REACTION OF ESTERS OF SULFOXYLIC ACID WITH ETHYL α-BROMOACETOACETATE

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Sulfoxylic acid esters (I) react with alkyl halides to form sulfinic acid esters RS(O)·OR [1]. We are the first to show that the reaction of (I) with ethyl α-bromoacetoacetate (II) occurs by a fundamentally different scheme for increasing the coordination of the sulfur atom. This reaction gives vinyl esters of sulfurous acid (III).

$$\underset{\text{(I)}}{(RO)_2S} + \underset{\text{(II)}}{MeC(O)CHBrC(O)OEt} \rightarrow \underset{\text{(III)}}{ROS(O)OC(Me) = CHC(O)OEt} + RBr$$

$$R = Et,\ i\text{-}Pr$$

The PMR spectra of (II) in CCl_4 in the region for vinyl protons H–(C=C) show two singlets at 5.57-5.53 ppm (0.45 H) and 5.06-5.00 ppm (0.55 H), which indicates the separation of (III) as a 45:55 mixture of E and Z isomers, respectively. Analogous spectral behavior has been reported for enol phosphates [2]. The low yield of (III) (25.27%) is related to disproportionation upon the separation of (III) by distillation, analogously to other mixed sulfites [3], with the formation of symmetrical sulfites, in particular, dialkyl sulfites $(RO)_2SO$. The formation of sulfinic acid esters was not observed during this reaction.

A sample of 0.2 mole (I) was heated for 20 h at 85-90°C in an argon atmosphere with 0.2 mole (II) with distillation of RBr formed. The residue was distilled in vacuum. When R = Et, the yield of (III) was 10.4 g (25%), bp 67-68°C ($7 \cdot 10^{-3}$ mm), n_D^{20} 1.4712. Found, %: C 43.1; H 6.2; S 14.2. $C_8H_{14}O_5S$. Calculated, %: C 43.24; H 6.3; S 14.41. IR spectrum (ν, cm^{-1}): 12.55 (S=O), 1625 (C=C), 1720 (C=O). When R = i-Pr, the yield of (III) was 12.7 g (27%), bp 74-75°C ($3 \cdot 10^{-3}$ mm), n_D^{20} 1.4830. Found, %: C 45.2; H 6.4; S 13.3. $C_9H_{16}O_5S$. Calculated, T: C 45.76; H 6.77; S 13.5. IR spectrum (ν, cm^{-1}): 1250 (S=O), 1630 (C=C), 1725 (C=O).

LITERATURE CITED

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