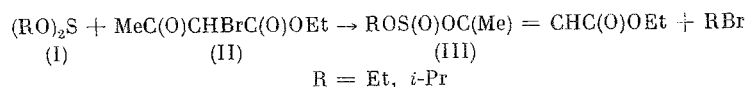


REACTION OF ESTERS OF SULFOXYLIC ACID WITH ETHYL α -BROMOACETOACETATE

S. V. Baires, V. B. Ivanov, L. T. Vil'danova,
and B. E. Ivanov

UDC 542.91:547.368

Sulfoxylic acid esters (I) react with alkyl halides to form sulfinic acid esters $RS(O) \cdot$ 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).



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

1. E. Wenschuh, R. Fahsl, and R. Hohne, *Synthesis*, **12**, 829 (1976).
2. H. Kolind-Andersen and S.-O. Lawesson, *Acta Chem. Scand.*, **29**, 430 (1975).
3. G. Berti, *J. Am. Chem. Soc.*, **76**, 1213 (1954).