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PHOTOCHEMICAL REARRANGEMENTS OF SUBSTITUTED THIOCHROMANONE SULFOXIDES

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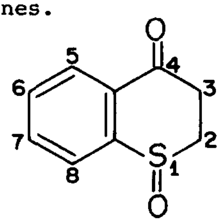
There have been a number of recent reports dealing with photochemical investigations of cyclic keto sulfides (1-4). Much of the interest in these systems stems from the likelihood of charge-transfer excited state interaction between the sulfur-atom and the carbonyl group (5). Relatively few reports have appeared concerning the photochemical reactions of sulfoxides (6,7), but the recent work of Morin and Spry on the non-photochemical rearrangements of benzothiazine sulfoxides (8) prompts us to report our own photochemical investigation of some keto sulfoxides related to thiochroman-4-one 1-oxide, 1. A number of interesting transformations were discovered when a series of 2- and 3-substituted thiochromanone sulfoxides were subjected to irradiation. Indeed, the relative profusion of reactions which we now present contrasts sharply with an earlier investigation of a series of related sulfones (9), where only bimolecular (pinacol) reduction was observed. The contrast between the two series may be attributable to the operation of charge-transfer effects in the sulfoxide series (10). There is no very marked difference between the ultraviolet absorption spectra of the respective sulfoxides and sulfones.



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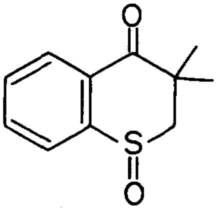

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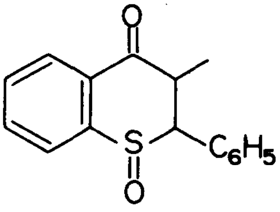

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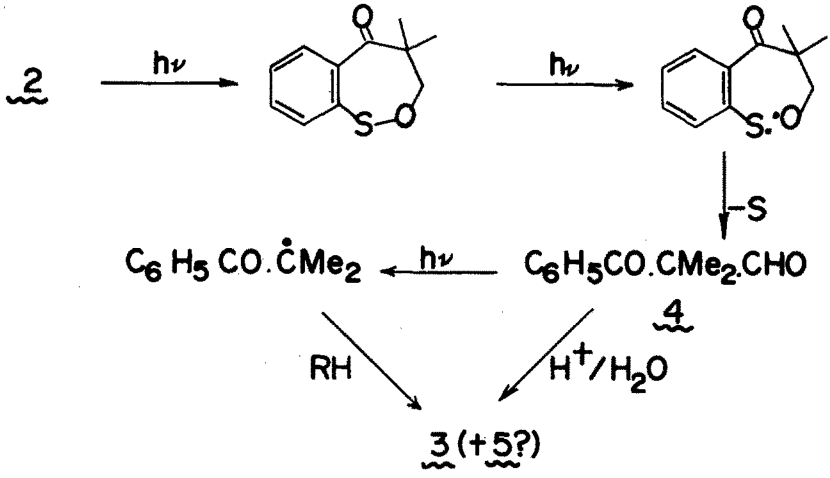
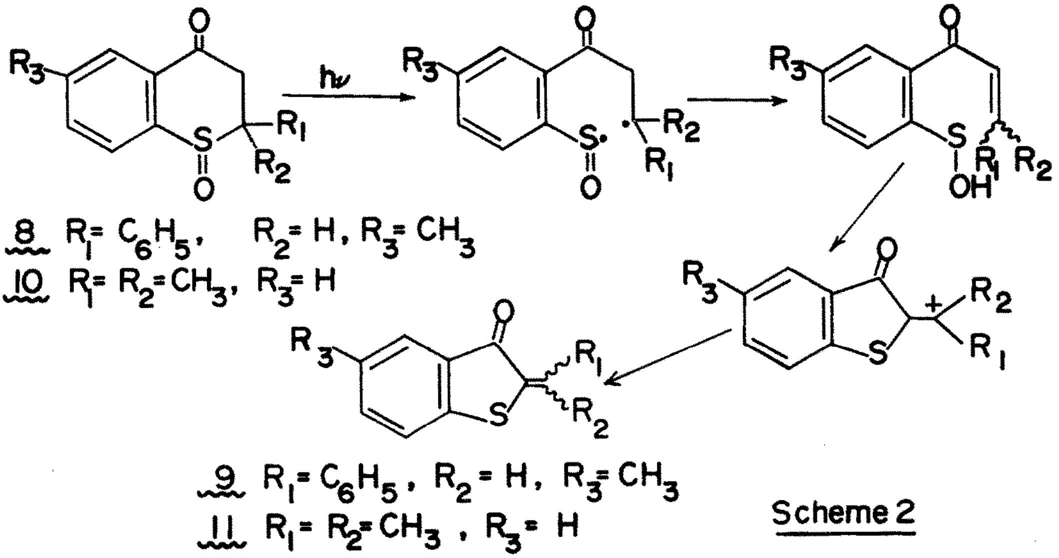
Irradiation of 3,3-dimethylthiochroman-4-one 1-oxide 2 in benzene solution, using a Hanovia 115W medium pressure mercury arc with a Vycor filter, led to a mixture (∿50%) containing three products, accompanied by some polymerization. These products (11) were shown to be isobutyrophenone 3 (7%), 2-benzoylisobutyraldehyde 4 (31%), and benzoic acid 5 (12%). A possible mechanistic route to these products is proposed in Scheme 1. The mass spectral rearrangement of aromatic sulfoxides to sulfenates has been reported (12) and the conversion of 4 to 3 finds some analogy in the work of Anderson and Reese (13) on the photochemistry of phenacyl halides. Further support for the intermediacy of 4 as a primary photoproduct is indicated by our preliminary results on the irradiation of authentic 4, prepared from isobutyraldehyde (morpholino) enamine and benzoyl chloride. Under irradiation conditions identical to these used in the irradiation of 2, we found that 4 could rapidly be converted to isobutyrophenone (40%) and benzoic acid (20%), the remainder being polymeric. Similar results were obtained when we irradiated 3-methylthiochroman-4-one 1-oxide 6 and 3,6-dimethylthiochroman-4-one 1-oxide 7. The formation of m-tolyl ethyl ketone from 7 in very similar yield to the isobutyrophenone obtained from 2 demonstrates that the aromatic rings present in products of type 3 - 5 are not derived by incorporation of solvent benzene.

Scheme 1



The 2-substituted thiochromanone sulfoxides 8 and 10 gave as the sole identifiable products (in each case accompanied by extensive polymerization) the ring-contracted thiaindanones 9 (3%) and 11 (13%) respectively. Other authors (6,15) have previously reported the non-photochemical, acetic anhydride catalyzed conversion of 10 to 11. 2-Methylthiochroman-4-one 1-oxide gave only polymeric material in contrast to the 3-methyl analogue 2.

Among the other related compounds which we have investigated 3-methyl-2-phenylthiochroman-4-one 1-oxide 12 was the only one bearing substituents at both the 2- and 3-positions. One might reasonably conclude that an unsubstituted 3-position is necessary to obtain products of the thiaindanone type because in contrast to 8 no ring-contraction was observed and the β-diketone 1,1-dibenzoylethane 13 was isolated as the sole product in 35% yield. Other sulfoxides which we have irradiated under similar conditions include the parent compound 1, isothiochroman-4-one 2-oxide, and 5-methylthiochroman-4-one 1-oxide. In the first two instances extensive polymerization occurred, while in the latter case we obtained almost complete recovery of starting material. This latter result we attribute to photoenolization which has been reported previously for o-methyl substituted aryl ketones (14).



8 $R_1 = C_6H_5$, $R_2 = H$, $R_3 = CH_3$
10 $R_1 = R_2 = CH_3$, $R_3 = H$

9 $R_1 = C_6H_5$, $R_2 = H$, $R_3 = CH_3$
11 $R_1 = R_2 = CH_3$, $R_3 = H$

Scheme 2

The mechanistic pathways tentatively suggested (Schemes 1, 2) are an attempt to account for the observed dichotomy between the two series. Initial α-cleavage of the sulfoxide and formation of an intermediate sulfenic acid

(15) can lead to products of type 9 and 11 only if the 3-position in the original sulfoxide is unsubstituted. On the other hand, if the 3-position is originally disubstituted, as in 2, ring-expansion via the sulfenate ester (Scheme 1) appears to be predominant. Both mechanisms could account for the substantial degree of polymerization observed in all cases, although we have as yet no direct evidence for the intermediates postulated in Scheme 2. Further work on the elucidation of the mechanisms involved in these reactions is continuing.

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