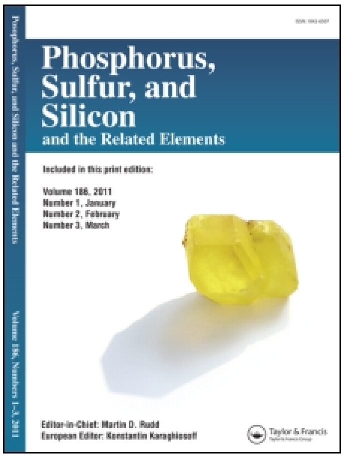

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S. Inoue[a]; T. Tezuka[b]; S. Oae[b]
[a] Department of Chemistry, Tokyo Kyoiku University, Tokyo, Japan [b] Department of Chemistry, The University of Tsukuba, Ibaraki, Japan

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A NEW TYPE OF PHOTOCHEMICAL ADDITION REACTION OF ELEMENTAL SULFUR TO OLEFINS

S. INOUE

Department of Chemistry, Tokyo Kyoiku University, Tokyo, Japan

and

T. TEZUKA and S. OAE

Department of Chemistry, The University of Tsukuba, Sakura-mura, Ibaraki 300–31, Japan

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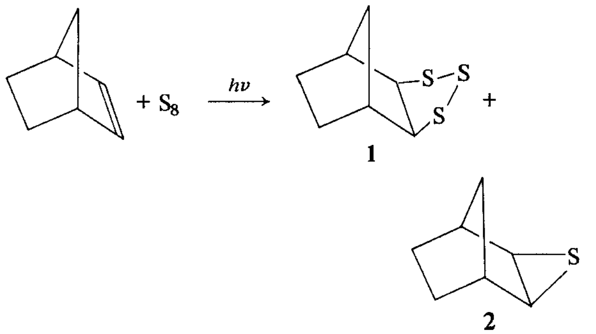
Photochemical reactions of elemental sulfur with several olefins were studied. Irradiation of a mixture of elemental sulfur and norbornylene with 3500 Å light afforded 3,4,5-trithiatricyclo[5.2.1.0]decane (**1**) and 2,3-epithionorbornane (**2**). Similarly, several thiane derivatives (**4–6**) were found to be formed by the photolysis of a mixture of cyclohexene and sulfur.

It has long been known that elemental sulfur reacts with olefins to give sulfides.[1] Recently, Shields and Kurtz reported the formation of trithiane (**1**) by amine-catalyzed thermal reaction of elemental sulfur with norbornylene.[2] Unlike the thermal reaction, there is practically no work on photochemical reactions of elemental sulfur with olefins. We wish to report a novel photo-reaction of sulfur with olefins, that affords thianes and related compounds.

When a mixture of elemental sulfur and norbornylene in carbon disulfide was irradiated with 3500 Å light, 3,4,5-trithiatricyclo[5,2,1,0] decane (**1**) and 2,3-epithionorbornane (**2**) were formed in 77 and 8% yield respectively.[3] The structure of **1** was confirmed by comparison of spectral data with those of an authentic sample prepared by a known method.[2] The structure **2** was assigned on the basis of the elemental analysis and by comparison of the spectral data.[4]



In the initial stage of the reaction, the compound **2** could not be detected by VPC; nevertheless a small amount of **1** was formed. A rough kinetic analysis by VPC demonstrated that compound **2** was gradually formed after **1** started to accumulate (Figure 1). These

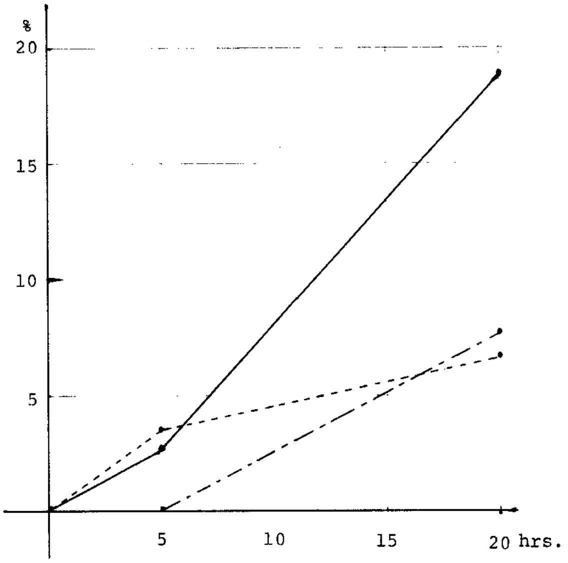
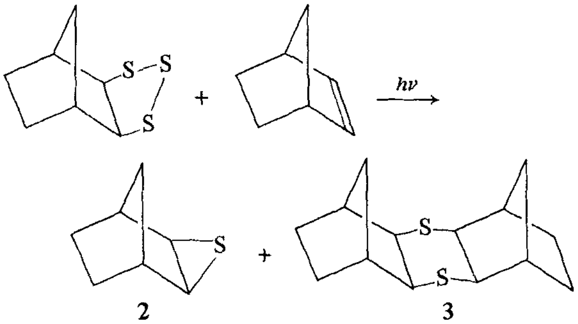


FIGURE 1 The % yields of **1** and **2** *vs.* time by photolysis of sulfur and norbornylene in benzene or DMF-NH_3 solution. ——— yield of **1** in benzene solution. – – – – – yield of **2** in benzene solution. ------ yield of **1** in DMF–NH_3 solution.

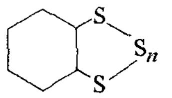
observations suggest **2** to be a secondary product from **1**. In fact, when a benzene solution of **1** and norbornylene (large excess) was irradiated under the same photolytic conditions, **2** was formed in 35% yield together with a small amount of dithiane **3**, the structure of which was assigned by mass spectroscopy. A control experiment revealed that **2** was not formed from **1** by thermal reaction and that **1** was not converted to **2** in the absence of norbornylene even under photolytic conditions. Thus it is clear that **2** is formed by the reaction of an excited molecule of **1** with norbornylene.



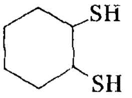
2 **3**

Compound **2** is considered to be derived by the transfer of a sulfur atom from **1** to norbornylene. The thermally induced transfer of a sulfur atom from stilbene episulfide to cyclohexene has already been reported.[5] Thus the photo-reaction of **1** with several olefins such as cyclohexene, 2-methyl-2-butene, and cyclooctene were tested, with the expectation of obtaining the respective episulfides. However, in the photo-reaction the consumption of **1** was extremely slow, and the corresponding episulfide could not be detected with mass spectroscopy.

Thiane derivatives may also be obtained by photo-reactions of elemental sulfur with other olefins. For example, when a mixture of elemental sulfur and cyclohexene was irradiated with 3500 Å light, several products were formed, from which **4-6** were identified by GC mass spectroscopy. Thus, the mass spectral fragment ion peaks of the compound **4**, which is a major VPC component of the reaction mixture, were at m/e 242 (M), 210 (M-S), 178 (M-S_2), 146 (M-S_3), 114 (M-S_4) and 81 (M-S_5H). Similarly, **5** and **6** were assigned to the second major and minor components, respectively. VPC retention times and mass spectral degradation patterns of **4**, **5** and **6** were in accord with those of authentic samples prepared by a known method.[6] Since the isolation of these compounds was rather difficult, the reaction mixture was reduced with $LiAlH_4$ (LAH) for identification and dithiol **7** was formed.



4; $n = 3$
5; $n = 2$
6; $n = 1$



7

Photochemical formation of the thiane derivatives from elemental sulfur and olefin has no precedent and hence is of particular interest. In the thermal addition reaction of sulfur to norbornylene, addition of ammonia increased the yield of **1**.[2] In contrast, in the photo-reaction, the addition of ammonia did not accelerate the formation of **1**. As shown in Figure 1, the amount of **1** and **2** formed by the photo-reaction in benzene solution increased with time. In contrast, the amount of **1** formed in DMF-NH_3 solution by photolysis was extremely low, in which **2** was not formed even under prolonged irradiation. It is now clear from this observation that the mechanistic path of the photochemical formation of **1** is different from that of the thermal reaction. In view of the reddish color formation in the photo-reaction of sulfur and norbornylene in CS_2, one tends to consider that such allotropes[7] as S_3 and S_4, formed by the photolysis, are attacking the olefinic double bond to give the adducts. However further investigation with individual sulfur allotropes are necessary to understand the nature of these photo-reactions.

EXPERIMENTAL

Photo-reaction of sulfur with norbornylene. A degassed mixture of elemental sulfur (350 mg) and norbornylene (73 mg) in carbon disulfide (2.2 g) was irradiated with 3500 Å light (Rayonet 108) for 70 hours at 40°C. Vacuum distillation of the reaction mixture afforded 3,4,5-trithiatricyclo[5.2.1.0]decane (**1**), bp 89° (0.1 mm), and 2,3-epithionorbornane (**2**), mp 32° in 77 and 8% yield, respectively.

1: m/e 190 (M), 126 (M-S_2), and 93 (M-S_3H), nmr ($CDCl_3$), δ 2.42 (2H, m.), 3.60 (2H, d.). **2**: Anal. *Found.*; C, 66.60; H, 8.07; S, 25.42%. *Calcd.* for $C_7H_{10}S$: C, 66.61; H, 7.99; S, 25.40%. m/e 126 (M) and 93 (M-SH); nmr ($CDCl_3$), δ 2.36 (2H, m.) and 2.63 (2H, d.).

Photo-reaction of 3,4,5-trithiatricyclo[5.2.1.0]decane (1) with norbornylene. A mixture of **1** (32.6 mg) and norbornylene (588.6 mg) in benzene (64 mg) was irradiated as described above. The epithio derivative **2** was identified by comparison of the VPC retention time and mass spectral degradation pattern with those of the authentic sample. The yield of **2** was estimated by integrating the VPC peak using biphenyl as an internal standard. The mass spectrometric analysis indicated that the dithiane derivative (**3**), m/e 252 (M), 158 (M-norbornylene), 126 (M-norbornylene-S), 93 (M-norbornylene-S_2H), was present in the reaction mixture with **2**.

Photo-reaction of sulfur with cyclohexene. A mixture of sulfur (53 mg) and cyclohexene (390 mg) was irradiated with 3500 Å light for 14 hr at 50°C. Several trials to separate the thiane derivatives were carried out but in vain. Then the reaction mixture was analyzed by means of the GC mass spectrometer. The thiane derivatives **4**, **5** and **6** were identified as a major, second major, and minor components, respectively.

5: *m/e* 210 (M), 178 (M-S), 141 (M-S_2), 114 (M-S_3), 81 (M-S_4H).

6: *m/e* 178 (M), 141 (M-S), 114 (M-S_2), 81 (M-S_3H).

LAH reduction of a reaction mixture obtained from the photo-reaction of sulfur and cyclohexene. A reaction mixture obtained from sulfur and cyclohexene by photolysis was stirred with LAH in absolute ether overnight. The usual work-up afforded an oil, in which dithiol **7** was identified by comparison of the VPC retention time and fragmentation pattern of the mass spectrum with those of the authentic sample prepared from cyclohexene episulfide and hydrogen sulfide.

Monitoring the photo-reaction of sulfur with norbornylene in benzene and in DMF-NH_3 solution. A degassed benzene (650 mg) solution of sulfur (37 mg) and norbornylene (63 mg), or an ammonia-saturated dimethylformamide (700 mg) solution of sulfur (48 mg) and norbornylene (82 mg) in Pyrex tubes was irradiated at 3500 Å in a Rayonet "merry-go-round" reactor for several hours. Samples were taken at intervals, and the amounts of **1** and **2** formed were analyzed by means of VPC (SE-30) using biphenyl as an internal standard. The results are presented in Figure 1.

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