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Photodesulfurization of a Sulfoxide

Sir:

Photoracemization of sulfoxides,[1] dehydrative photorearrangements of thiachroman 1-oxides,[2] and photocleavage of an episulfoxide[3] have been reported. Photochemical loss of sulfur monoxide from a sulfoxide has not been described.[4] We felt it would be of interest to attempt this type of extrusion reaction by the sensitized photolysis of *cis*- and *trans*-1,3-dihydro-1,3-diphenyl-2-thiaphenalene 2-oxides (I).[5] On sensitized irradiation, sulfoxide I did not undergo loss of sulfur monoxide but rather suffered an unusual photodesulfurization reaction.

Purified benzene solutions (0.04 *M*) of either *cis*- or *trans*-I (E_T = 58.5 kcal/mol)[6] irradiated with 366-mμ light absorbed only by benzophenone (0.055 *M*) gave rise to 1-benzoyl-8-benzylnaphthalene (II, E_T = 58.2 kcal/mol),[6] mp 139°, as the sole reaction product (80% isolated yield).[7] The structure of II was confirmed by its oxidation to 1,8-dibenzoylnaphthalene (III).[8] No photoepimerization between the two isomers of I was observed during the course of reaction.[9]

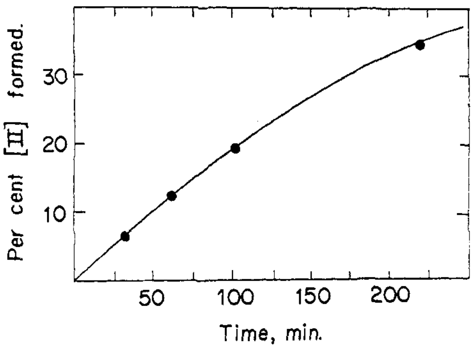
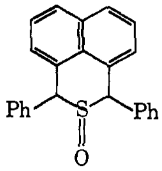


Figure 1. Plot of per cent [II] formed *vs.* time.

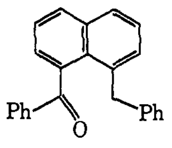
A water-cooled Hanovia Type L 450-W medium-pressure lamp fitted with Corning color filters O-52 and 7-54 was employed as the 366-mμ light source. The quantum yield for the benzophenone-sensitized decomposition of *cis*-I was found to be 0.23 while that of *trans*-I was 0.10.[10] All of the above reactions were run on a merry-go-round apparatus in sealed Pyrex tubes degassed by three freeze–thaw cycles at 10^{-5} torr. The actinometer used for these measurements was the benzophenone-sensitized isomerization of 0.10 *M* *trans*-stilbene ($\Phi = 0.43$).[11]

The decomposition of I seemed most likely to occur by initial carbon–sulfur bond rupture of the sulfoxide, giving rise to the diradical IV. We have been unable to obtain any evidence for the presence of long-lived intermediates derived from IV in this reaction. During the reaction, no significant coloration developed, and only the presence of sulfoxide, ketone, and sensitizer could be detected by careful spectroscopic and chromatographic (thin layer) examination. Furthermore, a zero-order plot of the formation of II against time using a constant intensity lamp gave a straight line, as shown in Figure 1. These results may be explained by: (1) a one-quantum process in which no long-lived intermediate is involved in the formation of ketone from IV; (2) a two-quantum mechanism which proceeds by way of a thermally stable intermediate which is photochemically transformed into ketone II. This transformation could be sensitized not only by benzophenone but also by the triplet states of sulfoxide I and ketone II, assuming the E_T value of the intermediate was <58 kcal/mol.[12]

Benzophenone-sensitized irradiation of *cis*-I in benzene solution also was carried out with various concentrations of either *cis*-piperylene or 1,3-cyclohexadiene present. These data show (Table I) that with the concentrations of piperylene or cyclohexadiene which were used the reaction does not proceed through a quenchable excited state of the sulfoxide (I*). Again,



I



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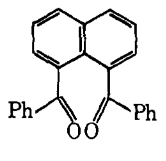

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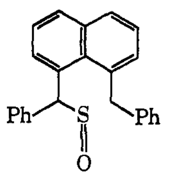

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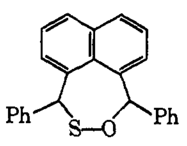

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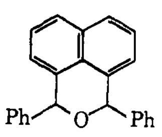

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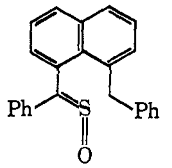

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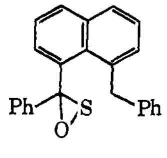

VIII

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(1) R. S. Cooke and G. S. Hammond, *J. Am. Chem. Soc.*, **90**, 2958 (1968), and references cited therein.

(2) R. A. Archer and B. S. Kitchell, *ibid.*, **88**, 3462 (1966).

(3) D. C. Dittmer, G. C. Levy, and G. E. Kuhlmann, *ibid.*, **89**, 2793 (1967).

(4) For the thermal extrusion of sulfur monoxide from a sulfoxide, see R. M. Dodson and R. F. Sauers, *Chem. Commun.*, 1189 (1967).

(5) R. H. Schlessinger and A. G. Schultz, *J. Am. Chem. Soc.*, **90**, 1676 (1968).

(6) We are deeply indebted to Dr. W. G. Herkstroeter for determination of the emission spectra.

(7) All melting points are uncorrected. Satisfactory analyses were obtained for all new compounds. Sulfoxide I has no absorption above 350 mμ. The same results were obtained for sulfoxide I when Michler's ketone was used as the sensitizer. Fluorenone did not sensitize the decomposition of sulfoxide I.

(8) W. Schlenk and J. Holtz, *Ber.*, 50, 268 (1917).

(9) The base-catalyzed epimerization of *cis*-I to *trans*-I has been reported; see ref 5.

(10) Analyses were carried out using nmr. Compound II showed sharp singlet resonance for the methylene protons at δ 4.17. The nmr spectra of *cis*- and *trans*-I are given in ref 5.

(11) G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964).

(12) For analogies to this mechanism, see Robert O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1968, pp 106–154, and references cited therein.

Table I

No.	[*cis*-I][a]	[Ph_2CO][a]	[Quencher][a] or [Q]	[Quencher]/ [*cis*-I]	Statistical[b] Φ/Φ_0	Obsd Φ/Φ_0	Φ/Φ_0(obsd)/ Φ/Φ_0(stat)
1	3.60	5.56					
2	3.80	5.48	3.18[c]	0.84	0.54	0.71	1.3
3	3.77	5.48	4.28[c]	1.14	0.47	0.68	1.4
4	3.66	5.48	8.34[c]	2.28	0.31	0.55	1.8
5	3.89	5.44	14.80[c]	3.81	0.21	0.37	1.8
6	3.56	5.65	2.04[d]	0.57	0.64	0.73	1.1
7	3.53	5.48	3.90[d]	1.11	0.48	0.54	1.1
8	3.46	5.63	7.70[d]	2.23	0.31	0.37	1.2

[a] Concentration $\times 10^{-2}$ *M*. [b] Φ/Φ_0 = [*cis*-I]/[*cis*-I] + [Q]). [c] *cis*-Piperylene. [d] 1,3-Cyclohexadiene.

ketone II was the sole product of reaction, and no evidence for an intermediate was observed. Thus, the two-quantum process (mechanism 2) would seem to be ruled out since the presence of a quencher should result in the increase of intermediate at the expense of product. Therefore the one-quantum mechanism shown below most adequately accounts for all of the above observations.

$$Ph_2CO + h\nu \longrightarrow Ph_2CO^{*3} \qquad (1)$$

$$Ph_2CO^{*3} + Q \longrightarrow Ph_2CO + Q^{*3}\ (Q = \text{quencher}) \qquad (2)$$

$$Ph_2CO^{*3} + I \longrightarrow I^* + Ph_2CO$$
$$(I^* = \text{excited nonquenchable state of I}) \qquad (3)$$

$$I^* + Q \not\longrightarrow \qquad (4)$$

$$I^* \longrightarrow I \qquad (5)$$

$$I^* \longrightarrow [IV] \longrightarrow II \qquad (6)$$

The absence of quenching (reaction 4) implies that the initially formed triplet state of I (E_T = 58.5 kcal/mol) undergoes rapid relaxation to a lower triplet state which cannot be effectively quenched by piperylene or cyclohexadiene. Relaxation of this type is known for the stilbenes.[11]

The detailed pathway by which ketone II is formed from the diradical IV has not been determined. However, it is felt that the reaction probably goes through a short-lived intermediate species. One possible intermediate of this type would be the heterocycle V. A reaction path involving V does not appear to be favorable since it could decompose in a dark reaction to both ketone II (hydrogen transfer followed by loss of sulfur) and oxide VI[13] (loss of sulfur). Oxide VI has been found to be completely inert to both sensitized and direct irradiation and can be readily detected in very small quantities. No oxide has been found in the photoreactions of I.

The sulfine VII could be an intermediate in the reaction of I also. Sulfines are known to thermally decompose to give olefins[14] and photochemically to undergo loss of sulfur to give carbonyl compounds.[15] Assuming its thermal behavior is similar to previously reported examples, VII would not appear to be an intermediate either.

We feel that the most viable intermediate in this reaction is the three-membered-ring heterocycle VIII which may be formed directly from the diradical IV. Loss of sulfur from VIII in a dark reaction would be expected to be facile even at room temperature.

Several other experiments including flash photolysis and direct irradiation of I are being carried out to test these hypotheses. In addition, the scope and utility of this reaction are being investigated with several other sulfoxides.

Acknowledgments. This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation and by the Petroleum Research Fund (Grant No. 756-G).

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(13) V. Boekelheide and G. Vick, *J. Am. Chem. Soc.*, **78**, 653 (1956).

(14) W. A. Sheppard and J. Diekmann, *ibid.*, **86**, 1891 (1964).

(15) J. Strating, L. Thijs, and B. Zwanenburg, *Rec. Trav. Chim.*, **83**, 631 (1964).

(16) Author to whom inquiries should be addressed.

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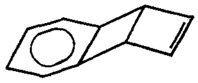
Strained Ring Systems. VII.[1] Benzobicyclo[2.2.0]hexa-2,5-diene (Hemi Dewar Naphthalene)

Sir:

Benzobicyclo[2.2.0]hexa-2,5-diene ("hemi Dewar naphthalene") (**1**) has been of interest to us in that it is a simple entry into a family of compounds which incorporate two of the classically proposed structures of benzene fused in a single molecule.[2] It is half-way to "Dewar naphthalene" (**2**), and offers a convenient route to the synthesis of substituted benzobicyclo[2.2.0]hex-2-enes (**3**) for other studies.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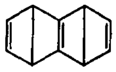
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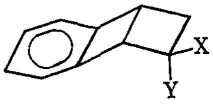

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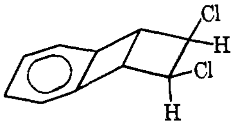

4

Our synthesis of **1** began with the reaction of benzyne and *cis*-3,4-dichlorocyclobutene.[3] The adduct **4**, mp 79–79.5° (sealed tube), is assigned the *cis-exo* structure on the basis of its nmr spectrum[4] which exhibits absorptions centered at τ 2.80 (aromatic, multiplet, J =

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(1) For paper VI in this series see R. N. McDonald and G. E. Davis, *Tetrahedron Letters*, 1449 (1968).

(2) D. E. Applequist and R. Searle, *J. Am. Chem. Soc.*, **86**, 1389 (1964), have reported the synthesis of a "Dewar anthracene." The preparation of "hemi Dewar biphenyl," a compound in which the moieties are joined but not fused, has been described by G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965).

(3) M. Avram, I. Dinulescu, M. Elian, M. Farcasiu, E. Marcia, G. Mateescu, and C. D. Nenitzescu, *Ber.*, **97**, 372 (1964).

(4) Carbon tetrachloride solution with internal TMS.