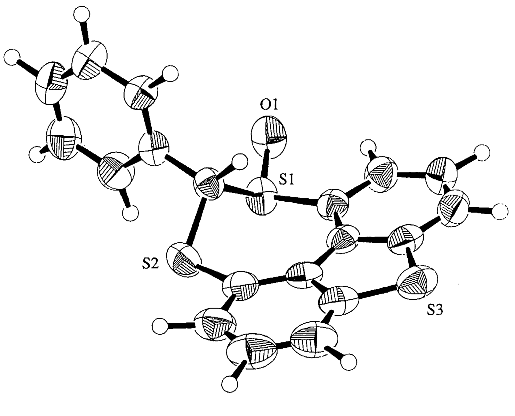
Mechanism for Photodecomposition of 4,8,10-Trithiadibenzo[*cd,ij*]azulene 8-oxides

Takayoshi Fujii, Hiroki Kusanagi, and Naomichi Furukawa*
Tsukuba Advanced Research Alliance Center, Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305

(Received March 27, 1996)

4,8,10-Trithiadibenzo[*cd,ij*]azulene 8-oxides were prepared and their photolysis provided a convenient procedure to yield the corresponding aldehydes and ketones together with 4,8,9-trithiacyclopenta[*def*]phenanthrene.



Trans isomer
Config. *Rs, Sc* or *Ss, Rc*

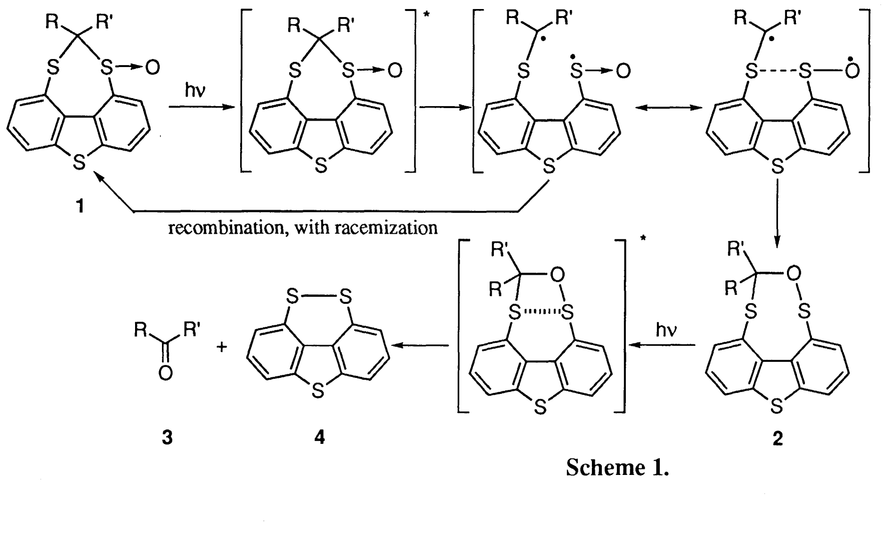
Figure 1. ORTEP drawing of **1a**.

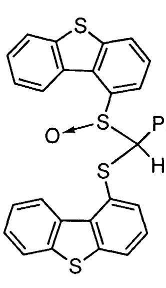
In the course of our studies with respect to the generation of dication *via* through-space interaction using 1,8-disubstituted naphthalene and 1,9-disubstituted dibenzothiophene,[1] we have succeeded in the generation of reactive species on photolysis of 1,8-bis(alkylthio)- and 1,8-bis(alkylseleno)naphthalene, and 1,9-bis(alkylthio)dibenzothiophene derivatives.[2] Furthermore, we found that 4,8,10-trithiadibenzo[*cd,ij*]azulene 8-oxides underwent photo-rearrangement of the sulfinyl-oxygen atom to give the corresponding carbonyl compounds quantitatively together with 4,8,9-trithiacyclopenta[*def*]phenanthrene. We report this new method for the generation of aldehydes and ketones from cyclic dithioacetals S-oxide together with the mechanism of its photolysis.

Typically, 9-phenyl-4,8,10-trithiadibenzo[*cd,ij*]azulene 8-oxide (**1a**) was prepared according to the following procedure. Reduction of 4,8,9-trithiacyclopenta[*def*]phenanthrene (**4**) with sodium borohydride in THF-ethanol at room temperature gave almost quantitatively 1,9-dibenzothiophenedithiol (**5**). 9-Phenyl-4,8,10-trithiadibenzo[*cd,ij*]azulene (**6a**) was prepared by the reaction of **5** and benzaldehyde in the presence of $SiCl_4$ in CH_2Cl_2 in 79% yield. Compound **1a** was obtained in 84% yield as the diastereoisomer (**1a** : **1a'** = 2 : 1) by oxidation of **6a** using *m*-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2 at -20 °C. The structure of the major diastereoisomer **1a** was determined by X-ray crystallographic analysis (Figure 1).[3] The molecular structure of **1a** is a *trans*-isomer with a phenyl group and a sulfinyl-oxygen atom occupying the equatorial positions (R_S,S_C and S_S,R_C configurations). The S(1)•••S(2) distance of **1a** is 2.9 Å which is markedly shorter than the sum of the van der Waals radii (3.7 Å) of sulfur atoms.

Although the compounds **6** were thermally and photochemically stable molecules, the corresponding monooxides **1** were found to decompose on exposure to a high pressure Hg lamp (400 W) to the corresponding aldehydes and ketones quantitatively with complete recovery of **4** in benzene (Scheme 1 and Table 1). Solvent effects were examined on photolysis of **1a** using protic and aprotic solvents including ethanol, acetonitrile, THF, CH_2Cl_2, and benzene. The photodecomposition reactions gave **3a** and **4** quantitatively regardless of the solvent used. Although benzaldehyde bis(1-dibenzothiophenyl) dithioacetal S-oxide **7** underwent photodecomposition under identical conditions, the products obtained were a mixture of intractable compounds separation of which were not possible by a simple procedure. These results imply that the through-space interaction between the two sulfur atoms at the 1,9-positions of dibenzothiophene plays an important role for the formation of **4** and **5** quantitatively.

Photolysis of **1a** under irradiation with a high pressure Hg





7

Scheme 1.

Table1. Photolysis of **1**[a]

1	R	R'	Yield of **3** (%)[b]	Yield of **4** (%)[b]
a	Ph	H	>99	>99
b	*p*-Tol	H	>99	>99
c	$CH_3(CH_2)_5$	H	>99	>99
d	PhCH=CH	H	>99	>99
e	2-furyl	H	>99	>99
f	Ph	CH_3	>99	>99
g	$-(CH_2)_3-$		>99	>99
h	$-(CH_2)_4-$		>99	>99
i	$-(CH_2)_5-$		>99	>99
j	$-(CH_2)_6-$		>99	>99

[a] 400W high pressure Hg lamp $\lambda > 300$ nm, [Substrate] = 2.0×10^{-2} M.
[b] Yields were determined by HPLC and ^{1}H-NMR spectroscopy.

lamp (500 W, λ = 313 nm) in deoxygenated CH_2Cl_2 was monitored by HPLC at various time intervals (Figure 2). The peak of the starting material **1a** gradually reduced, while the peaks of **3a** and **4**, which were identified by comparing the retention times with those of the authentic compounds, appeared after a delay of *ca.* 10 min. When the photolysis of **1a** was stopped at the optimum point of conversion of **1a** to **2a**, the intermediate **2a** could be obtained by preparative HPLC of the reaction mixture and its structure was determined by ^{1}H-NMR and mass spectroscopy.[4] The apparent mass balance dipped and rose again in a manner completely consistent with the formation of the intermediate **2a**. It is well known that many photochemical reactions of sulfoxides proceed *via* an initial formation of sulfenic esters as intermediates.[5] Recently, several sulfenic esters were isolated after photolysis of acyclic[5c] and cyclic sulfoxides.[5b,6] The quantitative mass balance observed in the present photolysis was reproducibly achieved on extended photolysis. The quantum yields for the consumption of **1a** and the formation of **3a** and **4**, and the isomerization of **1a** to **1a'** under above photochemical conditions were measured by comparison with fulgide actinometry to be 0.34, 0.04, 0.04, and 0.05, respectively, being also indicative of the existence of an intermediate on photolysis of **1a** leading to **3a** and **4**.[7] Furthermore, the loss of **1a** was proportional to the first power of the intensity of 313 nm light and the formation of **3a** and **4** was proportional to the square of the light intensity as shown in Figure 3. These results imply that the consumption of **1a** proceeds by a one-photon process to give an intermediate **2a**, which seems to be formed by a stepwise or a concerted rearrangement in the primary photochemical step. Thereafter, the intermediate **2a** should be converted to the corresponding **3a** and **4** *via* the S•••S through-space interaction in the secondary photochemical step.

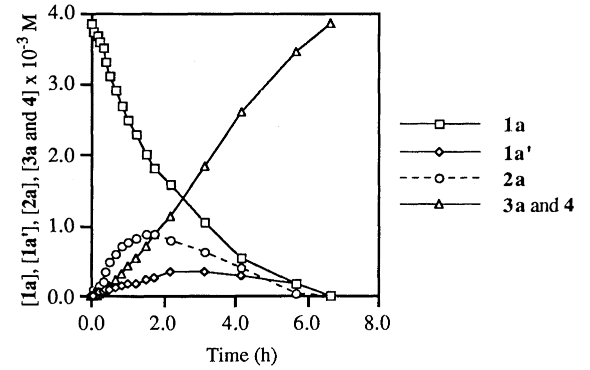


Figure 2. Time course of photolysis of **1a** (3.84×10^{-3} M **1a** in $CDCl_3$).

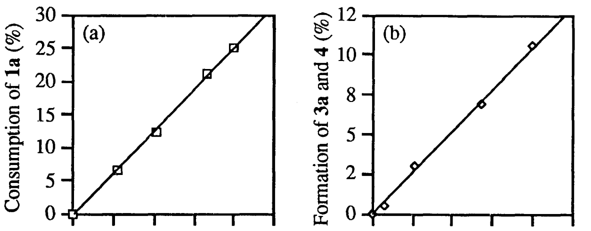


Figure 3. Light intensity dependence on the consumption of **1a** (a) and the formation of **3a** and **4** (b) (4.02×10^{-3} M **1a** in CH_2Cl_2).

The advantage of our present procedure is not only a promising method to regenerate aldehydes and ketones in high yields in neutral solvents but also is that it does not require the use of malodorous alkyl dithiols, toxic heavy metals or strong acids for deprotection.[8] Furthermore, compound **4** can be recovered completely and recycled to the starting materials after reduction and treatment with aldehydes.

We are grateful to Associate Professor Hirochika Sakuragi of University of Tsukuba for his constant advice and discussions during this work. This work was supported by a special grant from University of Tsukuba [TARA project] and a Grant-in-Aid from the Ministry of Education, Science, and Culture of Japan (No. 07404035).

References and Notes

1 a) H. Fujihara, J. -J. Chiu, and N. Furukawa, *Chem. Lett.*, **1990**, 2217; b) H. Fujihara, M. Yabe, J. -J. Chiu, and N. Furukawa, *Tetrahedron Lett.*, **32**, 4345 (1991); c) N. Furukawa, T. Kimura, Y. Horie, S. Ogawa, and H. Fujihara, *Tetrahedron Lett.* **33**, 1489 (1992).

2 a) H. Fujihara, M. Yabe, and N. Furukawa, *J. Org. Chem.*, **58**, 5291 (1993); b) N. Furukawa, T. Fujii, T. Kimura, and H. Fujihara, *Chem. Lett.*, **1994**, 1007; c) T. Fujii, T. Kimura, and N. Furukawa, *Tetrahedron Lett.*, **36**, 1075 (1995); d) T. Fujii, H. Sakuragi, and N. Furukawa, *Tetrahedron Lett.*, **36**, 8039 (1995); e) T. Kimura, Y. Ishikawa, K. Ueki, Y. Horie, and N. Furukawa, *J. Org. Chem.*, **59**, 7117 (1994).

3 Crystal data for **1a**: $C_{19}H_{12}O_1S_3$; monoclinic, $P2_1/c$, a=14.846(2) Å, b=5.105(1) Å, c=20.727(16) Å, β=95.21(2)°, V=1564.3 Å^3, z=4, Dx=1.50 g/cm^3, μ(Mo-Kα)=4.1 cm^{-1}, R=0.042 (R_w=0.041), unique reflections = 3117.

4 The intermediate **2a** is an unstable, acid-sensitive and oily material, and its photolysis provided the corresponding **3a** and **4**.
Compound **2a**: ^{1}H-NMR (270 MHz, $CDCl_3$, 55 °C) δ 6.38 (bs, 1H), 7.22-7.41 (m, 8H), 7.67 (d, J = 8.7 Hz, 1H), 7.69 (d, J = 8.7 Hz, 1H), 7.78 (d, J = 8.7 Hz, 1H); MS (m/z) 352 (M^+).

5 a) I. W. J. Still, in "The chemistry of sulphones and sulphoxides," ed by S. Patai, Z. Rappoport, and C. J. M. Stirling, John Wiley & Sons Ltd., Chichester (1988), p. 873 and references therin; b) A. G. Schultz and R. H. Schlessinger, *J. Chem. Soc., Chem. Commun.*, **1970**, 1294; c) Y. Guo and W. S. Jenks, *J. Org. Chem.*, **60**, 5480 (1995).

6 a) R. Kowalewski and P. Margaretha, *Helv. Chim. Acta*, **76**, 1251 (1993) b) N. K. Capps, G. M. Davies, P. B. Hitchcock, R. W. McCabe, and D. W. Young, *J. Chem. Soc., Chem. Commun.*, **1983**, 199.

7 The quantum yields for the consumption of **1a'** and the formation of **3a** and **4**, and isomerized **1a** were 0.39, 0.05, 0.05, and 0.06, respectively. The measurement of quantum yield was carried out using the output of a 500 W high pressure Hg lamp filtered through a Toshiba UVD33S filter and a monochromator set at 313 nm under conditions of complete light absorption. The fulgide, (*E*)-a-(2,5-dimethyl-3-furylethylidene)(isopropylidene)succinic anhydride, which has a quantum yield of 0.20 for its photocoloration at 313 nm in toluene was used as an actinometer. See, H. G. Heller and J. R. Langan, *J. Chem. Soc., Perkin Trans 2*, **1981**, 341.

8 a) B.-T. Grobel and D. Seebach, *Synthesis*, **1977**, 357; b) D. Seebach and E. J. Corey, *J. Org. Chem.*, **40**, 231 (1975) and references therin; c) K. Ogura, M. Yamashita, M. Suzuki, S. Furukawa, and G. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, **57**, 1637 (1984)