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LETTERS TO THE EDITOR

An Unexpected Reaction Pattern of Divinyl Sulfoxide with Potassium *O*-Alkyl Carbonodithioates under Microwave Assistance

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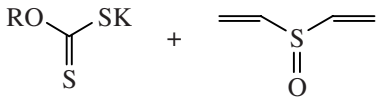
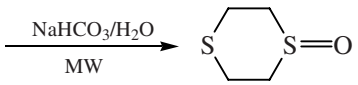
The selective monoaddition of carbonodithioate anions to readily available divinyl sulfoxide (**I**) [1, 2] in the H_2O–$NaHCO_3$ or H_2O–C_6H_6–$NaHCO_3$ systems, leading to *O*-alkyl *S*-[2-(vinylsulfinyl)ethyl] carbonodithioates, has been reported [3].

In the present work we found that the same reaction under microwave irradiation (450 W, 10 min) affords $1\lambda^4$,4-dithiane 1-oxide (**II**) in a yield of up to 31%.



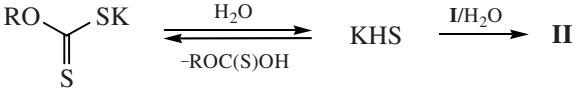
I



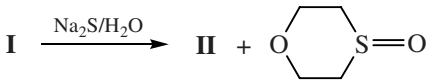
II

R = Et, Bu.

Apparently, the reaction begins with hydrolysis of the starting potassium salts of xanthic acid to form hydrosulfide anions which further react with divinyl sulfoxide (**I**) by the addition-cyclization scheme to give heterocycle **II**.



Dithiane oxide **II** was prepared independently by heating divinyl sulfoxide (**I**) with sodium sulfide in water (50–55°C, 5 h). Along with **II**, $1,4\lambda^4$-oxathiane 4-oxide (**III**) was formed under these conditions via the known reaction of divinyl sulfoxide with water [4].



III

The IR, ^{1}H NMR, and mass spectra of compounds **II** and **III** were identical to those described in the literature [4–7].

$1\lambda^4$,4-Dithiane 1-oxide (**II**). A round-bottom flask equipped with a reflux condenser was charged with 3 mmol of **I**, a solution of 4 mmol of $NaHCO_3$ in 4 ml of water, and a solution of 4 mmol of potassium *O*-butyl carbonodithioate in 4 ml of H_2O. The mixture was placed into a microwave oven and irradiated at 450 W for 10 min, after which it was cooled, extracted with benzene (5 × 10 ml), and dried over $MgSO_4$. Benzene was removed under reduced pressure, and the residue was dried in a vacuum. Sublimation gave 0.13 g (31%) of compound **II** as colorless crystals, mp 125–126°C (125–127°C [6]). IR spectrum (KBr, cm^{-1}): 2962, 2913, 2861 ν(CH_2); 1744, 1462, 1406, 1324 δ(CH_2); 1274, 1212, 1169, 1128; 1021 ν(S=O); 628, 510 ν(C–S). ^{1}H NMR, δ, ppm: 2.50–2.54 m (2H, CH_2S), 2.96–3.02 m (2H, CH_2S=O), 3.09–3.14 m (2H, CH_2S=O), 3.54–3.61 m (2H, CH_2S). Found, %: C 35.66; H 5.88; S 46.83. *M* 136.22. $C_4H_8OS_2$. Calculated, %: C 35.27; H 5.92; S 47.07. Mass spectrum (electron impact, 70 eV), *m/z* (I_{rel}, %): 136 $[M]^+$ (53),

119 (4), 108 (3), 92 (8), 87 (43), 77(56), 73 (24), 64 (9), 63 (15), 61 (25), 60 (98), 59 (72), 58 (24), 53 (5), 50 (3), 48 (13), 47 (22), 46 (42), 45 (100), 41 (12), 35 (5).

The reaction with potassium *O*-ethyl carbonodithioate gave 18% of compound **II**.

Reaction of divinyl sulfoxide with sodium sulfide. A solution of 0.72 g of $Na_2S{\cdot}9H_2O$ and 0.305 g of sulfoxide **I** in 10 ml of H_2O was stirred at 50–55°C for 5 h. After cooling, the reaction mixture was diluted with water (~10 ml), extracted with chloroform (5 × 10 ml), and dried with potassium carbonate. Chloroform was removed under reduced pressure, and the residue was dried in a vacuum to obtain 0.09 g (22%) of a mixture of heterocycles **II** and **III** in a 12:1 ratio (GC–MS data).

The ^{1}H NMR spectra were recorded on a Bruker DPX 400 spectrometer (400 MHz) for solutions in $CDCl_3$, internal standard HMDS. The IR spectra were obtained on a Bruker IFS 25 instrument in KBr pellets. The electron impact mass spectra were taken on a SHIMADZU GCMS-QP5050A instrument, ionizing energy 70 eV. The microwave-assisted reac-tions were carried out in a modified Samsung 181 DNR household microwave oven.

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