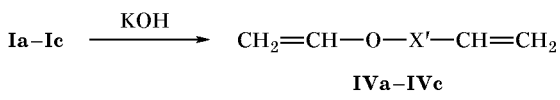
Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia

Received January 9, 2002

According to the data of [1], monovinyl ethers **I** derived from diols react with epichlorohydrin in the presence of alkali to give 1,2-epoxy-3-(vinyloxyalkoxy)propanes **II** and 1,3-bis(vinyloxyalkyl) glycerol ethers **III**.



While attempting to obtain by the same procedure [1] a series of compounds **II** [X = $(CH_2CH_2O)_n$, where n = 2 (**a**), 3 (**b**), 4 (**c**) as monomers for radical copolymerization, we have found that this reaction is very sensitive to temperature. Ethers **II** were formed only at 50–55°C, whereas at room temperature divinyl diethers $CH_2{=}CHOXCH{=}CH_2$ [**IV**, X = $(CH_2CH_2O)_2$ (**a**), $(CH_2CH_2O)_5$ (**b**), $(CH_2CH_2O)_4$ (**c**)] were obtained. Moreover, compounds **IV** were also formed in the absence of epichlorohydrin. No products **III** were detected.



The structure of compounds **IV** was proved by the NMR spectra. We observed no CH signals other than from the vinyl CH group in the *J*-modulated spin echo ^{13}C NMR spectra. The length of the X chain was determined from the CH_2CH_2O and $CH_2{=}CH$ signal intensity ratio in the ^1H NMR spectra.

Formally, the formation of diethers **IV** is the result of intermolecular dehydration of the initial monovinyl ethers. However, the X′ group in **IVa**–**IVc** is shorter than the double X group in **Ia**–**Ic**; these findings suggest that the reaction is accompanied by elimination processes.

Vinyl ethers are known to be inert toward nucleophiles [2]. On the other hand, Trofimov *et al.* [3] showed that monovinyl ethers derived from diols are capable of undergoing transformations involving the vinyloxy group by the action of alkali metal hydroxides [3]. Diol divinyl diethers, e.g., 1,2-bis(vinyloxy)ethane, lose acetaldehyde molecule in superbasic medium (KOH–DMSO) at 130°C under pressure [4]. Probably, other divinyl diethers behave similarly. Moreover, these reactions can occur under considerably milder conditions (atmospheric pressure, 50°C) than those reported in the literature due to increased mobility of the side chain in monovinyl ether and greater probability for elimination of acetaldehyde. Thus the formation of diol divinyl ethers in the reaction of monovinyl ethers of diols with alkali may be explained by concurrent elimination of vinyl alcohol and intermolecular dehydration.

Preparation of diol monovinyl ethers I. A high-pressure reactor was charged with 0.75 mol of diol and solid KOH (5 wt % with respect to the diol). The reactor was purged with nitrogen and acetylene, and acetylene was supplied at a pressure of 14–15 atm. The mixture was kept for 3–4 h at 120°C, cooled, and distilled under reduced pressure. The purity of the products was checked by GLC.

Preparation of 2,3-epoxypropyl ethers II. Ether **I**, 0.5 mol, and freshly distilled epichlorohydrin,

1070-4280/02/3805-0754 $27.00 © 2002 MAIK "Nauka / Interperiodica"

2 mol, were added to a solution of 0.63 mol of NaOH in 100–150 of water. The mixture was stirred for 4–5 h at 50–55°C and filtered, excess epichlorohydrin was distilled off, and the residue was distilled under reduced pressure. The purity of the products was checked by GLC.

11,12-Epoxy-3,6,9-trioxa-1-dodecene (IIa). Yield 61%, bp 130°C (5 mm), n_D^{20} = 1.4510. ^{1}H NMR spectrum, δ, ppm: 2.55 d.d (1H, 12-H$_{trans}$, *J* = 2.8, 5.2 Hz), 2.72 d.d (1H, 12-H$_{cis}$, *J* = 5.0, 5.2 Hz), 3.08 m (1H, 11-H), 3.36 d.d (1H, 10-H$_A$, *J* = 6.4, 11.6 Hz), 3.40–3.85 m (9H, 10-H$_B$, OCH$_2$), 3.98 d.d (1H, 1-H$_{cis}$, *J* = 2.0, 6.8 Hz), 4.20 d.d (1H, 1-H$_{trans}$, *J* = 2.0, 14.4 Hz), 6.51 d.d (1H, 2-H, *J* = 6.8, 14.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 43.88 (C^{12}), 50.97 (C^{10}), 68.20 (C^4), 69.99 (C^5), 71.04 (C^7), 71.10 (C^8), 72.61 (C^9), 86.73 (C^1), 152.62 (C^2). Found, %: C 57.55; H 8.49. $C_9H_{16}O_4$. Calculated, %: C 57.43; H 8.56.

14,15-Epoxy-3,6,9,12-tetraoxa-1-pentadecene (IIb). Yield 58%, bp 135°C (5 mm), n_D^{20} = 1.4532. ^{13}C NMR spectrum, δ_C, ppm: 43.91 (C^{15}), 51.04 (C^{14}), 68.24 (C^4), 70.04 (C^5), 71.06 (C^7), 71.07 (C^{10}), 71.12 (C^8), 71.17 (C^{13}), 72.68 (C^{11}), 86.68 (C^1), 152.69 (C^2). Found, %: C 56.46; H 8.80. $C_{11}H_{20}O_5$. Calculated, %: C 56.88; H 8.68.

17,18-Epoxy-3,6,9,12,15-pentaoxa-1-octadecene (IIc). Yield 59%, bp 140°C (5 mm), n_D^{20} = 1.4545. ^{1}H NMR spectrum, δ, ppm: 2.52 d.d (1H, 18-H$_{trans}$, *J* = 2.8, 5.2 Hz), 2.70 d.d (1H, 18-H$_{cis}$, *J* = 5.0, 5.2 Hz), 3.06 m (1H, 17-H), 3.33 d.d (1H, 16-H$_A$, *J* = 6.4, 11.6 Hz), 3.57–3.69 m (14H, OCH$_2$), 3.73 d.d (1H, 16-H$_B$, *J* = 3.0, 11.6 Hz), 3.81 m (2H, 4-H), 3.95 d.d (1H, 1-H$_{cis}$, *J* = 2.0, 6.8 Hz), 4.18 d.d (1H, 1-H$_{trans}$, *J* = 2.0, 14.3 Hz), 6.49 d.d (1H, 2-H, *J* = 6.8, 14.3 Hz). ^{13}C NMR spectrum, δ_C, ppm: 43.89 (C^{18}), 51.00 (C^{17}), 68.20 (C^4), 69.99 (C^5), 71.01–71.07 (C^7–C^{13}), 71.12 (C^{16}), 72.62 (C^{14}), 86.68 (C^1), 152.65 (C^2). Found, %: C 56.42; H 8.61. $C_{13}H_{24}O_6$. Calculated, %: C 56.51; H 8.75.

Preparation of diol divinyl diethers IV. Epichlorohydrine, 0.1 mol, was added to a mixture of 0.1 mol of ether **I** and 0.12 mol of KOH. The mixture was stirred for 5 h at room temperature, diluted with an ice–water mixture, and extracted with diethyl ether. The extract was washed with ice water, dried over Na_2SO_4, and subjected to fractional distillation. The purity of the products was checked by GLC.

Bis(2-vinyloxyethyl) ether (IVa). Yield 32%, bp 110°C (2 mm), n_D^{20} = 1.4531. ^{1}H NMR spectrum, δ, ppm: 3.72 m (4H, CH$_2$OCH$_2$), 3.84 m (4H, CHOC**H**$_2$), 3.97 d.d (2H, CH$_2$=, *J* = 4.8 Hz), 4.20 d.d (2H, CH$_2$=, *J* = 12.8 Hz), 6.47 d.d (2H, =CH, *J* = 6.4 Hz). ^{13}C NMR spectrum, δ_C, ppm: 68.25 (CHO**C**H$_2$), 70.11 (CH$_2$OCH$_2$), 86.80 (CH$_2$=), 152.66 (CH=). Found, %: C 60.52; H 8.75. $C_8H_{14}O_3$. Calculated, %: C 60.74; H 8.92.

3,6,9,12,15,18-Hexaoxa-1,19-eicosadiene (IVb). Yield 22%, bp 125°C (1 mm), n_D^{20} = 1.4540. ^{1}H NMR spectrum, δ, ppm: 3.57 m (16H, 5-H, 7-H, 8-H, 10-H, 11-H, 13-H, 14-H, 16-H), 3.79 m (4H, 4-H, 17-H), 3.92 d.d (2H, 1-H, 20-H, *J* = 4.8 Hz), 4.15 d.d (2H, 1-H, 20-H, *J* = 10.8 Hz), 6.48 d.d (2H, 2-H, 19-H, *J* = 7.2 Hz). ^{13}C NMR spectrum, δ, ppm: 70.16, 70.62, 71.23, 71.87 (C^4–C^{17}), 86.74 (C^1, C^{20}), 152.87 (C^2, C^{19}). Found, %: C 57.41; H 8.95. $C_{14}H_{26}O_6$. Calculated, %: C 57.91; H 9.02.

3,6,9,12,15-Pentaoxa-1,16-heptadecadiene (IVc). Yield 20%, bp 145°C (4 mm), n_D^{20} = 1.4548. ^{1}H NMR spectrum, δ, ppm: 3.56 m (8H, 7-H, 8-H, 10-H, 11-H), 3.64 d.d (4H, 5-H, 13-H, *J* = 2.0 Hz), 3.78 d.d (4H, 4-H, 14-H, *J* = 2.0 Hz), 3.91 d.d (2H, 1-H, 17-H, *J* = 4.8 Hz), 4.14 d.d (2H, 1-H, 17-H, *J* = 12.4 Hz), 6.45 d.d (2H, 2-H, 16-H, *J* = 7.2 Hz). ^{13}C NMR spectrum, δ_C, ppm: 68.16 (C^8, C^{10}), 69.99 (C^7, C^{11}), 71.05 (C^5, C^{13}), 71.08 (C^4, C^{14}), 86.65 (C^1, C^{17}), 152.61 (C^2, C^{16}). Found, %: C 58.37; H 8.89. $C_{12}H_{22}O_5$. Calculated, %: C 58.52; H 9.00.

The NMR spectra were obtained on a Varian VXR-500S instrument at 500 MHz for ^{1}H and 125 MHz for ^{13}C; acetone-d_6 was used as solvent, and HMDS, as internal reference. GLC analysis was performed on an LKhM-8 chromatograph equipped with a thermal conductivity detector; carrier gas helium; 3000 × 3-mm columns packed with 5% of SE-30 on Chromaton N-AW-DMCS.

REFERENCES

1. Shostakovskii, M.F., Atavin, A.S., Vyalykh, E.P., Trofimov, B.A., and Tatarinova, A.F., *Zh. Org. Khim.*, 1967, vol. 3, no. 11, pp. 1972–1976.
2. Shostakovskii, M.F., *Vinilovye efiry* (Vinyl Ethers), Moscow: Akad. Nauk SSSR, 1952.
3. Trofimov, B.A., Oparina, L.A., and Parshina, L.N., *Zh. Org. Khim.*, 1986, vol. 22, no. 8, pp. 1583–1585.
4. Trofimov, B.A., Oparina, L.A., Parshina, L.N., Vins, V.V., and Lavrov, V.I., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, no. 12, pp. 2873–2874.