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Photoreaction of *S*-Butyl 3-Methoxy-2-butenethioate. Competitive 1,5-Methyl Migration and *O*-Demethylation

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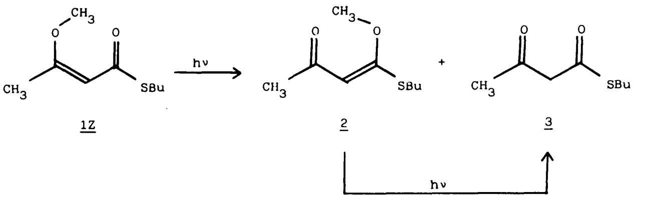
Synopsis. Irradiation of *S*-butyl (*Z*)-3-methoxy-2-butenethioate (**1Z**) *gave the* 1,5-*methyl migration product* **2** and the *O*-demethylation product **3**. The photo-1,5-methyl migration occured competitively with the *O*-demethylation from the π, π* excited triplet state of **1Z**. The migration product **2** underwent the secondary photoreaction to **3** in a nondegassed benzene solution.

Recently we reported the photoreaction of *S*-alkyl 3-oxobutanethioates to the corresponding disulfides.[1] The photoreaction occurred only from the keto form though the 3-oxobutanethioates exhibit keto-enol tautomerism. Irradiation of a model compound for the enol form, *S*-butyl (*Z*)-3-methoxy-2-butenethioate (**1Z**), under nitrogen gave no disulfides but an *O*-demethylated product. Although the photoreactions of enol esters have been well studied,[2] those of enol ethers have received only little attention.[3] We investigated the further details of the enol ether **1Z** and found thst **1Z** underwent the unusual 1,5-methly migration competing with the *O*-demethylation. The migration was followed by the secondary photoreaction in the presence of dissolved oxygen. In this paper we will descrive these results of the photoreaction of **1Z**.

Irradiation of a degassed benzene solution of **1Z** in a sealed Pyrex tube with a 450 W high-pressure mercury lamp gave 4-butylthio-4-methoxy-3-butene-2-one (**2**) and *S*-butyl 3-oxobutanethioate (**3**) in 65 and 25% yield, respectively.[4] The structure of **2** was elucidated by spectral data and by elemental analysis. The IR spectrum of **2** showed the characteristic absorption of α,β-unsaturated carbonyl at 1680 cm^{-1}. The ^{1}H NMR spectrum of **2** showed two singlets at δ 2.28 and 3.64, attributable to the acetyl and the methoxyl group, respectively. The peak at δ 3.64 underwent large upfield shift in benzene-d_6 and was observed at δ 2.94. The ^{1}H NMR spectra of α,β-unsatulated compounds undrego large chaneges when these substances are dissolved in aromatic solvents.[5] The solvent effect of **2** can be explained in terms of the diamagnetic anisotropy of the aromatic nucleus in the intermolecular complex between the α,β-unsatulated carbonyl compounds and the aromatic solvent. The ^{13}C NMR spectrum of **2** showed a doublet at δ 99.3 and singlets at δ 169.9 and 187.8 attributable to α-, β-, and carbonyl carbon, respectively. These results supported the structure of **2**.



The photochemical reaction of **1Z** was pursured by quantitative analysis of the products and the starting material. The time-conversion curves are given in Figs 1 and 2. Since no quantitative measurement was taken of the intensity of the light for irradiation and absorption of the light by the enol form of the product 3-oxobutanethioate **3**, only the relative reactivity will be discussed here. Figure 1 shows that both the compound **2** and **3** were formed even at low conversion percentage of **1Z**. The figure also shows that the amount of **2** and **3** were nearly constant after the staring material had completely disappaered. Therefore, the migration from **1Z** to **2** competes with the demethylation to **3**. The formation of both **2** and **3** from **1Z** were efficiently and equally quenched with 1,3-pentadiene and sensitized with *p*-methoxy acetophenone, so that both **2** and **3** formations take place from the same triplet state of **1Z**.

The ratio of photoproduct **2** to **3** was strongly affected by the irradiation conditions. Figure 2 shows that compound **2** converts to compound **3** by prolonged

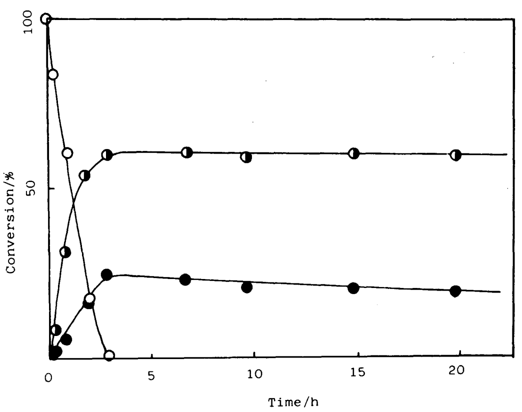


Fig. 1. Time-conversion curves for the photochemical reaction of **1Z** in degassed benzene-d_6
—○—: 1Z, —◑—: 2, —●—: 3.

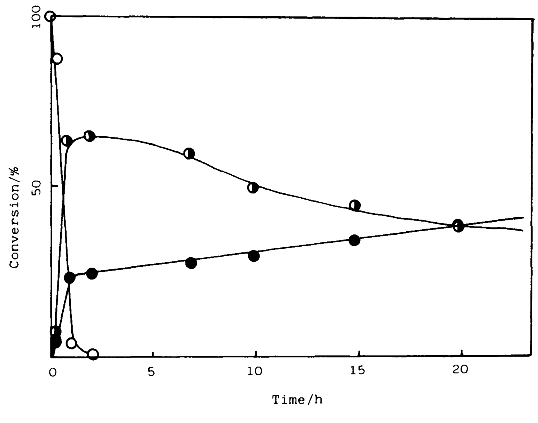


Fig. 2. Time-conversion curves for the photochemical reaction of **1Z** in nondegassed benzene-d_6
—○—: 1Z, —◑—: 2, —●—: 3.

iradiation in a nondegassed benzene solution. Dissolved oxyen might causes the transformation of **2** to **3**. The Figure also shows that the rate of disappearance of the starting compound **1Z** is enhanced in the nondegased benzene. Ethyl bromide also accelerated the photoreaction of **1Z** and the secondary photoreaction of **2**. The compounds containing heavy atoms enhance the rate of π,π^* $S \rightarrow T^*$ intersystem crossing, and no heavy-atom enhancement of the rate of intersystem crossing takes place in the n,π^* excited state of ketones.[6] The external heavy atom effects on photoreactions of **1Z** and **2** suggest both the primary and the secondary photoreaction proceed from the π,π^* excited triplet state. Dissolved oxygen in solution probably operates through the catalysed intersystem crossing.[7]

The formation of **3** can be explained in terms of homolytic carbonoxygen bond cleavage from the π,π^* excited triplet state of **1Z**. Biphenyl could be detected by GLC analysis of a reaction mixture of a degassed benzene solution of **1Z**. This result supports the above mechanism for the formation of **3**. The formation of the methyl migration product **2** may be explained in terms of either the concerted 1,5-sigmatropic reaction or the nonconcerted radical rearrangement. Although the 1,5-sigmatropic reactions with inversion at the migration center are photochemically allowed,[8] the reactions in general do not take place from the $^3\pi,\pi^*$ states.[9] Therefore, the nonconcerted radicalrearrangement seems to be probable for the mechanism of the 1,5-methyl migration of **1Z**.

Irradiation of a benzene solution of the *E*-isomer 1E gave the *O*-demethylated product **3** in 58% yield.[10] No methyl migration products could be detected. Abcence of the methyl migration products in photolysis of the *E*-isomer seems to be explained in terms of the principle of least motion.[11] The distance separating the methoxyl and the carbonyl group should be larger in the *E*-isomer than in the *Z*-isomer. Therefore, the 1,5-methyl migration occurs easily in the case of the *Z*-isomer. The cage radical pair from the *E*-isomer seems to diffuse to free radicals.

Experimental

The IR spectra were recorded on a JASCO A-3 spectrometer. The UV spectra were taken on a JASCO HUN-790 spectrometer. The ^{1}H and the ^{13}C NMR spectra were measued on a JEOL FX-90Q spectrometer using TMS as an internal standard. Irradiation was carried out with an Ushio 450 W high-pressure mercury lamp.

Chemicals. The butenethioate **1Z** and **1E** were prepared by treatment of the 3-oxobutanethioate **3** with diazomethane in the usual way.[12] The *E*- and *Z*-configuration were deduced by ^{1}H NMR spectroscopic data.[13]

S-Butyl (E)-3-Methoxy-2-butenethioate (1E): Mp 44.6—45 °C; IR (KBr) 1430, 1510, 1660 cm^{-1}; UV $\lambda_{\max}^{\mathrm{EtOH}}$ 293 nm (ε 6360); ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, CH_3), 1.1—1.8 (4H, m, CH_2), 2.14 (3H, s, CH_3), 2.82 (2H, t, SCH_2), 3.83 (3H, s, OCH_3), 5.68 (1H, s, olefinic); ^{13}C NMR ($CDCl_3$) δ= 13.6 (q), 22.0 (t), 28.3 (t), 30.5 (q), 31.7 (t), 58.2 (q), 97.7 (d), 173.8 (s), 194.3 (s); Found: C, 57.23; H, 8.64%. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.65%.

S-Buthyl (Z)-3-Methoxy-2-butenethioate (1Z): Mp 41.5—42 °C; IR (KBr) 1380, 1600, 1660 cm^{-1}; UV $\lambda_{\max}^{\mathrm{EtOH}}$ 273 nm (ε 6960); ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, t, CH_3), 1.1—1.8 (4H, m, CH_2), 2.01 (3H, s, CH_3), 2.86 (2H, t, SCH_3), 3.85 (3H, s, OCH_3), 5.24 (1H, s, olefinic); ^{13}C NMR ($CDCl_3$) δ= 13.7 (q), 18.7 (q), 22.1 (t), 28.0 (t), 32.0 (t), 56.2 (q), 105.1 (d), 165.1 (s), 186.1 (s); Found: C, 57.24; H, 8.60%. Calcd for $C_9H_{16}O_2S$: C, 57.41; 8.65%.

Preparative Irradiation of 1Z. A solution of **1Z** (300 mg, 1.60 mmol) in benzene (5 cm^3) was placed in a 15×150 mm Pyrex culture tube. The solution was degassed by three freeze-pump-thaw cycles, sealed and irradiated for 2 h with a high-pressure mercury lamp. After removal of the solvent, the residual oil was chromatographed on silica gel. Elution with benzene–ethyl acetate (4:1) gave **2** (195 mg, 65%) and **3** (70 mg, 25%). **2**: bp 220 °C/10 Torr (1 Torr≈ 133.322 Pa); IR (neat) 1680 cm^{-1}; UV $\lambda_{\max}^{\mathrm{EtOH}}$ 263 nm (ε 5360); ^{1}H NMR ($CDCl_3$) δ=0.92 (3H, t, CH_3), *ca.* 1.2—1.8 (4H, m, CH_2), 2.28 (3H, s, CH_3CO), 2.88 (2H, t, SCH_2), 3.64 (3H, s, OCH_3), 5.39 (1H, s, olefinic); ^{1}H NMR (C_6D_6) δ=0.81 (3H, t, CH_3), *ca.* 1.1—1.7 (4H, m, CH_2), 2.28 (3H, s, CH_3CO), 2.88 (3H, s, OCH_3), 2.94 (2H, t, SCH_2), 5.26 (1H, s, olefinic); ^{13}C NMR ($CDCl_3$) δ=13.7 (q), 19.7 (q), 22.1 (t), 28.4 (t), 32.2 (t), 55.4 (q), 99.3 (d), 169.9 (s), 187.8 (s); Found: C, 57.51; H, 8.61%. Calcd for $C_9H_{16}O_2S$: C, 57.41; H, 8.56%.

Preparative Iradiation of 1E. A solution of **1E** (12 mg, 0.65 mmol) in benzene (5 cm^3) was irradiated for 10 h with a high-pressure mercury lamp. The usual work-up gave the unreacted **1E** (62 mg) and **3** (32 mg, 58%).

Quantitative Analysis of Photoreaction of 1Z. A degassed/nondegassed benzene-d_6 solution of **1Z** (0.30 mol/L) in a sealed NMR tube was irradiated. The amounts of **1Z**, **2**, and **3** were determined by ^{1}H NMR spectroscopy.

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