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PHOTOLYTIC REARRANGEMENT OF CARBONYL-STABILIZED SULFONIUM YLIDES

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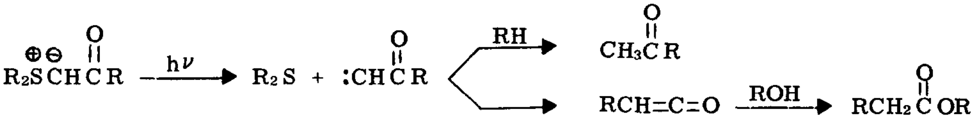
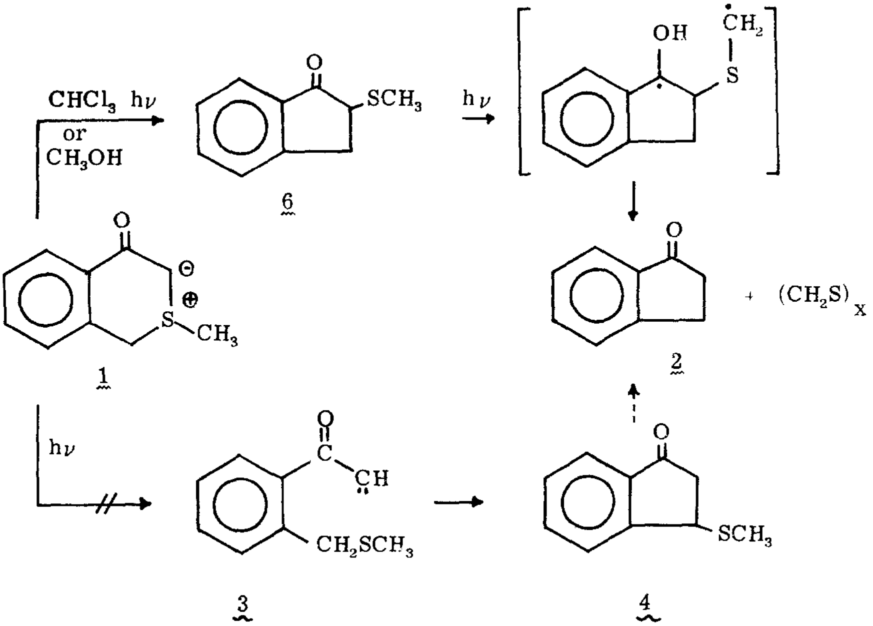
One of the many interesting properties of β-ketosulfonium ylides is their susceptibility to photochemical cleavage of the dipolar sulfur-carbon bond to give products derived from ketocarbene and ketene intermediates (1, 2). These products are reported to include methyl ketones formed from ketocarbenes by abstraction of hydrogen from the solvent (2), and esters formed (in alcohol solvents) by rearrangement of ketocarbenes to ketenes with subsequent addition of the solvent (1, 2).



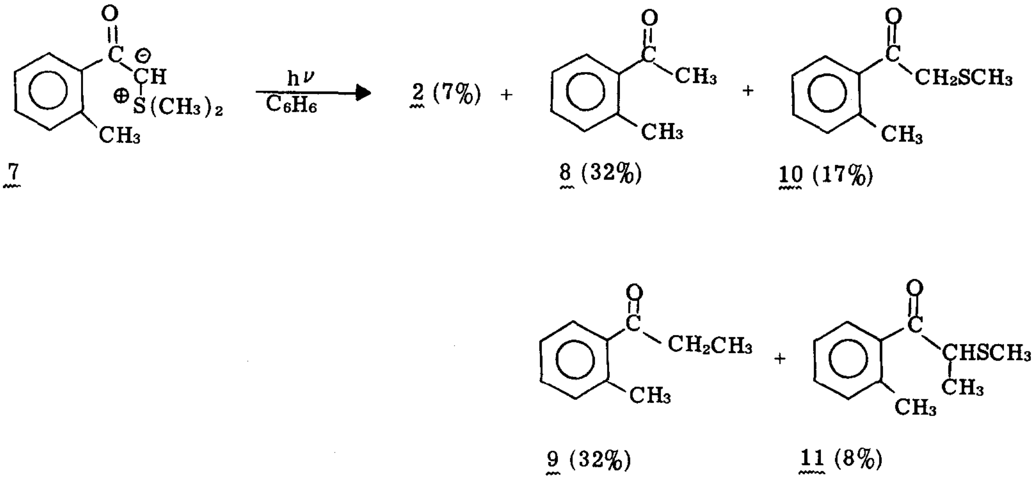
$$R_2\overset{\oplus}{S}\overset{\ominus}{C}H\overset{\overset{O}{\|}}{C}R \xrightarrow{h\nu} R_2S + :CH\overset{\overset{O}{\|}}{C}R \begin{cases} \xrightarrow{RH} CH_3\overset{\overset{O}{\|}}{C}R \\ \longrightarrow RCH{=}C{=}O \xrightarrow{ROH} RCH_2\overset{\overset{O}{\|}}{C}OR \end{cases} \qquad (1)$$

We have recently investigated the photolysis of 2-methylisothiochroman-4-one-3-ylide, 1, in both chloroform and anhydrous methanol (3), and were surprised to obtain 1-indanone 2 as the *only* volatile product (45%). No methyl ester or methyl ketone anticipated from cleavage of the type shown in equation 1 was obtained. Absence of these products does not preclude cleavage of the dipolar C–S bond of 1 since the intermediate ketocarbene 3 could insert into the benzylic C–H to give 3-thiomethyl-1-indanone 4 which might decompose photolytically to 2. We reject this possibility, however, on the basis that the suggested photolysis of γ-keto sulfides is without precedent (4) and that photolysis of 1, dideuterated at the benzylic position, gave 1-indanone-3-d_2.



We suggest, therefore, that photolysis of **1** results in cleavage of the *benzylic* C–S bond with formation of 2-thiomethylindanone **6** which photolyzes to **2** under the reaction conditions (5). There is ample precedent for the photoelimination of β-keto sulfides to give ketones (6, 7, 8), and we have independently verified that **6** does indeed photolyze to give **2**. Thus, **6** was prepared from 2-bromoindanone and sodium methiolate, and it was found to photolyze rapidly in chloroform to give a quantitative yield of **2** (3). Although we have no supporting evidence, we suggest that the conversion of **6** to **2** involves a Type II photoelimination (9). The sulfur is probably eliminated as thioformaldehyde which is known to polymerize readily--hence no attempt was made to isolate it.

The photolysis of the acyclic analog of **1** , namely **7**, was also investigated (3). In chloroform, *o*-methylacetophenone **8** was the only volatile product obtained. In benzene, however, *nine* products were detected by glpc, and the five major ones (90% overall) were collected preparatively and identified as **8**, **9**, **2**, **10** and **11**.



7

8 (32%)

10 (17%)

9 (32%)

11 (8%)

Products 9 and 11 very probably arise by photoinduced rearrangement and elimination reactions analogous to the transformations 1 → 6 → 2. Formation of 8 and 10 is less easily explained. The precursor to 8 could be the ketocarbene or the β-keto sulfide 10. The latter alternative is preferred since the likelihood of efficient hydrogen abstraction from benzene by a ketocarbene seems small. Indanone is probably the only product that may reasonably be derived from the ketocarbene in benzene. Just how 10 is formed and what relationship, if any, it has to the photoinduced rearrangement of 7 to 11 is not known. This and the deeper question of the nature of the photoinduced rearrangement of sulfur ylides (10) is under investigation. The thermal equivalent of the photochemical reaction is the Stevens rearrangement (11), but the mechanisms of the two processes may be unrelated.

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References

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(2) B. M. Trost, ibid., **88**, 1587 (1966); **89**, 138 (1967).

(3) A 200 watt Hanovia lamp type S was used with a pyrex filter.

(4) The photolytic behavior of several γ-keto sulfides is described by P. Y. Johnson and G. A. Berchtold, J. Am. Chem. Soc., **89**, 2761 (1967).

(5) To our knowledge, a similar photochemical rearrangement and elimination sequence was first proposed by Trost (2) to explain minor amounts of propiophenone formed in the photolysis of dimethylphenacylsulfonium ylide.

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(8) J. R. Collier and J. Hill, Chem Commun., 700 (1968).

(9) J. G. Calvert and J. N. Pitts, "Photochemistry," Wiley, New York, N. Y., 1966, pp 382-385.

(10) Photochemical rearrangement of a nitrogen ylide has been reported by P. de Mayo and J. J. Ryan, Tetrahedron Letters, 827 (1967). Photolysis of oxythiobenzoyl chloride to benzoyl chloride [J. F. King and T. Durst, J. Am. Chem. Soc., **85**, 2676 (1963)] may be classified as a photolylic rearrangement of a sulfur ylide.

(11) See for example K. W. Ratts and A. N. Yao, J. Org. Chem., **33**, 70 (1968), and references to the Stevens rearrangement cited therein.