LETTERS TO THE EDITOR

SYNTHESIS OF TRIMETHYLETHYLENE SULFIDE

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The widely accepted data on the properties of trimethylethylene sulfide (I) (bp 145-150°C, d_4^0 0.927; for example, see [1]), which is obtained in 60% yield by thiocyanation of 2,3-dibromo-2-methylbutane by means of NH_4CNS and subsequent treatment with Na_2S_2, raise doubts in connection with the anomalously high boiling point of I in the homologous series of methyl-substituted episulfides. Our attempts to obtain episulfide I by the method in [2] (even when the reaction conditions were changed) were unsuccessful because of side reactions that occur even during the thiocyanation of 2,3-dihaloalkanes [3].

We were able to obtain I [bp 106-108, 53° (100 mm), d_4^{25} 0.8842] only by reaction of trimethylethylene oxide with KCNS via a modified method [4].

Episulfide I polymerizes via an ionic mechanism to give stereoregular polymers only on anionic catalysis.

EXPERIMENTAL

Trimethylethylene Sulfide (I). A 24.1-g (0.28 mole) sample of trimethylethylene oxide [5] (bp 75°, d_4^{20} 0.8204, n_D^{20} 1.3834) and a solution of 27.2 g (0.28 mole) of KCNS in 40 ml of 50% ethanol were maintained in a sealed ampoule at constant rotation in the vertical position for 50 h. The upper layer was separated, the same amount of the KCNS solutions was added, and the mixture was stirred for 24 h. The upper layer was then separated and dried with calcium chloride in a refrigerator. Vacuum distillation with a fractionating column (normal distillation is accompanied by decomposition of I) gave 14.6 g (51%) of colorless episulfide I (91% pure according to gas–liquid chromatography with bp 53° (100 mm), n_D^{25} 1.4644, and d_4^{25} 0.8842. UV spectrum (in heptane): λ_{max} 263 nm, ε 32.3 IR spectrum (thin layer): 2980, 2995 cm^{-1} (ν_{C-H} of the methylidyne group of the episulfide ring), 950, 972 cm^{-1} (episulfide ring bands). The splitting of the band at 1375 cm^{-1} indicates the presence of a gem-dimethyl group. PMR spectrum (of the pure substance): δ 1.50 (doublet, J = 5 Hz), 1.54 and 1.56 (singlets), 2.76 (quartet). Found: C 58.8; H 9.8; S 31.4%. $C_5H_{10}S$. Calculated: C 58.8; H 9.8; S 31.4%.

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