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SHORT
COMMUNICATIONS

Hydrolysis of 2-[2-(Vinyloxy)ethoxymethyl]oxirane in the Presence of Sodium Hydrogen Sulfate

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2-[2-(Vinyloxy)ethoxymethyl]oxirane (**I**) is known as a highly reactive difunctional monomer and starting compound in the synthesis of many uncommon compounds and advanced materials for new technologies [1]. To extend the scope of application of compound **I** in organic synthesis, it is important to know the nature of products formed as a result of its hydrolysis in the presence of different catalysts at different pH values.

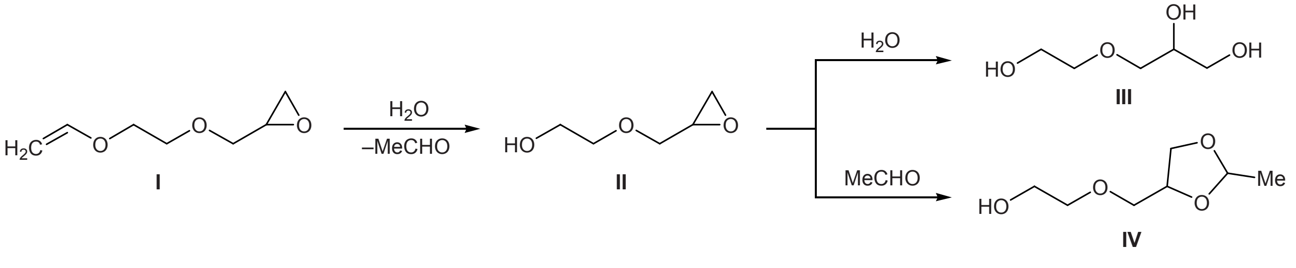
It was reported previously that hydrolysis of **I** at 20–35°C by the action of hydrochloric acid taken in a catalytic [2] or larger amount [3] gives 2-(oxyran-2-ylmethoxy)ethanol (**II**) and acetaldehyde. The hydrolysis rate constants determined by UV spectroscopy and polarography, following the disappearance of ether **I** or accumulation of acetaldehyde, were almost identical. It was also noted [3] that no appreciable differences in the kinetics of the process were observed in experiments performed in open cells and sealed ampules, despite volatility of acetaldehyde. The hydrolysis of vinyl ether **I** in distilled water at 70°C gave 3-(2-hydroxyethoxy)propane-1,2-diol (**III**) in 39% yield and a water-soluble resin [4].

We have found that hydrolysis of vinyl ether **I** in the presence of sodium hydrogen sulfate even in an open vessel at room temperature gives 4-(2-hydroxyethoxymethyl)-2-methyl-1,3-dioxolane (**IV**) as a mixture of *trans* and *cis* isomers at a ratio of 1.2 : 1 (according to the ^{1}H NMR data) in an overall yield of up to 30%.

It is known that 1,3-dioxolanes are formed by acid-catalyzed reactions of aldehydes with alkyloxiranes or 1,2-diols [5]. In the latter case, the process is reversible, and removal of liberated water from the reaction mixture is necessary [6]. Therefore, we presumed that in our case dioxolane **IV** is formed via reaction of acetaldehyde with 2-(oxyran-2-ylmethoxy)ethanol (**II**).

A mixture of 20 g of a saturated solution of $NaHSO_4$ (pH 1.9), 29 g (0.2 mol) of vinyl ether **I**, and 50 ml of water was stirred for 8 h without external heating. The mixture turned homogeneous. Another portion of ether **I**, 58 g (0.4 mol), was added in 0.5–1.0-ml portions over a period of 14 h, and the mixture was stirred for 2 h more (it remained homogeneous). The mixture was treated with 10 g of anhydrous potassium carbonate, the precipitate was filtered off, and the filtrate was extracted with diethyl ether (3 × 40 ml).

3-(2-Hydroxyethoxy)propane-1,2-diol (III) was isolated by distillation of the aqueous phase. Yield



27%, bp 163–165°C (1 mm), d_4^{20} = 1.2084, n_D^{20} = 1.4730; published data [4]: bp 153–157°C (1 mm), d_4^{20} = 1.1690, n_D^{20} = 1.4720; MR_D = 31.61, calcd. 31.52. Found, %: C 43.98; H 8.97. $C_5H_{12}O_4$. Calculated, %: C 44.11; H 8.88.

2-(2-Methyl-1,3-dioxolan-4-ylmethoxy)ethanol (IV) was isolated from the ether extract by distillation. Yield 30%, bp 88–90°C (2 mm), d_4^{20} = 1.0932, n_D^{20} = 1.4455; published data [7]: bp 113–115°C (8 mm), n_D^{20} = 1.4453. IR spectrum, ν, cm^{-1}: 3400, 2990, 2920, 2865, 1470, 1450, 1400, 1360, 1330, 1305, 1260, 1205, 1130, 1105, 1050, 1010, 920, 860, 715, 690, 610, 520. ^{1}H NMR spectrum, δ, ppm: 1.35 d (1.4H, Me, *cis*, ^3J = 4.8 Hz), 1.38 d (1.6H, Me, *trans*, ^3J = 4.8 Hz), 2.90 br.s (1H, OH), 3.6–4.3 m (9H, OCH$_2$, 4-H), 5.01 q (1.1H, 2-H, *trans*, ^3J = 4.8 Hz), 5.11 q (0.9H, 2-H, *cis*, ^3J = 4.8 Hz). ^{13}C NMR spectrum, δ_C, ppm: *trans* isomer: 19.74 (CH_3), 61.57 (CH_2OH), 67.14 (C^5), 72.16 (4-CH_2), 72.89 (**C**H_2CH_2OH), 75.05 (C^4), 102.07 (C^2); *cis* isomer: 19.79 (CH_3), 61.57 (CH_2OH), 67.24 (C^5), 71.64 (4-CH_2), 72.89 (**C**H_2CH_2OH), 74.66 (C^4), 101.48 (C^2). Found, %: C 51.96; H 8.73. $C_7H_{14}O_4$. Calculated, %: C 51.84; H 8.70.

The IR spectra were recorded on a Specord 75IR spectrometer from thin films. The ^{1}H and ^{13}C NMR spectra were measured on a Bruker DPX-400 instrument at 400 and 100 MHz, respectively, using $CDCl_3$ as solvent and HMDS as internal reference.

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