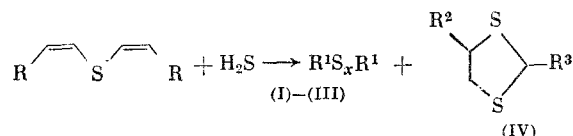


THIYLATION OF DIVINYL SULFIDE AND ITS DERIVATIVES BY HYDROGEN SULFIDE IN LiOH/DMSO

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We have found that H_2S in LiOH/DMSO reacts with divinyl sulfide and di(propen-1-yl) sulfide to form di- (I), tri- (II), and tetrasulfides (III) as well as 1,3-dithiolanes (IV).



$R = H$; $R^1 = Et$, $R^2 = H$, $R^3 = Me$, $x = 2$ (Ia), 3 (IIa), 4 (IIIa), (IVa); $R = Me$; $R^1 = Pr$, $R^2 = Me$, $R^3 = Et$, $x = 2$ (Ib), 3 (IIb), 4 (IIIb), (IVb).

The addition of H_2S or its disproportionated form, disulfane, to diallyl sulfide leads apparently to 1-propen-1-ylthio-1-propanethiol (V) and 1-propen-1-ylthio-1-propane hydrosulfide (VI). Intermediates (V) and (VI) in the LiOH-DMSO- H_2S oxidation-reduction system [1] may split to give propanethiol and propane hydrosulfide, which are oxidized to (I)-(III). Hemithioacetal (V) may also undergo intramolecular cyclization to form (IV), but this reaction is secondary in nature.

Hydrogen sulfide was rapidly passed into a mixture consisting of 10.2 g divinyl sulfide, 6.8 g LiOH and 150 ml DMSO at about 20°C for 4 h. The reaction mixture was diluted with water and extracted with ether. The ethereal extracts were dried over $CaCl_2$. Ether was distilled off. Vacuum distillation gave a fraction of 11.8 g which was analyzed by gas-liquid chromatography on a column packed with 15% Carbowax 20 M on Chromaton N-AW-DMCS. The distillate was found to contain 5.7 g (39.3%) (Ia), 3.7 g (20.2%) (IIa), 1.6 g (7.2%) (IIIa), and 0.8 g (5.6%) (IVa).

The reaction of di(propen-1-yl)sulfide with H_2S under analogous conditions leads to 46.2% (Ib), 16.7% (IIb), and 6.3% (IVb). Product (IIIb) was detected in the mixture by chromatomass spectrometry. For structural study, the compounds were isolated by preparative gas-liquid chromatography on a 2 m × 6 mm column packed with 15% Carbowax 20 M on Chromaton N-AW-DMCS.

PMR spectrum in $CDCl_3$ (δ , ppm, HMDS): 2.68 q, 2.87 q, 2.95 q, 2.66 t, 2.84 t, CH_2S in (Ia), (IIa), (IIIa), (Ib) and (IIb), respectively; 1.30 t, 1.37 t, 1.39 t, 0.98 t, 1.00 t, Me in (Ia), (IIa), (IIIa), (Ib), and (IIb), respectively; 1.69 m, 1.77 m CH_2 in (Ib) and (IIb), respectively. The chemical shifts for the 1,3-dithiolanes were in accord with the data of Keskinen et al. [2].

LITERATURE CITED

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