Photolysis of Benzylic Sulfur Compounds. The Formation of Phenanthrene from *cis*-Stilbene Sulfide

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One of the most extensively studied fields of photochemistry has been the photo-cyclization reaction of *cis*-stilbene(1) and related compounds(2) to give a phenanthrene structure by an irradiation reaction in the presence of a suitable oxidant, such as oxygen or iodine. The reaction mechanism, which assumes an intermediacy of 4a, 4b-dihydrophenanthrene (III) (or equivalent structures), requires the presence of an unsaturated linkage connecting the two aryl groups in a cis relationship. In attempting to determine the scope and limitation of this reaction, we wished to know the extent to which a modification in the olefinic bond is allowed and also the possibility of an alternative mechanism being operative. Thus we have examined the photochemistry of [2.2]metacyclophane(3) and *o*-terphenyl,(4) each a model compound of *cis*-stilbene whose olefinic moiety has been replaced by a single bond or incorporated in an aromatic ring system. By carrying out irradiation reactions in a cyclohexane or benzene solution in the presence of iodine, it has been shown that they afford 4, 5, 9, 10-tetrahydropyrene and triphenylene respectively in high yields. In contrast to the *cis*-stilbene-phenanthrene reaction, no cyclization could be attained, however, by irradiation reactions carried out in an oxygen atmosphere, indicating the importance of iodine. In view of the facile cleavage reaction of the carbon-sulfur bond in

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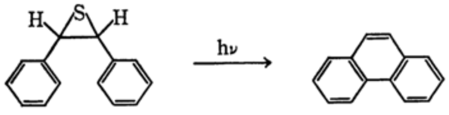
1) a) F. R. Stermitz in O. L. Chapman ed. "Organic Photochemistry," Vol 1, Mercel Dekker, Inc., New York (1967), p. 249. b) F. B. Mallory, C. S. Wood and J. T. Gordon, *J. Am. Chem. Soc.*, **86**, 3094 (1964) and papers citedtherein.

2) W. Carruthers and H. N. M. Stewart, *Tetrahedron Letters*, **1965**, 301; F. B. Mallory and C. S. Wood, *ibid.*, **1965**, 2643; G. Galiazzo, P. Bortolus and G. Cauzzo, *ibid.*, **1966**, 3717; R. E. Doolittle and C. K. Bradsher, *J. Org. Chem.*, **31**, 2616 (1966).

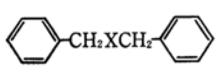
3) T. Sato, E. Yamada, T. Okamura, T. Amada and K. Hata, This Bulletin, **38**, 1049 (1965).

4) T. Sato, Y. Goto and K. Hata, *ibid.*, **40**, 1994 (1967).

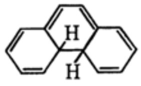
benzylic sulfur compounds during irradiation,[5–7] it occurred to us that further structural modification might be possible and that such compounds as I and II might become potential precursors to generate a phenanthrene structure.



I



IIa X = S
b X = SO
c X = SO₂



III

A cyclohexane solution of *cis*-stilbene sulfide (I), which had been prepared according to the method of Ketcham and Shah[8] and which contained a small amount of iodine, was irradiated in a quartz vessel with a high-pressure mercury arc lamp under a current of nitrogen. After a 20 hr irradiation, phenanthrene was isolated in a 60% yield. *trans*-Stilbene sulfide was not subjected to the photolysis studies since the compound was so unstable as to be decomposed into *trans*-stilbene and sulfur even when handled at room temperature. A recent paper[9] has described the photolysis of *trans*-dibenzoylstilbene sulfide, which afforded desulfurization products, *cis*- and *trans*-dibenzoylstilbenes, together with further transformation products. These facts suggested that the formation of phenanthrene from I proceeded through a desulfurization reaction to afford *cis*-stilbene, followed by cyclization *via* the well-established mechanism.[1b] In considering the oxidation step of the key intermediate III, it might be attractive to assume the participation of sulfur, which is eliminated during irradiation, as an oxidant. Although it has already been shown that elemental sulfur is not effective in bringing about an aryl coupling reaction in the case of *cis*-stilbene-phenanthrene,[1b] the atomic sulfur generated from I may be reactive enough to abstract the allylic hydrogens in III in the form of hydrogen sulfide. In accordance with this expectation, the irradiation reaction carried out using a degassed solution of I in cyclohexane in the absence of any added oxidant was also found to afford phenanthrene. The reaction was followed by UV spectra measurements, which indicated that those peaks ascribed to the phenanthrene structure begin to develop within 15 min.

As has already been reported from these laboratories,[5] the main products from the irradiation reaction of sulfoxide IIb for 14 hr were benzaldehyde (37%) and dibenzyl disulfide (14%). A further examination with gas chromatography revealed that small amounts of bibenzyl, *trans*-stilbene, and phenanthrene were also present, together with benzyl alcohol. Recent papers[6,7] have described the photolysis studies of sulfide IIa, which also produced the above mentioned three hydrocarbons, together with other materials. Phenanthrene and stilbene were considered to be formed *via* α-benzylthio- and α-benzylsulfinylbibenzyl respectively. On the other hand, the photolysis of sulfone IIc under similar conditions gave bibenzyl as one of the products, neither stilbene nor phenanthrene being formed. Thus the main reaction in this case may be the evolution of sulfur dioxide, followed by a recombination of benzyl radicals.

Experimental

Photolysis of *cis*-Stilbene Sulfide (I). Isomeric stilbene sulfides were obtained by the method of Ketcham and Shah[9] starting from the corresponding stilbene oxides. Of these, the *trans*-isomer (mp 41—45°C) tended to decompose even when handled at room temperature and so was not subjected to photochemical studies.

a) A solution of 215 mg (1.0 mmol) of I (mp 76.5—77°C) and 50.5 mg (0.2 mmol) of iodine in 60 m*l* of cyclohexane was irradiated in a quartz vessel with a Wako HBC-1000 high-pressure mercury arc lamp for 20 hr at 9°C. By column chromatography on alumina, using *n*-hexane as an eluent, 108 mg (60% yield) of phenanthrene (mp 97—100°C) were then isolated.

b) An evacuated solution of I in cyclohexane (5×10^{-4} M) under a vacuum of 10^{-4} mmHg was irradiated with the unfiltered light of Toshiba SHL-100 high-pressure mercury lamp at 30°C. The reaction was followed by UV spectra determination. The displacement of the λ_{max} value of I at 264 mμ by those bands ascribed to phenanthrene was seen to occur within 15 min. The photolysis was then continued for 3 more hr, until the characteristic bands of phenanthrene occurring at 250, 275, 283, 300, 337, and 347 mμ were clearly recognized.

Photolysis of Benzyl Sulfoxide (IIb). A solution of 1.0 g (4.4 mmol) of IIb in 50 m*l* of benzene was photolyzed in a quartz vessel with a HBC-1000 high-pressure mercury lamp for 14 to 40 hr. Benzaldehyde was determined by converting it to the 2, 4-dinitrophenylhydrazone; it was found to be formed in 37 and 19% yields after 14 and 40 hr respectively. The reaction mixture of the 14 hr irradiation was then analyzed by column chromatography on alumina; bibenzyl (1%), dibenzyl disulfide (14%), and benzyl alcohol (4%) were eluted successively. Gas chromatography using a Carbowax 1500-chromosorb W or 5% SE-30 column operated at 185 and 180°C demonstrated the presence of *trans*-stilbene and phenanthrene in small amounts (less than 1%).

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[5] T. Sato, E. Yamada, T. Akiyama, H. Inoue and K. Hata, *ibid.*, **38**, 1225 (1965).

[6] W. H. Laarhoven and Th. J. H. M. Cupper, *Tetrahedron Letters*, **1966**, 5003.

[7] W. Carruthers, *Nature*, **209**, 908 (1966).

[8] P. Ketcham and V. P. Shah, *J. Org. Chem.*, **28**, 229 (1963).

[9] A. Padwa, D. Crumrine and A. Shubber, *J. Am. Chem. Soc.*, **88**, 3064 (1966).