

PHOTOCHEMICAL REARRANGEMENT OF 8-METHYLTHIOCHROMAN-4-ONE 1-OXIDE:

EVIDENCE FOR THE EXISTENCE OF SULFENATE INTERMEDIATES IN SULFOXIDE PHOTOLYSES

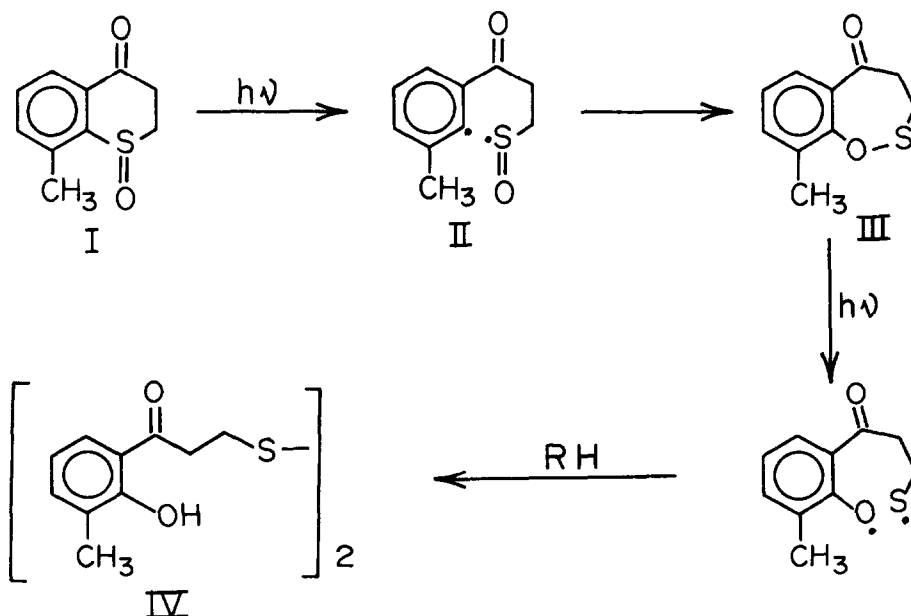
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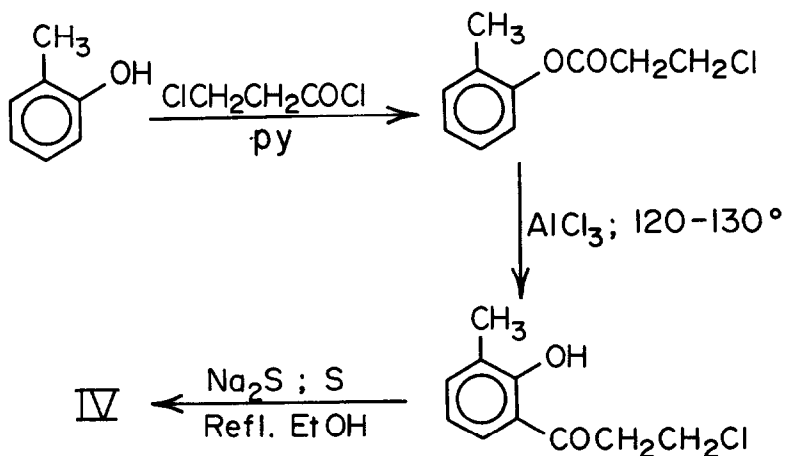
The photochemical behavior of compounds containing the sulfoxide chromophore has attracted increased attention in recent years.¹⁻⁵ Among the interesting photochemical reactions observed for the sulfoxide group was the reported conversion of a cyclic sulfoxide to a ring expanded cyclic sulfenate.⁶ Earlier reports described the photochemical conversion of di-*n*-butyl and dibenzyl sulfoxides into the corresponding disulfides^{7,8} and Block⁹ later proposed a sulfenate rearrangement pathway to explain the former rearrangement. We have now observed an apparently analogous rearrangement of certain cyclic sulfoxides in the thiochroman-4-one series in which an unusual aryl C-S bond cleavage appears to be involved. Indeed, the results now described for 8-methylthiochroman-4-one 1-oxide (I) and other aryl substituted thiochromanone sulfoxides show a remarkably different pattern of photochemical behavior from those we had described earlier for the 2- and 3-substituted sulfoxides in the same series.¹⁰

Scheme 1



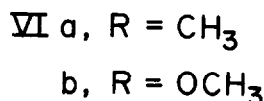
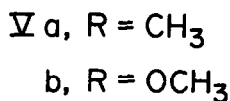
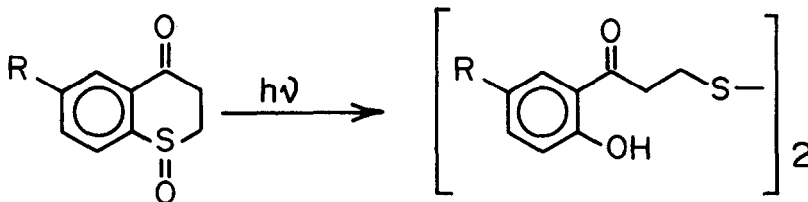
Ultraviolet irradiation¹¹ of a 1% solution of (I) in benzene for 24 hours, followed by chromatography on silica gel, afforded a single crystalline product, m.p. 133-134°, in 10% yield.¹² Starting material (40%) and uncharacterizable products accounted for the balance of the material. The product showed broad hydroxyl absorption in the i.r. and a carbonyl band at 1634 cm^{-1} and n.m.r. signals at δ 2.23 (s, 6H), 3.21 (m (A_2B_2), 8H), 6.79 (t, $J = 8\text{ Hz}$, 2H), 7.34 (br d, $J = 8\text{ Hz}$, 2H), 7.62 (br d, $J = 8\text{ Hz}$, 2H) 12.46 (br s, 2H) p.p.m. The carbonyl band position is at considerably lower frequency than that of the starting material and very close to that for *o*-hydroxyacetophenone. Further evidence for the presence of a phenolic hydroxyl group was given by the solubility of the product in alkali and the characteristic bathochromic shift of the u.v. spectrum in alkali. A possible isomeric peroxide structure could be ruled out on the basis of both the mass spectrum and the starch-iodide test, which was negative even after prolonged exposure to strong acid.¹³ This evidence has led us to assign the disulfide structure (IV) to the photo-product, and this assignment has been confirmed by an unambiguous synthesis (Scheme 2) from *o*-cresol.

Scheme 2



The novel photochemical reaction observed for 8-methylthiochroman-4-one 1-oxide might be due to the steric or electronic influence of the 8-methyl group or even some special effect, such as photoenolization at the sulfoxide chromophore, in the manner of *o*-methylacetophenone derivatives. It had earlier been noted¹⁴ that the mass spectrum of (I) differs in significant aspects from those

of the parent, unsubstituted sulfoxide and its 2- and 3-methyl analogues. Photolysis of the 6-methyl- and 6-methoxythiochroman-4-one 1-oxides (V a,b) has been found to lead, under similar conditions, to the analogous disulfides (VI a,b) in yields of 4% and 5% respectively. Irradiation of 8-methoxycarbonylthiochroman-4-one 1-oxide, however, gave none of the corresponding disulfide product.



The evidence obtained from the foregoing experiments appears to indicate that the electronic influence of the aromatic ring substituents is predominant. Accordingly, we propose the mechanistic pathway outlined in Scheme 1, involving initial excitation and C-S bond cleavage to the aryl sulfinyl biradical (II), which presumably is stabilized by the presence of an electron-releasing substituent at the 8-, or the 6-, position. Reclosure to the cyclic sulfenate (III), O-S bond cleavage and subsequent dimerization and hydrogen abstraction would account for the formation of (IV). If the alternative C-S bond cleavage, leading to a biradical isomeric with (II), does occur it may well only lead to intractable polymeric product, similar to that arising as the sole photochemical product from thiochroman-4-one 1-oxide itself.¹⁵ Further work on the detailed mechanism of this and related rearrangements is currently in progress.

Acknowledgment

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References

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12. Satisfactory analytical and mass spectral data were obtained for all new compounds.
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