

Letters to the Editor

An unexpected reaction of divinyl ether of ethylene glycol with hydrogen sulfide

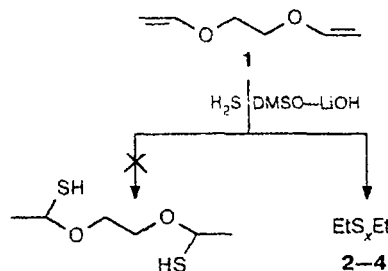
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It is known that the reactions of divinyl ethers of diols with thiols occur *via* addition at the vinyl group. For example, the reactions of 1,2-di(vinyloxy)ethane (**1**) with thiols result in the formation of the corresponding oxygen-containing sulfides.^{1–3}

We have found that compound **1** reacts with hydrogen sulfide in a DMSO–LiOH system to give diethyl polysulfides, instead of the expected 3,6-dioxaoctane-2,7-dithiol, in an overall yield of 65% and a diethyl disulfide (**2**) : diethyl trisulfide (**3**) : diethyl tetrasulfide (**4**) ratio of 3 : 1 : 1.5 (GLC data).

Reaction of 1,2-di(vinyloxy)ethane with hydrogen sulfide. Compound **1** (3 g, 0.03 mol) was added to a suspension of LiOH (1 g, 0.04 mol) in DMSO (150 mL), and hydrogen sulfide was passed at 30 °C for 5 h. The reaction mixture was cooled to –20 °C, diluted with water, and extracted with ether. The ether extracts were washed with water and dried with CaCl₂. The ether was distilled off, and the residue was fractionated to give a mixture (2.4 g) with b.p. 90 °C (2 Torr). According to the GLC analysis with authentic samples, the mixture contained compounds **2**, **3**, and **4** in the ratio 3 : 1 : 1.5, respectively.



$x = 2$ (**2**), 3 (**3**), 4 (**4**)

¹H NMR, δ : 1.30 (t), 1.36 (t), 1.40 (t) [CH_3 in compounds **2**, **3**, and **4**, respectively], 2.69 (q), 2.89 (q), 2.99 (q) [CH_2 in compounds **2**, **3**, and **4**, respectively]. These results are in accordance with the data on the downfield shift of the chemical shifts of protons as the number of sulfur atoms in the molecule increases.⁴ Nonidentified products (7%) have meth-

ylene protons with δ 3.45 and 3.57. Based on the GLC-MS data, we can attribute them to compounds of the EtS_nSH type.

Along with molecular ions (m/z) 1, 122; 2, 154; and 3, 186; GLC-MS revealed the presence of a compound with m/z 94 in the reaction mixture, which most likely has the structure EtSSH .

The analytical chromatographic analysis was carried out on a Khrom-5 chromatograph using helium as the carrier gas (katharometer as the detector, column 1 m \times 4 mm, 15% Carbowax 20 M on Chromaton N-AW-DMCS, temperature of the column 90 °C).

^1H NMR spectra were recorded in CDCl_3 on a Tesla BS-567 spectrometer (100 MHz).

References

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