Tetrahedron Letters No. 27, pp. 2523-2526, 1971. Pergamon Press. Printed in Great Britain.

PHOTOCHEMISTRY OF β-KETOSULFOXIDES

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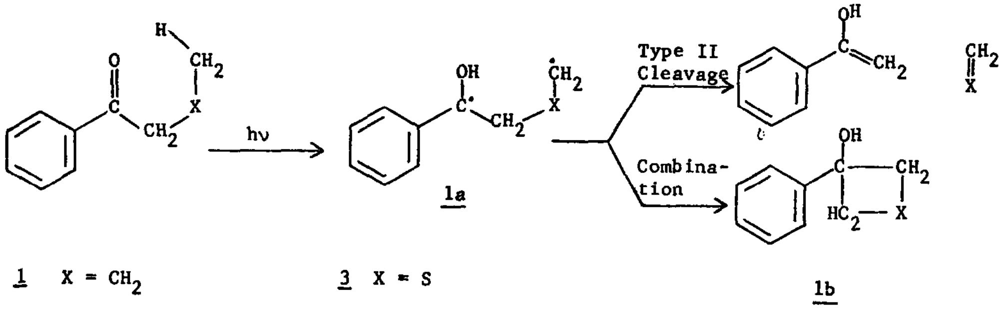
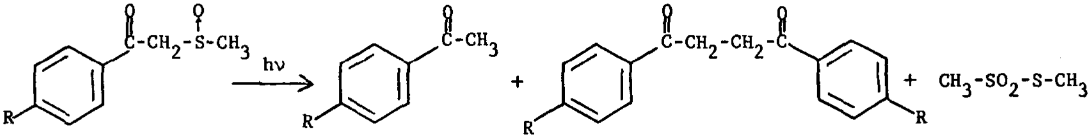
(Received in USA 27 April 1971; received in UK for publication 8 June 1971)

Photochemical behavior of carbonyl compounds containing γ-hydrogens (1) has been well documented.[1,2] The primary process, in the absence of electronic factors, involves abstraction of a γ-hydrogen atom producing a diradical intermediate (1a), which either undergoes cleavage (Type II cleavage) and/or radical combination to a cyclobutanol derivative.[3] Similar processes have recently been shown to take place in the case of ω-ethoxyacetophenone[4] (2) and ω-ethylthioacetophenone[5,6] (3). Contrary to this general behavior, β-sulfonylacetophenones[7] (4) have been found to be inert to γ-hydrogen abstraction. In this report we wish to present some preliminary observations on the photochemistry of ω-sulfinylacetophenones (5).



1 X = CH_2
2 X = O
3 X = S
4 X = SO_2
5 X = S→O

ω-Methylsulfinylacetophenones were prepared by the addition of DMSO anion to the corresponding benzoic acid ester in THF according to the procedure reported by Corey and Chaykovsky.[8] A dilute solution of ω-methylsulfinylacetophenone (5) in dry benzene was irridiated under argon gas with a 450 w Hanovia medium pressure Hg lamp using a Pyrex filter. The progress of the reaction was followed by analyzing ailquots of the reaction mixture by TLC. The loss of the starting material was accompanied by the appearance of three products which were identified as acetophenone (6), 1,2-dibenzoylethane (7) and methyl methanethiolsulfonate (8). Compound (8) possessed two singlets of equal intensity in its nmr spectrum at 3.3 and 2.7 δ. The infrared spectrum of this material showed characteristic bands for a sulfone at 1320 and 1140 cm^{-1}. The mass spectrum revealed a molecular weight of 126. Finally, the structure of this compound was confirmed by comparison of its spectral properties with those of an authentic sample prepared by esterification of methanesulfonylchloride with methanethiol in pyridine. The other two products, (6) and (7), were identified by comparison of their physical and spectral properties with authentic samples. Irradiation of ω-methylsulfinyl-p-methylacetophenone (9) gave rise to similar products (10, 11 and 8).

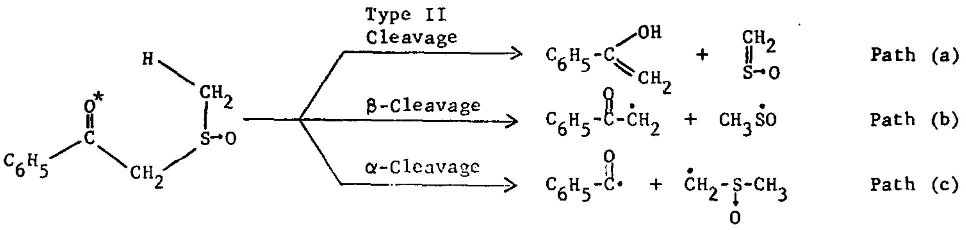


5 R = H 6 R = H 7 R = H 8

9 R = CH_3 10 R = CH_3 11 R = CH_3

The possible similarity of this photodecomposition reaction to that of butyrophenone requires comments on the mechanism of this cleavage reaction. The three possible decomposition pathways available for an excited β-sulfinyl ketone are represented in Scheme I.

Scheme I



The first pathway (a) involves γ-hydrogen abstraction followed by cleavage to give the enol form of acetophenone and a sulfine.[9] Simple sulfines have been reported to be unstable[10] so no attempts were made to isolate it. The second pathway (b) involves the cleavage of β-carbon-sulfur bond to give benzoylmethyl and methylsulfinyl radicals. The benzoylmethyl radical could either undergo H-abstraction to give acetophenone and/or dimerization to give 1,2-dibenzoylethane. Since the latter product has been isolated in the photolysis reaction, the β-cleavage process seems to be important. Methylsulfinyl radicals produced by this cleavage could undergo dimerization to an unstable S,S'-dioxide which would rapidly disproportionate to the corresponding thiolsulfonate. Barnard and Percy[11] have explained the formation of thiolsulfonates from the oxidation of a monooxide of an alkyl or aryl disulfide (RSOS R') on the basis of rearrangement of the sulfinyl radicals produced by S-S fission (cf. Ref. 12). The third pathway (c) involves α-cleavage to produce benzoyl and methylsulfinylmethyl radicals. Since products derived from this cleavage have not been obtained, this process will be considered unimportant. Thus, there exist two possible mechanisms (paths a and b) for the formation of acetophenone. Since benzene is a poor hydrogen atom donor, it is not likely that H-abstraction by benzoylmethyl radical from this solvent has occurred. This lends support to the Type II elimination mechanism.[13]

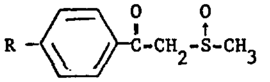
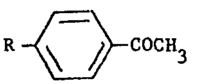
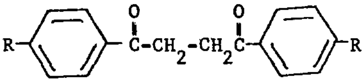
Since increase in solvent polarity has been shown to enhance the quantum efficiency of Type II elimination of butyrophenones,[2] an attempt was made to study the effect of solvent polarity on the formation of acetophenone, and the results are shown in Table I.

From the data, it can be seen that polar solvents favor the β-cleavage process which results in the formation of large amounts of diaroylethane. 2-Propanol, being an excellent hydrogen atom donor, facilitates the formation of aryl methyl ketone (H-abstraction by carbonyl oxygen either before or after β-cleavage would give the same result). By analogy with butyrophenone and other carbonyl compounds, perhaps the reactive excited state here is the n,π* triplet of the carbonyl group. If this were the case, hydrogen abstraction from reactive solvents, methanol and acetonitrile, would be expected to be competitive to γ-hydrogen abstraction and β-cleavage, and to increase acetophenone yields. The very fact that these two solvents lower the yields of aryl methyl ketones suggests interaction of the solvent with ground or excited state β-sulfinyl ketone; and furthermore, such interaction seems to facilitate β-cleavage.

Thus, it seems apparent that β-ketosulfoxides (5 and 9) upon photolysis primarily undergo β-cleavage in methanol or acetonitrile as evidenced by the isolation of diaroylethanes and methyl methanethiolsulfonate. The results in benzene suggest the Type II elimination mechanism as the major pathway.

Detailed studies concerning the nature of the excited state and the mechanism of the cleavage process are in progress.

Table 1. Relative Yields[a] of Products Formed in the Photolysis[b] of β-Sulfinyl Ketones[c]

	Solvent		
R = H	Benzene	67.5	32.5
R = H	Methanol	28	72
R = H	CH_3CN	36	64
R = H	2-Propanol	78	22
R = CH_3	Benzene	68.5	31.5
R = CH_3	Methanol	34	66
R = CH_3	2-Propanol	84	16

a. Calculated from glpc and nmr analyses and confirmed by isolation of the diaroylethane.

b. The photolyses were carried out for 1 hr by which time all the starting material disappeared.

c. In each case (except in 2-propanol) methyl methanethiolsulfonate (8) was formed in 25-30% yield relative to the other products. Low yields of 8 are due to its instability under the irradiation conditions. In fact, prolonged photolysis leads to complete disappearance of this product. Together the three products accounted for over 80% of the total mixture.

Acknowledgment. Technical assistance provided by Mr. James R. Westrich is gratefully acknowledged.

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9. Possible intermediacy of the thietaneoxide derivative (1b, X = $S\rightarrow O$) in the formation of acetophenone has been excluded by studying the photochemical behavior of the α-methyl derivative of (5). Full details will be furnished in a forthcoming paper.
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13. However, the possibility that hydrogen atom transfer from methylsulfinyl radical to benzoyl methyl radical immediately after their formation to produce acetophenone is a moot point; see Reference 6.