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Photochemical Reaction of *S*-Alkyl 3-Oxobutanethioate

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Synopsis. Irradiation of *S*-alkyl 3-oxobutanethioate (**1**) in benzene or ethanol yielded the disulfide **2**. Irradiation of *S*-alkyl α-bromothioacetate also gave the disulfide **2**. The photochemical reaction of the 3-oxobutanethioate **1** involves the Norrish Type I reaction followed by rapid fragmentation of the radical $\cdot CH_2COSR$ to the thiyl radical **5**.

The Norrish Type I reaction of ketones has been thoroughly investigated[1] and work has also been done on the photochemistry of α-substituted β-dicarbonyl compounds.[2] However, β-dicarbonyl compounds which possess no α-substituents are inert toward the Type I reaction.[3,4] We report here that *S*-alkyl 3-oxobutanethioates **1**, which possess no α-substituents, undergo the Type I reaction to give the disulfides **2**, but no thioacetates **6**.

When a benzene solution of *S*-propyl 3-oxobutanethioate (**1a**) was irradiated under nitrogen with a 450 W high-pressure mercury lamp through a Pyrex filter, dipropyl disulfide (**2a**) was obtained in 26% yield. Similarly, irradiation of the 3-oxobutanethioates **1b**—**e** under the same conditions gave the corresponding disulfides **2b**—**e**. In these cases no *S*-alkyl thioacetates, which are expected to be produced through the Type I reaction, and no thiolactones, which are expected to be formed *via* δ-hydrogen abstraction by ketone carbonyl, were detected.

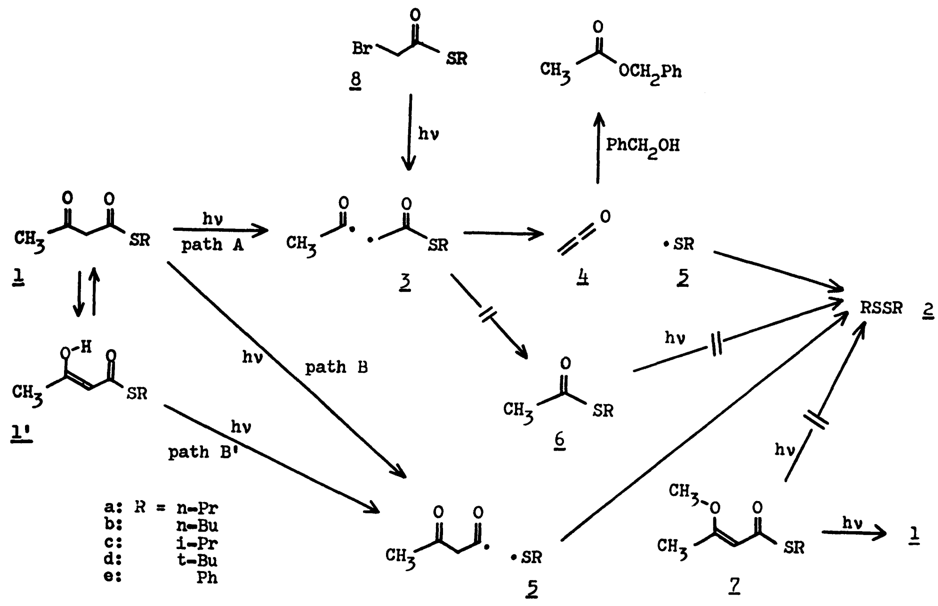
Formation of the disulfide **2** can be explained in terms of the Type I reaction of the 3-oxobutanethioate **1** followed by the fragmentation of the radical $\cdot CH_2COSR$ (**3**) to the thiyl radical **5** (path A).

An alternative path B, which involves the direct cleavage of the sulfur-acyl bond, may be considered. The sulfur-acyl bond of the excited enethiol esters cleaves homolitically to give enethiyl radicals.[5] However, the path B seems to be improbable because the direct or acetone-sensitized irradiation of *S*-propyl thioacetate **6a** in benzene gave no disulfides. More evidence for exclusion of the path B mechanism has been obtained. Loveridge *et al.* reported that irradiation of *S*-phenyl thioacetate in benzene gave diphenyl disulfide; however, no products were obtained when the thioacetate was irradiated in alcohols.[5b] Their results prompted us to investigate the photoreaction of the 3-oxobutanethioate **1** in alcohols. Irradiation of *S*-phenyl 3-oxobutanethioate (**1e**) in ethanol also gave the disulfide **2e** in 22% yield. Similarly, irradiation of the 3-oxobutanethioate **1b** in ethanol gave the disulfide **2b** in 14% yield. These results indicate that the mechanism of the photoreaction of 3-oxobutanethioate **1** is different from that of the photolysis of the enethiol esters. Therefore, path B, which involves the direct sulfur-acyl bond cleavage, seems to be excluded.

Table 1. The yields of the disulfide **2** in the photolysis of **1** and **8**

Compound	Solvent	Yield/% of **2**[a]
1a	PhH	26
1b	PhH	59
	EtOH	14
1c	PhH	5
1d	PhH	2
1e	PhH	49
	EtOH	22
8b	PhH	37
8e	EtOH	19

a) Conversion yield.



Scheme 1.

The other pathway which involves the direct cleavage of the sulfur-acyl bond from the enol form of the 3-oxobutanethioates may be considered (path B′). The 3-oxobutanethioates **1** exhibited keto-enol tautomerism. The 3-oxobutanethioate **1b** contained 71% of the keto form and 29% of the enol form in deuterated chloroform. However, this pathway seems to be improbable for the following reasons. When a benzene solution of *S*-butyl 3-methoxy-2-butenethioate (**7**), which is a model compound for the enol form of the 3-oxobutanethioate **1b**, was irradiated under the same conditions, *O*-demethylated product **1b** was obtained in 86% yield. A trace of the disulfide **2b** was detected by GLC; however, the disulfide **2b** seems to be a secondary photoproduct from the 3-oxobutanethioate **1b** because of the very low yield.

Although the attempt to trap the radical **3** from **1b** and **1e** with ethanethiol was unsuccessful, evidence in support of the above mechanism (path A) was obtained from the following experiments. When the 3-oxobutanethioate **1b** was irradiated in benzene containing 20% of benzyl alcohol, the ketene **4** was trapped as benzyl acetate which was detected by GLC. Irradiation of an ethanol solution of *S*-phenyl α-bromothioacetate (**8e**), which is expected to form the radical **3**,[6] gave the disulfide **2e** in 19% yield. In this case *S*-phenyl thioacetate could not be detected. Similarly, irradiation of *S*-butyl α-bromothioacetate (**8b**) in benzene gave the disulfide **2b** in 37% yield. These results suggest that the 3-oxobutanethioate **1** undergoes the Type I reaction to yield the radical $\cdot CH_2COSR$ (**3**) and the radical **3** rapidly fragments to the thiyl radical **5**.

The photoreaction of the 3-oxobutanethioate **1b** was efficiently quenched with 1,3-pentadiene, so that the Type I reaction takes place from the n,π* triplet state of the keto form of the 3-oxobutanethioate **1**.

Experimental

Chemicals. The 3-oxobutanethioates **1a**—**e**, the thioacetate **6a**, and the α-bromothioacetates **8b** and **8e** were prepared according to previously described methods.[7,8] The butenethioate **7** was prepared by treatment of **1b** with diazomethane.[9]

General Procedure for Photolysis of 3-Oxobutanethioate 1 and α-Bromothioacetate 8. A 3-oxobutanethioate **1** or a thioacetate **8** (300 mg) in benzene or ethanol (70 ml) was irradiated for about 100 h under nitrogen with a 450 W high-pressure mercury lamp (Ushio Elec. Co.) through a Pyrex filter. After removal of the solvent, the residue was chromatographed on silica gel. Elution with benzene gave a disulfide **2**. The structure of **2** was determined by direct comparison with authentic samples.[10]

Photoreaction of S*-Butyl 3-Methoxy-2-butenethioate (7).* A solution of **7** (101 mg) in benzene (50 ml) was irradiated in a Pyrex vessel under nitrogen for 28 h. After removal of the solvent, the residue was chromatographed on silica gel (benzene–ethyl acetate 5 : 1) to give 80 mg of **1b**.

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