Photodesulphurization of Sulphoxides into Aldehydes

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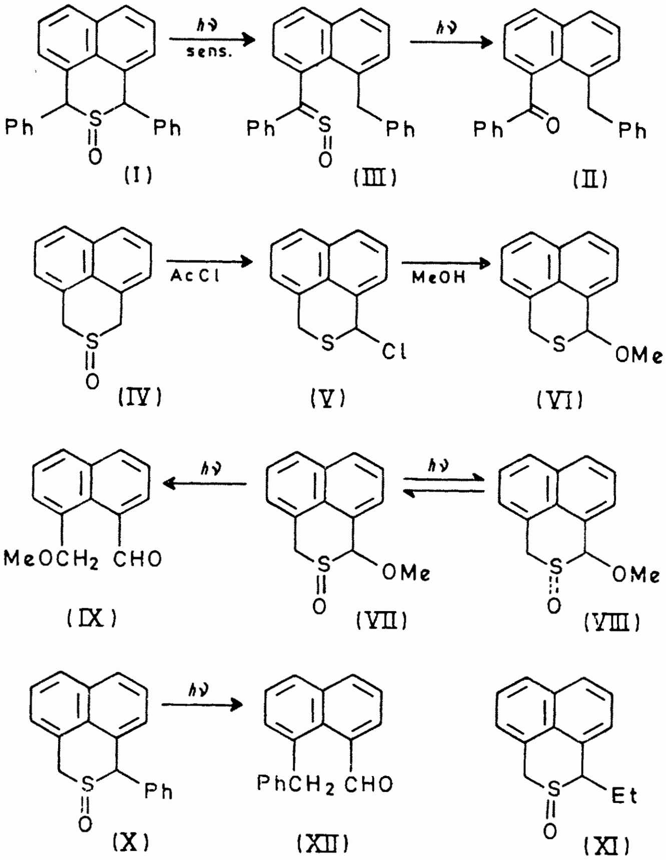
Summary A potentially useful synthetic photoconversion of sulphoxides into aldehydes is described.

RECENTLY, we found that sensitized irradiation of the sulphoxide (I) gives the ketone (II) by a unique photodesulphurization process.[1] This reaction proceeds from triplet-state sulphoxide to sulphine (III) which then undergoes singlet-state collapse into ketone (II) accompanied by loss of sulphur.[2] To explore the synthetic utility of this photodesulphurization reaction, we have examined the sensitized photolysis of other sulphoxides related to (I) in the hope that aldehydes would be obtained as the photoproducts.

Treatment of a methylene chloride solution of sulphoxide (IV)[3] with 1 equiv. of acetyl chloride gave the highly unstable α-chlorosulphide (V) in nearly quantitative yield.† Reaction of (V) with anhydrous methanol in methylene chloride solution afforded, in 85% overall yield from the sulphoxide (IV) a single crystalline substance identified as the α-methoxy-sulphide (VI), m.p. 94°.

Controlled oxidation of (VI) with *m*-chloroperbenzoic acid afforded in 95% yield the α-methoxy-sulphoxides (VII), m.p. 220°, and (VIII), m.p. 95°. Peroxy-acid oxidation of (VII) and (VIII) gave a single crystalline α-methoxy-sulphone in 90% yield. The n.m.r. spectrum of this sulphone closely resembles those of sulphide (VI) and sulphoxide (VII). These results show that (VII) and (VIII) are pyramidal isomers which differ only in the configuration of the sulphoxide group.

Two different and easily distinguished photochemical reactions have been observed for (VII) and (VIII). Benzophenone-sensitized irradiation (366 nm) of either sulphoxide in degassed chloroform solution gave rise to a photostationary state of both pyramidal isomers.‡ The quantum yields for interconversion of (VII) and (VIII) were 0·70 and 0·35, respectively.§ Prolonged sensitized irradiation led to nearly complete photodesulphurization of (VII) and (VIII) accompanied by the formation of a single liquid photoproduct, the aldehyde (IX), isolated as its semicarbazone, m.p. 195°, in 80% yield. A quantum yield of 0·04 was found for the formation of (IX) from (VII) and (VIII).¶



(I) (III) (II)

(IV) (V) (VI)

(IX) (VII) (VIII)

(X) (XII) (XI)

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† Satisfactory analyses have been obtained for all new compounds except sulphide V, and spectral data are in accord with the structures assigned.

‡ The ratio of (VII) and (VIII) at the photostationary state was 1 : 2·1.

§ For a description of the light source, actinometer, degassing procedure, and method of analysis, see ref. 1.

¶ The value 0·04 represents an overall quantum yield for the decomposition of sulphoxides (VII) and (VIII) into aldehyde (IX).

The sum of the quantum yields for pyramidal inversion (1·05) and photodesulphurization (0·04) is essentially unity (1·09). Thus, sulphoxide pyramidal inversion is a significant energy-wasting step in the formation of aldehyde (IX) from sulphoxides (VII) and (VIII).

Sulphoxides (X) and (XI) also give similar photochemical results. These compounds are readily prepared in high overall yield (70—80%) from (V) by treatment of the chlorosulphide with either phenylmagnesium bromide or ethylmagnesium bromide followed by oxidation of the resulting phenyl and ethyl sulphides with *m*-chloroperbenzoid acid.[4] Sensitized irradiation of sulphoxide (X) gives aldehyde (XII) in 80% yield, m.p. 180°, semicarbazone. Sulphoxide (XI) also gives a single liquid aldehyde on sensitized photolysis.

These results suggest that the photodesulphurization reactions described here could prove to be an interesting and efficient means of obtaining unsymmetrically substituted naphthalene derivatives.

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[1] A. G. Schultz, C. D. DeBoer, and R. H. Schlessinger, *J. Amer. Chem. Soc.*, 1968, **90**, 5314.

[2] A. G. Schultz and R. H. Schlessinger, *Chem. Comm.*, 1969, 1483.

[3] Sulphoxide (IV) is readily prepared in three steps from the anhydride of naphthalene-1,8-dicarboxylic acid. R. H. Schlessinger and I. S. Ponticello, *J. Amer. Chem. Soc.*, 1967, **89**, 3641.

[4] For examples of the conversion of α-chloro-sulphides into α-alkyl and aryl sulphides, see I. I. Lapkin and R. G. Mukhina, *Zhur. org. Khim.*, 1966, **2**, 385.