Photochemical rearrangements of substituted thiochromanone sulfoxides[1]

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The photochemical behavior of a number of substituted derivatives of thiochroman-4-one 1-oxide has been examined. In contrast to the analogous sulfones these sulfoxides undergo a variety of photochemical rearrangements. At least three distinct pathways have been recognized; β-hydrogen abstraction or rearrangement to cyclic sulfenates, which then undergo further reaction by homolysis of the S—O bond, appearing to be particularly favorable processes. In a small number of examples, photochemical deoxygenation is observed as a competing reaction. Mechanisms which attempt to account for the influence of structural variations on the particular pathway followed have been proposed.

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On a examiné le comportement photochimique d'un certain nombre de dérivés de la thiochromanone-4 oxyde-1 substituée. Par opposition avec les sulfones correspondantes, ces sulfoxydes subissent une variété de réarrangements photochimiques. On a reconnu, au moins trois chemins distincts; les processus qui semblent particulièrement favorables sont l'enlèvement d'un hydrogène-β ou le réarrangement en sulfénates cycliques qui subissent une réaction ultérieure par homolyse du lien S—O. Dans un petit nombre d'exemples on observe une désoxygénation photochimique comme réaction compétitive. On propose des mécanismes qui tentent d'expliquer l'influence des variations structurales sur les chemins particuliers suivis au cours des réactions.

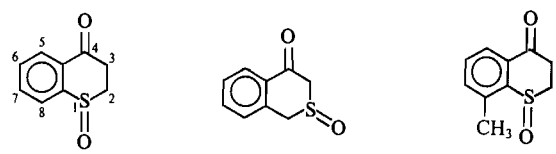
[Traduit par le journal]

Introduction

Interest in the photochemistry of cyclic sulfoxides has increased dramatically since the work of Archer and Kitchell (1) on the rearrangement of 2,2-dimethylthiochroman 1-oxide appeared in 1966. Schultz and Schlessinger (2, 3), Lawesson and co-workers (4), and Ganter and Moser (5) have been among the workers active in this area, while the topic has been reviewed by Block (6). We wish now to report our own results, obtained upon irradiation of a series of thiochromanone sulfoxides, which have been the subject of earlier communications (7, 8). Evidence will be presented in support of three distinct types of rearrangement pathway, in each of which the sulfoxide group appears to undergo a formal α-cleavage reaction. The dependence of the particular pathway followed upon the (alkyl) substitution pattern and the possible reasons for this dependence will also be presented.

Results and Discussion

After some initial difficulties had been overcome a satisfactory general procedure for synthesizing sulfoxides in the thiochroman-4-one, **1**, and isothiochromanone, **2**, series was discovered. We have examined the effects of ultraviolet irradiation on close to 20 such compounds, most of which have not been reported previously.



1 **2** **3**

One very notable feature of the photochemistry of thiochromanone sulfoxides is that it differs dramatically from that of the analogous sulfides,

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[3]Taken in part from the Ph.D. thesis of M. T. Thomas, University of Toronto, 1970.

reported a few years ago by Berchtold and coworkers (9, 10), in which rearrangements via thiacyclobutanone intermediates and photofragmentation processes are common, and that of the analogous sulfones (11) for which simple photoreduction to pinacols predominates. Apart from a relatively small number of instances in which the sulfoxides were decomposed too rapidly to allow isolation of the photoproducts, it appears that we can sub-divide the photoreactions of these sulfoxides into three categories:

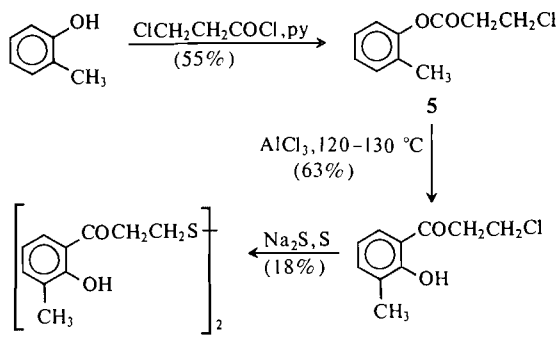
(*A*) those in which electron-releasing substituents (such as CH_3, OCH_3) are present at positions 6 or 8 of the thiochromanone system;

(*B*) those in which at least one substituent (CH_3) is present at the C-3 position, although another substituent (CH_3 or C_6H_5) may also be present at C-2;

(*C*) those in which at least one substituent (CH_3 or C_6H_5) is present at C-2, but C-3 is completely unsubstituted.

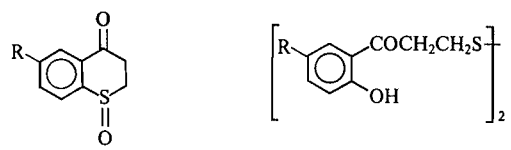
The first example of a reaction of type *A* was encountered on photolysis in benzene of 8-methylthiochroman-4-one 1-oxide, **3** (8). The only characterizable product, isolated in 10% yield from this reaction, showed a molecular ion at *m/e* 390, indicative of a dehydrodimer type structure. The possibilities of a disulfide or a peroxide type structure presented themselves, but the latter was rejected when the usual organic peroxide tests proved negative. (Intuitively, the formation of a peroxide which was not only stable at its mp (133–134 °C), but showed a molecular ion with intensity 13% of the base peak, had seemed highly improbable.) The spectral evidence, particularly the low frequency for the carbonyl group in the ir, pointed towards the disulfide structure **4**. This was confirmed by a relatively straightforward synthesis from *o*-cresol (Scheme 1). The Fries rearrangement conditions could be controlled to obtain predominantly *ortho*-migration of the 3-chloropropanoyl group in the ester **5**. No attempt to optimize the yield in the conversion of **6** into **4** has been made. The sample of **4** obtained by this route was identical in all respects with the photoproduct described above. A considerable amount (40%) of the starting sulfoxide was recovered from the irradiation of the 8-methyl sulfoxide.

Similarly, photolysis of 6-methyl- and 6-methoxythiochroman-4-one 1-oxide (**7***a*, **7***b*) gave the analogous disulfide products (**8***a*, **8***b*) in yields of

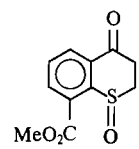


SCHEME 1

6 and 7.5%, respectively. On the other hand, no such product could be isolated from the irradiation of 8-carbomethoxythiochroman-4-one 1-oxide, **9**. These facts suggested an electronic rather than a steric effect of the substituent in the aromatic ring and we thus propose the mechanism shown in Scheme 2 in which an electron-



7*a* R = CH_3 **8***a* R = CH_3
7*b* R = OCH_3 **8***b* R = OCH_3



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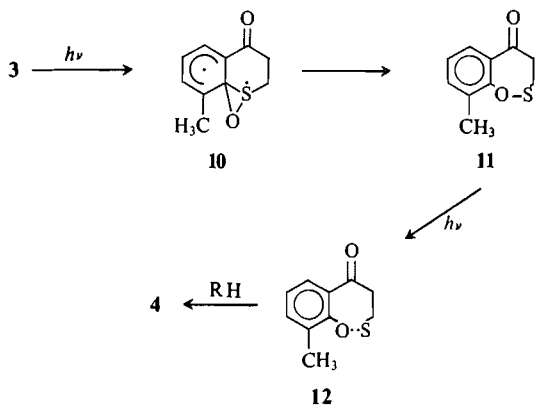
releasing group at position 8 (or 6) would be expected to stabilize the initially produced cyclohexadienyl radical **10** (or, possibly, a simple phenyl radical produced by α-cleavage of the sulfoxide). Collapse of **10** to the cyclic sulfenate **11**,[4] followed by a second photolytic step would lead to the biradical **12**. Coupling of the thiyl radicals, and hydrogen abstraction (from solvent or other substrate molecules) by the phenyloxy radicals would lead to **4**. It is a necessary consequence of this proposal that the sulfoxide oxygen becomes the phenolic OH group in the product.

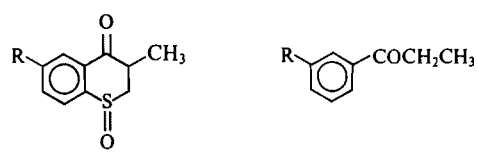
[4]As discussed later for the 3-methyl substituted case, we cannot at present rule out the possibility of a concerted rearrangement of **3** to **11**.

We have confirmed that this is the case by repeating the irradiation, under otherwise identical conditions, on the ^{18}O-labelled sulfoxide, prepared by the procedure of Montanari and coworkers (12). The mass spectral fragmentation pattern (see Experimental) strongly supports the exclusive location of the ^{18}O-label on the phenolic hydroxyl group.



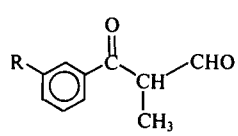
SCHEME 2

Photolysis of the 3-methylthiochroman-4-one 1-oxide, **13***a*, is typical of a number of 3-substituted sulfoxides which, like the sulfoxides already discussed, give products derived by opening of the hetero-ring, but from which in addition the sulfur atom has been subsequently lost (type *B* reaction). Irradiation of 3-methylthiochroman-4-one 1-oxide in benzene (7) was found to give three identifiable products, along with recovered starting material (15%). The least polar product eluted on chromatography was a mobile liquid with a single carbonyl band



13*a* R = H
13*b* R = CH_3

14*a* R = H
14*b* R = CH_3



15*a* R = H
15*b* R = CH_3

(1685 cm^{-1}) and the characteristic pattern of an ethyl group in the nmr. Direct comparison with an authentic sample showed unmistakably that this compound was propiophenone, **14***a*, and this was further confirmed by comparison of the semicarbazone derivatives of the two samples.

A second product isolated from the chromatography was a solid, with bands in the ir at 1724 and 1680 cm^{-1}, indicative of two carbonyl groups. That one of these was an aldehyde functionality was indicated by the characteristic singlet at δ 9.86 ppm in the nmr. The presence of a monosubstituted benzene ring and the molecular formula $C_{10}H_{10}O_2$ indicated that this product was probably 2-benzoylpropanal, **15***a*. This was confirmed by synthesizing the latter compound by base-catalyzed condensation of propiophenone and ethyl formate and direct spectral comparison of the two samples.

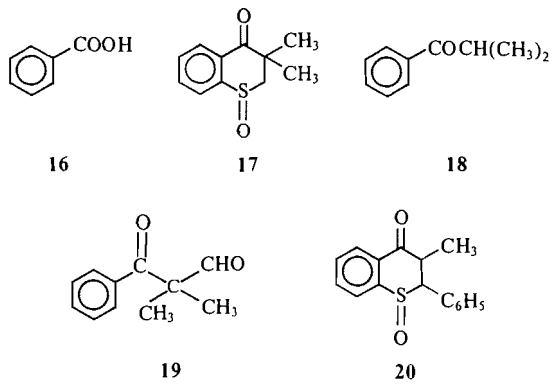
The third product, also a solid, was comparatively easily identified as benzoic acid, **16**, by virtue of its mp, molecular formula ($C_7H_6O_2$), and characteristic reaction with aqueous sodium bicarbonate.

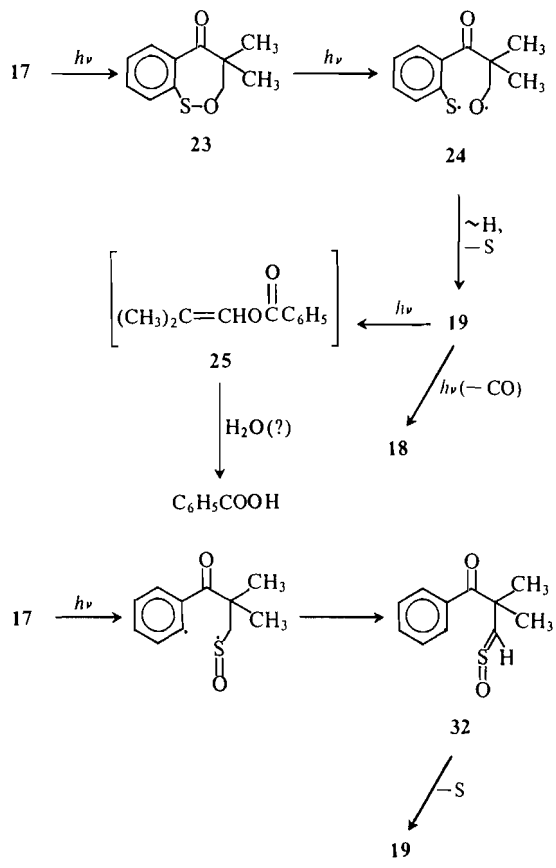
Our mechanistic proposal (Scheme 3) assumes that the initial photoproduct is 2-benzoylpropanal, **15***a*. Support for this suggestion was obtained by subjecting **15***a* independently to photolysis. Irradiation of **15***a* in dry benzene gave virtually no change after 30 h, but if the irradiation was conducted in benzene previously shaken with water, benzoic acid (67%) and propiophenone (13%) were isolated after 12 h. Some benzoic acid was also obtained when a sample of **15***a* was allowed to stand at 25 °C in the dark for 2 weeks. We are presently unable to advance a reason for the dramatic effect of added water on the photolysis of **15***a*, other than the obvious comment that it appears to require attack of water on an excited state of the keto-aldehyde.

The nature of the products obtained from the 3-methyl sulfoxide, and particularly the absence of sulfur, raised the possibility that these products might have arisen by complete photochemical cleavage of the hetero-ring, followed by attack of the fragments so produced on solvent benzene. This possibility could be eliminated following the photolysis of 3,6-dimethylthiochroman-4-one 1-oxide, **13***b*, which was found to produce only the expected propiophenone analogue, 1-*m*-tolyl-1-propanone, **14***b* (9%), and no

isomeric tolyl ethyl ketones, thus showing that the aromatic ring in the keto-aldehyde is that originally present in the sulfoxide. Photolysis of **13***b* also produced the expected keto-aldehyde **15***b* (7%) (although no *m*-toluic acid was found) and some recovered sulfoxide (13%).

Irradiation of 3,3-dimethylthiochroman-4-one 1-oxide, **17**, in benzene proceeded in an analogous manner. Chromatography again led to the isolation of three products, identified as isobutyrophenone, **18** (15%), 2-methyl-2-benzoylpropanal, **19** (15%), and benzoic acid (25%). The isobutyrophenone was identified by spectral comparison with an authentic sample and also by mp and mixture mp of the semicarbazone derivative. The keto-aldehyde structure **19** was initially assigned by analogy with the similar products obtained earlier, and finally confirmed by direct comparison with an authentic sample of 2-methyl-2-benzoylpropanal, synthesized by benzoylation of the morpholine enamine of isobutyraldehyde (13). The mp of the (mono) 2,4-dinitrophenylhydrazones of the two samples remained undepressed on admixture. A small amount of starting sulfoxide (8%) was also recovered in the later stages of the chromatography of the photolysate.



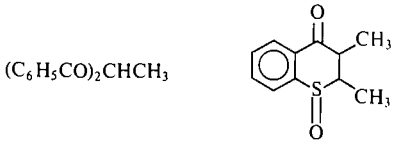


SCHEME 3

Once again, we attempted to establish the formation of 2-methyl-2-benzoylpropanal, **19**, as the primary photochemical process by independent irradiation of this compound in benzene. After only 1 h, decomposition was essentially complete and afforded isobutyrophenone (71%), accompanied by benzoic acid (14%). The possibility that some reaction is occurring by a ground state (acid- or base-catalyzed) pathway cannot be completely eliminated, in view of the well known susceptibility of non-enolizable β-keto aldehydes to hydrolytic cleavage (13). However, the results of deuterium-labelling experiments, to be discussed below, make it unlikely that this is anything more than a minor decomposition pathway. The high yield of isobutyrophenone obtained in the irradiation of **19** is surprising, in that it appears to be at variance both with the results of the original irradiation of **17** and also with the results of irradiation of the β-keto aldehyde **15***a*, where benzoic acid was the principal product. We can advance no really satisfactory explanation for the first anomaly but it is possible that the presence of a large amount of the hydroxymethylene tautomer of 2-benzoylpropanal makes attack of water at the ketone carbonyl (whether in the ground state or the excited state) greatly preferred in the latter case, accounting for the large amount of benzoic acid formed.

Irradiation of 3-methyl-2-phenylthiochroman-4-one 1-oxide, **20**, under similar conditions

produced a crystalline product (39%) for which elemental analysis indicated the formula $C_{16}H_{14}O_2$. Analogy with the previous results and the spectral properties of this compound indicated that it was the expected 1,1-dibenzoylethane, **21**. This was readily confirmed by direct comparison with an authentic sample of the latter prepared by (mono) methylation of dibenzoylmethane with methyl iodide – silver oxide (14). Unlike the keto-aldehydes which were the



21 **22**

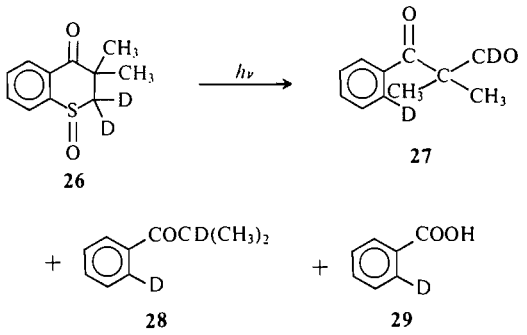
primary photoproducts in the earlier type *B* reactions, this β-diketone is not particularly susceptible to further photolysis, which accounts for both its relatively high yield and the almost complete absence (<0.5%) of benzoic acid in this photolysis. The only other product definitely identified in this reaction was recovered starting sulfoxide (12%).

Somewhat inadequate (spectral) evidence for the formation of the analogous 1-acetyl-1-benzoylethane was encountered in a small scale photolysis of 2,3-dimethylthiochroman-4-one 1-oxide, **22**. As the starting sulfoxide was difficult to synthesize and purify, no attempt has been made to confirm this result.

The results obtained from the photolyses of the 3-substituted thiochromanone sulfoxides lead us to postulate the alternative mechanisms shown in Scheme 3 for the type *B* photoreaction. Ring expansion of the 3,3-dimethyl sulfoxide **17**, for example, to the cyclic sulfenate **23** has ample analogy in mass spectrometry (15) and might proceed in either a concerted or a stepwise fashion. Further photolysis of the sulfenate leading to the biradical **24**, followed by desulfurization[5] and (intramolecular) hydrogen transfer from C-2 to the phenyl ring position vacated by sulfur, would lead to the initially formed keto-aldehyde **19**. Results of a deuterium-labelling experiment (to be discussed in detail below) further suggest that the secondary photochemical decarbonylation of **19** is either concerted (via a singlet excited state) or proceeds by a stepwise, cage-recombination process, since the formyl hydrogen (deuterium) is retained in the product **18**. The production of benzoic acid may be explained by α-cleavage of the benzoyl group, and recombination at oxygen rather than carbon, leading to the enol benzoate **25**. This possibility is supported by the report of the isolation of 2-butenyl acetate, albeit in low yield, from the photolysis of the β-diketone, 3-methyl-2,4-pentanedione (16). Finnegan and Hagan (17*a*) have reported the isolation of benzoylacetaldehyde, acetophenone, and benzoic acid from the photolysis of vinyl benzoate itself, the yields of the three products varying with the solvent used in the photolysis. Finnegan and Hagen have proposed a general category of photochemical rearrangement (of which the photo-Fries reaction is another example) of the type X—A—B=C → [A=B=C]· + X· → A=B—C—X, which may be reversible in certain instances.

An alternative proposal (Scheme 3) for the formation of **19** involves initial α-cleavage of the aryl C—S bond. Although this is the stronger of the two C—S bonds, the difference in bond energies is only about 7 kcal/mol and examples of aryl C—S bond cleavage in sulfides, sulfoxides, and sulfones have been reported by Kharasch and Khodair (17*b*). Hydrogen abstraction from C-2 by the reactive phenyl radical could then lead to an intermediate sulfine **32** (or the isomeric oxathiiran) which, from the work of Schultz and Schlessinger, would be expected to lose sulfur readily to give **19**.

Partial support for one of the above mechanisms was obtained by the photolysis of 2,2-di-



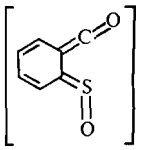
26 **27**

28 **29**

[5]As one of the referees has pointed out, this step appears significantly endothermic, and is perhaps, therefore, the major weakness in this suggested mechanism. However, we have not ascertained the fate of the extruded sulfur atom and Pryor and Walling have earlier shown the existence of the reaction RS· + A → R· + SA (*cf.* J. Am. Chem. Soc. **95**, 945 (1973)).

deuterio-3,3-dimethylthiochroman-4-one 1-oxide, **26**, synthesized by the procedure of Mock (18). This led to the deuterated keto-aldehyde **27** and the isobutyrophenone **28**, in each case with retention of the two deuterium atoms, and to the monodeuterated benzoic acid **29**, in yields comparable to those originally obtained for the unlabelled sulfoxide. Furthermore, attempts to incorporate external deuterium by conducting the photolysis of the unlabelled sulfoxide in benzene-d_6 or toluene-d_8 were without success. Thus the transfer of hydrogen from C-2 to the aryl ring, whatever the detailed mechanism of this step, must be *intra*molecular. Likewise, as postulated previously, the decarbonylation step must proceed without external incorporation of hydrogen (deuterium), and is thus presumably photochemical, not hydrolytic, in nature.

Other mechanistic studies conducted on the type *B* photolysis include an attempt to trap an



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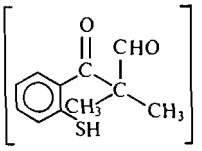

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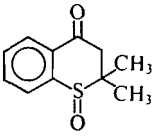
intermediate such as **30**, which might be formed by a photochemical fragmentation reaction analogous to that observed by Berchtold (10) for the keto-sulfides of similar structure or the mass spectrometric (*retro*-Diels–Alder) fragmentation observed earlier by us (19) for related sulfoxides. Trapping attempts (with methanol) were unsuccessful, as were attempts to isolate isobutylene from the effluent gas stream, indicating that **17** at least does not undergo significant photochemical reaction by this pathway. Preliminary attempts to carry out the irradiation of 3,3-dimethylthiochroman-4-one 1-oxide at lower temperatures (−10 °C) were not encouraging. Some evidence was obtained, however, in one experiment for a labile precursor to the keto-aldehyde **19**. Among the possible structures for this intermediate are the cyclic sulfenate **23**, the thiol **31**, or the sulfine **32**. A synthetic programme is currently in progress to attempt to identify sulfenates as real intermediates in these reactions.

The third well-defined category of photochemical behavior of thiochromanone sulfoxides



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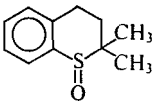

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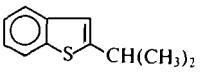

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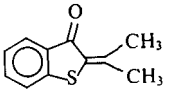

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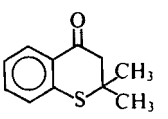
was first observed in the photolysis of 2,2-dimethylthiochroman-4-one 1-oxide **33**. As mentioned previously, Archer and Kitchell (1) had reported the photochemical ring contraction of 2,2-dimethylthiochroman 1-oxide, **34**, to 2-isopropylbenzothiophene, **35**, and also the conversion of **33** into 2-isopropylidene-3-thiaindanone, **36**, by heating with acetic anhydride (Pummerer reaction). We were interested to discover whether the presence of the carbonyl group in **33** would inhibit β-hydrogen abstraction by the excited sulfoxide chromophore at C-3, leading eventually, by the mechanism proposed by Archer and Kitchell, to **36**, or whether other photochemical processes would predominate. It may be noted that if β-hydrogen abstraction does occur it could also involve one of the C-2 methyl groups, leading to products other than **36**. We will return to this possibility later.

One other point concerning the synthesis of the 2,2-dimethylthiochroman-4-one 1-oxide (see Experimental) is worthy of brief comment. Cyclization of 3-methyl-3-phenylthiobutanoic acid to 2,2-dimethylthiochroman-4-one, **37**, the precursor of the desired sulfoxide **33**, failed completely if the reagent normally employed for such cyclizations, concentrated sulfuric acid, was used. Similarly poor results were obtained using polyphosphoric acid or phosphorus oxychloride which also have been successfully used for other thiochromanones and thioflavanones. A successful cyclization was achieved, however, with



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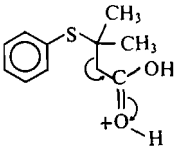

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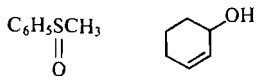
very dry phosphorus pentoxide in boiling benzene. We attribute the failure of the earlier attempts to fragmentation of the protonated butanoic acid derivative **38**, leading to the formation of a particularly stable (sulfur-stabilized) tertiary carbonium ion centre, and hence eventually to water-soluble products only.

Irradiation of 2,2-dimethylthiochroman-4-one 1-oxide in benzene showed considerable destruction of the sulfoxide band (ir) in 4 h. Chromatographic isolation of the products led to the isolation (in very low yield, 3%) of a crystalline ketone $C_{11}H_{10}OS$, shown by direct comparison with an authentic sample, to be identical with 2-isopropylidene-3-thiaindanone, **36**.

A crystalline product (8%), of similar polarity, was later shown to be identical with 2,2-dimethylthiochroman-4-one, **37**. This represents a product of formal deoxygenation of the starting sulfoxide. (The possibility that **37** was already present as an impurity in the starting sulfoxide has been eliminated.) Gurria and Posner (20) recently reported the photochemical deoxygenation of a number of diaryl sufoxides, and the mixed aryl alkyl sulfoxide **39**, in excellent yield. It may well be the case, based on the results of these authors and our own findings, that photochemical deoxygenation becomes an important pathway when other alternatives, such as β-hydrogen abstraction and α-cleavage processes, are impossible or disfavored in energy terms. Gurria and Posner (20) adduced evidence that the triplet excited state of their sulfoxides was responsible for the deoxygenation reaction and

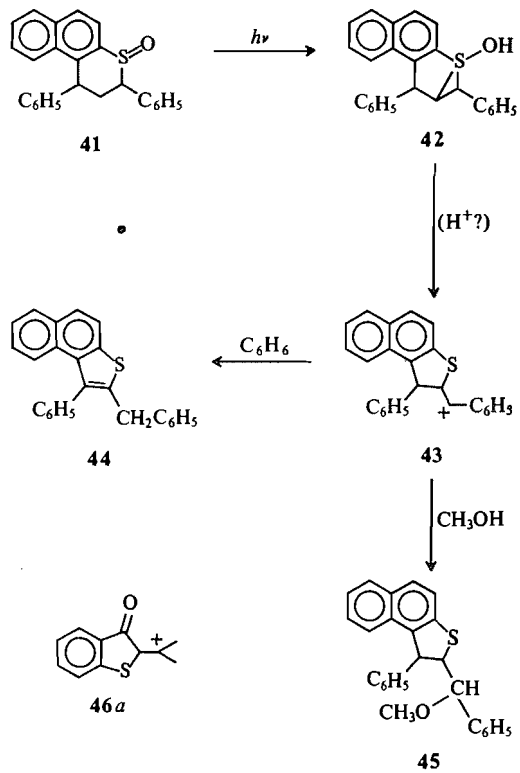


39 **40**

were also able to obtain evidence for the formation (direct or indirect) of singlet oxygen by a trapping experiment with cyclohexene. From the fact that they were able to isolate 2-cyclohexen-1-ol, **40**, in 41% yield by sodium iodide reduction of the photolysate, they concluded that formation of the corresponding hydroperoxide precursor indicated that the deoxygenation of the sulfoxides led to $^1O_2$, and not to atomic oxygen, which would be expected to react with cyclohexene to give the epoxide or cyclohexanone. We have attempted to carry out similar oxygen trapping experiments in the photolysis of **33**, without success. Since we have earlier shown (11), however, that thiochromanone sulfones are photolyzed only in the presence of a good hydrogen donor and are photochemically inert in benzene, we are quite confident in asserting that we have observed in the formation of **37** another genuine deoxygenation reaction, and not simply a disproportionation of the sulfoxide to equimolar amounts of sulfide and sulfone.

Some unreacted sulfoxide (46%) was recovered from the later stages of the chromatographic separation, and was the only other identifiable material present on photolysis of **33** in benzene.

Schultz and Schlessinger (21) have recently reported a similar photochemical ring contraction of a cyclic sulfoxide **41**. On the strength of a successful trapping experiment with methanol they propose a mechanism (Scheme 4) like that of Archer and Kitchell (1), involving β-hydrogen abstraction, ring closure to a highly strained tetracovalent sulfur species **42** and (acid-catalyzed?) rearrangement via the carbonium ion species **43** to the thiophene **44** (in benzene) or the dihydrothiophene **45** (in methanol). For this



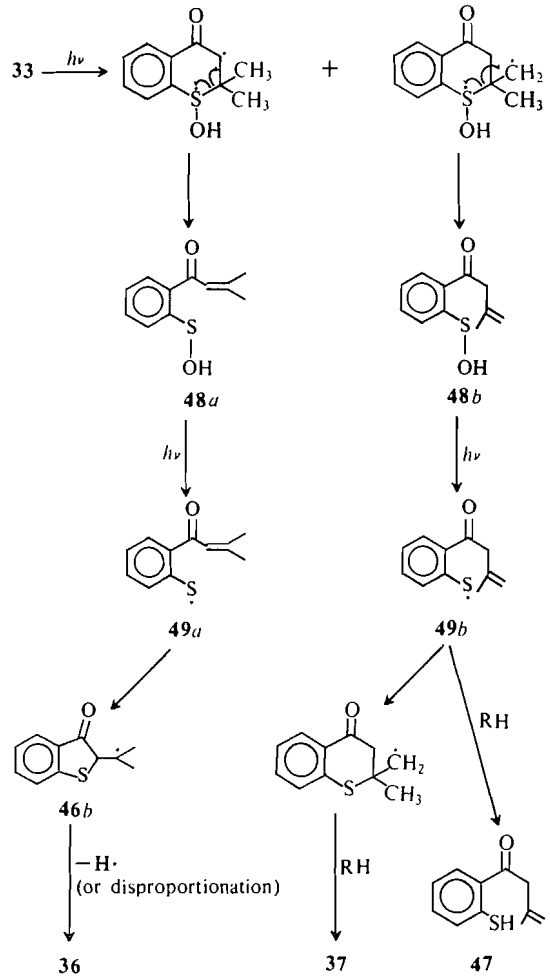
41 **42** **43** **44** **45** **46a**

SCHEME 4

reason, we have conducted the photolysis of 2,2-dimethylthiochroman-4-one 1-oxide, **33**, in methanol to see if products corresponding to the reaction of the (presumed) intermediate carbonium ion **46***a* could be obtained. We have so far been quite unsuccessful in this endeavour, thus suggesting that an entirely different mechanism is responsible for the formation of the ring-contraction product **36** or, possibly, that the intermediate involved in our case is not **46***a*, but a radical species of similar structure **46***b* (see Scheme 5).

From the irradiation of **33** in methanol (and also in various mixtures of methanol and benzene) we have isolated, however, a new product $C_{11}H_{12}OS$ in 6–11% yield, accompanied only by recovered starting sulfoxide (36%) and without formation of any of the deoxygenation product **37** or the ring-contraction product **36**. The presence of a weak band in the ir at 2450 cm^{-1} and of a singlet (1H) in the nmr at δ 1.58 ppm, completely removed by shaking with D_2O, led us to identify the new product as a thiol. The presence of an allylic CH_3 group (3H, s) at δ 1.58 and of the broadened doublet pattern characteristic of the $C{=}CH_2$ unit at δ 4.91 ppm, along with the mass spectral and analytical data, lead us to postulate the structure **47** for this compound. Since this product corresponds to a formal photoreduction process we repeated the irradiation of **33** in 50:50 isopropyl alcohol–benzene. Rather surprisingly, none of the thiol **47** appears to be formed under these conditions, although a small amount (4%) of the deoxygenation product **37** and recovered sulfoxide (30%) were isolated.

The foregoing results appear to point to a rather inefficient photochemical decomposition of **33**, characterized by the formation of free radical, rather than ionic, intermediates. The mechanistic scheme (Scheme 5) which we propose must be regarded as somewhat tentative but is more in accord with our findings than that proposed by Archer and Kitchell (1). Initial β-hydrogen abstraction from the two possible sites, followed by electronic reorganization, leads to two isomeric sulfenic acids **48***a* and **48***b*. This process, incidentally, is formally analogous to the formation of unsaturated aldehydes, following α-cleavage of cyclic ketones, and we certainly cannot rule out the possibility that α-cleavage precedes hydrogen abstraction. Homolytic decomposition of these unstable species by fission of the S—O bond would be expected to lead to the corresponding thiyl radicals. Cyclization of the thiyl radical **49***a* could lead to **46***b* and hence to **36**, and cyclization of **49***b* could eventually lead to the product of formal deoxygenation **37**. On the other hand, in the presence of a superior hydrogen donor (methanol) **49***b* is converted exclusively to the thiol **47**. We cannot at present answer the question as to why methanol does not appear to reduce the other thiyl radical **49***a* (or **46***b* for that matter) in a similar fashion. Nevertheless, although we cannot exclude other free-radical processes at this stage (including the involvement of a cyclic sulfenate), the mechanistic scheme which we propose satisfactorily accounts for the formation of all the products

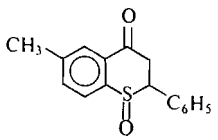


SCHEME 5

isolated and enables one to rationalize the rather surprising formation of the unconjugated thiol **47** and the absence of products arising from methanol addition more satisfactorily than a polar or ionic mechanism.

Similar irradiation of 2-methylthiochroman-4-one 1-oxide in benzene led, disappointingly, to a very rapid decomposition to a very viscous product from which no identifiable products could be obtained. A similar result was obtained with thiochroman-4-one 1-oxide, **1**, itself, which in this instance does resemble its sulfide analogue, earlier examined by Berchtold (10). Irradiation of 6-methyl-2-phenylthiochroman-4-one 1-oxide, **50**, however, in benzene afforded as the only identifiable product (14%) the ring-contracted analogue of **36**, 5-methyl-2-benzylidene-3-thiaindanone **51**, identified by comparison with an authentic sample prepared by aldol condensation of 5-methyl-3-thiaindanone with benzaldehyde. The stereochemistry of this compound has not been established; the vinylic proton signal is overlapped by the aromatic proton signals in the nmr, making an unambiguous assignment of the stereochemistry very difficult. The starting sulfoxide (44%) was also recovered in this irradiation.

Irradiation of isothiochromanone 2-oxide, **2**, and its 3,3-dimethyl derivative produced no isolable product, even when irradiation of the latter was conducted at −20 °C. We had also



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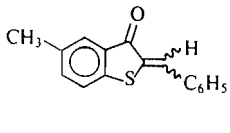

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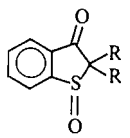

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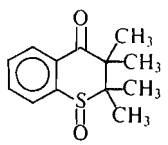
(R = H,CH_3)



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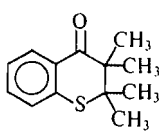

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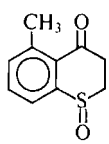

55

intended to examine the photochemical behavior of some thiaindanone sulfoxides **52**, but the unexpected difficulties encountered in their synthesis and the labile nature of the sulfide precursors induced us to abandon this attempt.

The irradiation of 2,2,3,3-tetramethylthiochroman-4-one 1-oxide, **53**, provides an example of a situation where both the 2- and 3-positions are completely substituted. In this case, of course, neither ring-contraction by β-hydrogen abstraction from C-3, nor the usual formation of β-dicarbonyl products from C-3 substituted analogues is possible. β-Hydrogen abstraction (from a C-2 methyl group) or γ-hydrogen abstraction (from a C-3 methyl group) remain formal possibilities but although we obtained liquid products showing spectral (nmr) evidence for vinylic protons, we were unable to isolate and separate any pure compounds from the photolysis mixture by any chromatographic technique, including glc.

Interestingly, the only product actually isolated, apart from small amounts of starting sulfoxide, was the product of deoxygenation, 2,2,3,3-tetramethylthiochroman-4-one, **54**, obtained in 33% yield. This yield was not significantly increased by changing the solvent to acetone. The isolation of the deoxygenation product, however, lends support to our suggestion that deoxygenation of the sulfoxide group is only likely when other photochemical pathways are impossible or disfavored.

The ultraviolet spectra of thiochromanone sulfoxides (Table 1) show a marked similarity to those of the analogous sulfones reported by us previously (11). However, in contrast to the sulfones, which are photochemically inert in solvents which are poor hydrogen-donors and give only moderate yields of pinacolic reduction products in alcoholic solvents, the foregoing discussion clearly reveals a very complex photochemistry for the keto-sulfoxides studied in this paper. In view of the fact that these photolyses proceed in essentially the same manner, albeit more slowly, in Pyrex as well as with Vycor filtration, and since the major emission bands of the (medium-pressure) mercury lamps being used are at 313 and 366 nm, it seems likely that absorption of light at approximately 290–295 nm (band B) is responsible for the photochemistry observed. The exact nature of this absorption is not known with certainty except that it appears

TABLE 1. Ultraviolet spectra of thiochromanone sulfoxides[a]

Sulfoxide	Band A nm (ε)	Band B nm (ε)	Band C nm (ε)
Thiochroman-4-one 1-oxide	243(10 300)	288(1920)	333sh(50)[b]
2,2-Dimethylthiochroman-4-one 1-oxide	243(10 500)[b]	296(1700)[b]	333sh(~100)[b]
3-Methylthiochroman-4-one 1-oxide	244(9040)	288(1910) 295sh(1790)	340(175)
6-Methylthiochroman-4-one 1-oxide	250(7950)	298(1780)	345(560)
8-Carbomethoxythiochroman-4-one 1-oxide	250sh(8600)	289(950) 298sh(830)	342(430)
2,2,3,3-Tetramethylthiochroman-4-one 1-oxide	242(—)[c]	301(—)[c]	[c]
Isothiochromanone 2-oxide	253(9880)	294(1580)	[c]

[a]In methanol or 95% ethyl alcohol.
[b]Reference 22.
[c]Not recorded.

likely to be some sort of combination band involving both the C=O and the S=O chromophores (22). The interesting possibility that essentially all of the light is absorbed by the carbonyl chromophore is suggested by our experience on irradiation of 5-methylthiochroman-4-one 1-oxide, **55**. In sharp contrast to the behavior of the other thiochromanone and isothiochromanone sulfoxides, even those which do not lead to identifiable products, **55** could be recovered in 90% yield after 24 h irradiation. This is believed due to the readiness with which *o*-methyl substituted aryl ketones undergo 'unproductive' photoenolization and suggests that the carbonyl group is playing an essential role, perhaps as an intramolecular sensitizer, in the photochemistry of the sulfoxide group which is ultimately observed.

The photochemical behavior of the S=O chromophore is frequently compared with that of the much better known carbonyl chromophore. Our results, and those of previous workers, suggest that the photochemical behavior of sulfoxides may indeed be as complex as that of ketones, but that there are important differences. The potential for the sulfoxide group to rearrange initially to bivalent sulfenate (or sulfenic acid) derivatives is formally analogous to the relatively rare formation of oxacarbenes, but the tendency for further homolysis of the much weaker S—O bond accounts for much of the unique photochemistry observed for sulfoxides. Recent evidence suggests that β-hydrogen abstraction processes may also be involved in the photochemistry of sulfoxides in certain cases, in contrast to that of the carbonyl group, in which γ-hydrogen abstraction is virtually the rule. Examination of Dreiding models of sulfoxides appears to confirm the likelihood of such processes occurring. Instances of γ-hydrogen abstraction involving the sulfoxide group, leading to fragmentation products akin to those in Norrish type II processes, however, have also been reported (6).

Experimental

General

The ir spectra (cm^{-1}) were recorded on a Perkin-Elmer 337 grating spectrophotometer and the low resolution mass spectra were obtained on a Bell and Howell 21-490 spectrometer. Accurate mass measurements were obtained on the A.E.I. MS-902 instrument. Nuclear magnetic resonance spectra (δ) were recorded on Varian T-60 and EM-360 spectrometers, with TMS as internal standard. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Box 25, DK 2730, Herlev, Denmark. A water-cooled Hanovia 115 W medium-pressure mercury arc lamp was normally employed as the light source in irradiation experiments, with the filter (Vycor or Pyrex) indicated. All melting points and boiling points are uncorrected.

Thiochromanones

Thiochroman-4-one is now available commercially and the syntheses of its 2-,3-,5-, and 8-methyl and 8-carbomethoxy analogues, and of isothiochromanone (11) as well as the 2,2- and 3,3-dimethylthiochromanones have been described previously (23,24). The synthesis of 3,3-dimethylisothiochromanone has also been described earlier (25). Two representative procedures (Methods *A*, *B*) are described below.

Sulfoxides

These were synthesized by oxidation of the appropriate thiochromanone by the same general procedure which we have already described (19,24) (see Table 2).

Method A

6-Methylthiochroman-4-one 1-Oxide

p-Toluenethiol (12.5 g) was added to a 20% aqueous

sodium hydroxide solution (20 ml), and β-propiolactone (7.2 g) added to the mixture at 0–5 °C, with stirring. After 3 h, the reaction mixture was acidified (HCl) and the product, 3-*p*-tolylthiopropanoic acid (11.0 g, 57%) collected by filtration as a white solid, mp 64–65 °C.

The thio acid (5.0 g) was then cyclized in concentrated sulfuric acid (75 ml) at 25 °C for 26 h. The dark red mixture was poured over crushed ice and extracted with ether. Washing the ethereal extracts with water, drying ($MgSO_4$), and evaporation gave a solid product which on recrystallization from petroleum ether (bp 60–70 °C) gave 6-methylthiochroman-4-one (3.3 g, 73%), mp 61–62 °C.

The sulfoxide was prepared by the usual procedure as a white solid (76%), which was recrystallized from benzene–petroleum ether, mp 110–111 °C; lit. mp (26) 110 °C.

Method B

3-Methyl-2-phenylthiochroman-4-one 1-Oxide

α-Methylcinnamic acid was prepared by the Perkin reaction by heating benzaldehyde (21.0 g), propionic anhydride (32.0 g) and freshly fused sodium propionate (20.0 g) at 130–135 °C for 30 h. The reaction mixture was poured into water and the solution neutralized with solid sodium carbonate. Removal of excess benzaldehyde by steam distillation and acidification gave the cinnamic acid (21.0 g, 64%).

α-Methylcinnamic acid (32.0 g), benzenethiol (30.0 g), and piperidine (4 ml) were refluxed in absolute alcohol (100 ml) for 72 h. Upon cooling, the p*H* was adjusted to 4–5 and excess thiol removed by steam distillation. The insoluble oily residue remaining in the distilling flask rapidly solidified and was recrystallized from benzene–petroleum ether. The 2-methyl-3-phenyl-3-phenylthiopropanoic acid so obtained (42.0 g, 76%) was a white solid, mp 119–120 °C.

The thio acid (7.0 g) was cyclized by heating with phosphorus oxychloride (30.0 g) at 100 °C for 1 h. After cooling and pouring the reaction mixture over crushed ice the crude product was extracted with ether. Washing the combined ethereal extracts (aqueous NaOH, H_2O), drying ($MgSO_4$), and evaporation gave the 2-phenyl-3-methylthiochroman-4-one (6.0 g, 89%).

Oxidation of the above product by the usual procedure gave a rather impure product in virtually quantitative yield. Purification by chromatography on silica gel and elution with 2–5% acetone in methylene chloride gave what appeared to be a diastereoisomeric mixture of the expected sulfoxide. The expected strong bands (1690, 1026 cm^{-1}) in the infrared were present and the expected molecular ion at *m/e* 270 was observed, but the nmr spectrum was more complex than expected for a single diastereomer: δ ($CDCl_3$) 1.2 (3H, dd), 3.2 (1H, q), 4.2 (1H, m), 7.3–8.2 (9H, m) ppm. No further purification was attempted and irradiation was carried out on the mixture (*q.v.*).

2,3-Dimethylthiochroman-4-one 1-Oxide

Oxidation of the sulfide (*cis/trans* mixture) obtained by the method already described (23) gave, after chromatography on silica gel, what was believed to be a mixture of diastereoisomeric sulfoxides (53%). The liquid mixture did not crystallize on prolonged cooling at −10 °C and was used directly for the irradiation (*q.v.*)

3,3-Dimethylisothiochromanone 2-Oxide

Oxidation of 3,3-dimethylisothiochromanone by the procedure used for isothiochromanone (*q.v.*) gave a liquid sulfoxide (86%) which decomposed on attempted distillation, but could be readily purified by chromatography on silica gel and elution with methylene chloride–acetone mixtures; ir (neat) 1681, 1047 cm^{-1}; nmr ($CDCl_3$) δ 1.50 (3H, s), 1.57 (3H, s), 4.26 (2H, AB quartet, J_{AB} = 10 Hz), 7.2–7.7 (3H, m), 8.08 (1H, dd, J = 2.0, 7.0 Hz) ppm.

Irradiation of 8-Methylthiochroman-4-one 1-Oxide

The sulfoxide (1.5 g) was irradiated (Vycor) under N_2 in dry, degassed benzene for 24 h, by which time the sulfoxide band in the ir at 1020 cm^{-1} had almost disappeared. After evaporation of the solvent the disulfide product (0.145 g, 10%) was obtained by chromatography on silica gel by elution with 1–2% acetone in methylene chloride. Apart from some brown polymeric material the only other compound isolated was the starting sulfoxide (40%), eluted with acetone.

Trituration of the crude disulfide with petroleum ether gave a white solid, which was recrystallized from petroleum ether (bp 60–70 °C), mp 133–134 °C; ir (Nujol) 1634, 1610 cm^{-1}; nmr ($CDCl_3$) δ 2.23 (6H, s), 3.07 (4H, t, J = 6 Hz), 3.43 (4H, t, J = 6 Hz), 6.85 (2H, t, J = 7.5 Hz), 7.38 (2H, d, J = 7.5 Hz), 7.66 (2H, d, J = 7.5 Hz), 12.46 (2H, s) ppm; λ_{max} (MeOH) 259(14 000), 330(5700) nm; *m/e* 390(M^+) (13), 163(63), 162(30), 161(13), 145(12), 135(100), 105(10), 79(17), 78(50), 77(36). *Anal.* calcd. for $C_{20}H_{22}O_4S_2$: C 61.22, H 5.61, S 16.32; found: C 61.47, H 5.80, S 16.47.

Attempts to form the semicarbazone, 2,4-dinitrophenylhydrazone, or oxime of the photoproduct were unsuccessful, and the compound showed no positive reaction with $FeCl_3$. Attempts to degrade the disulfide by employing various oxidizing agents, Raney nickel or acid-catalyzed hydrolysis were likewise unsuccessful. Essentially the same results were obtained when the irradiation was conducted in acetonitrile or acetone, and if the Vycor filter was replaced by Pyrex.

o-Tolyl 3-Chloropropanoate, 5

A mixture of *o*-cresol (10.8 g), 3-chloropropanoyl chloride (28.0 g) and pyridine (1 ml) were refluxed for 10 h in benzene (50 ml). After evaporation the residue was extracted with ether and the ethereal extracts washed thoroughly with water and dried ($MgSO_4$). After evaporation of solvent the ester (11.0 g, 55%) was collected at 90–92 °C/2 Torr; ir (neat) 1755 (C=O) cm^{-1}; nmr ($CDCl_3$) δ 2.16 (3H, s), 2.90 (2H, t, J = 6.5 Hz), 3.75 (2H, t, J = 6.5 Hz), 7.0–7.3 (4H, m) ppm. *Anal.* calcd. for $C_{10}H_{11}ClO_2$: C 60.45, H 5.54, Cl 17.88; found: C 60.52, H 5.60, Cl 17.84.

1-(2-Hydroxy-3-methylphenyl)-3-chloro-1-propanone, 6

The *o*-cresyl ester (2.0 g) was subjected to the Fries rearrangement by heating with anhydrous aluminum chloride (4.0 g) at 120–130 °C for 30 min. After cooling and cautious addition of water, the aqueous solution was extracted with ether. Washing (H_2O), drying ($MgSO_4$), and evaporation of the ethereal extracts gave the desired propiophenone derivative (1.3 g, 63%) as a white solid, mp 82–83 °C (95% EtOH); ir (Nujol) 1635 (C=O) cm^{-1};

TABLE 2. Analytical data

Sulfoxide	% Yield (from sulfide)	mp (deg)	Calculated			Found		
			C	H	S	C	H	S
Thiochroman-4-one 1-oxide	79	49–50	60.00	4.48	17.77	59.65	4.63	17.63
Isothiochromanone 2-oxide	62[a]	170–171[b]	60.00	4.48	17.77	60.15	4.64	17.63
2-Methylthiochroman-4-one 1-oxide	75	109–110[b]	61.86	5.15	16.49	61.61	5.08	16.52
3-Methylthiochroman-4-one 1-oxide (27)	73	116–117[c]	61.86	5.15	16.49	61.64	5.17	16.62
5-Methylthiochroman-4-one 1-oxide	60	112–113[c]	61.86	5.15	16.49	61.63	5.23	16.54
8-Methylthiochroman-4-one 1-oxide	90	83–84[c]	61.86	5.15	16.49	61.98	5.25	16.55
6-Methoxythiochroman-4-one 1-oxide	90[d]	98–99[c]	57.14	4.76	15.24	57.35	4.97	15.07
2,2-Dimethylthiochroman-4-one 1-oxide	49[e]	91–92[c]	63.46	5.77	15.38	63.45	5.81	15.37
3,3-Dimethylthiochroman-4-one 1-oxide	90	(bp) 140–142/0.5 Torr	63.46	5.77	15.38	63.85	6.02	14.97
3,6-Dimethylthiochroman-4-one 1-oxide	88	106–107[c]	63.46	5.77	15.38	63.15	5.62	15.40
6-Methyl-2-phenylthiochroman-4-one 1-oxide	33	140–141[c,f]	71.10	5.22	11.84	71.28	5.14	11.93
2,2,3,3-Tetramethylthiochroman-4-one 1-oxide	81	73–74[g]	66.08	6.83	13.55	66.20	6.68	13.59

[a]A much shorter time (2–4 h) is required for the oxidation in this case.
[b]Recrystallized from benzene.
[c]Recrystallized from benzene–petroleum ether (bp 60–70 °C).
[d]In the preceding cyclization step considerable demethylation occurred, leading to 6-hydroxythiochroman-4-one, mp 141–142 °C.
[e]The synthesis of 2,2-dimethylthiochroman-4-one has been reported (23) but the mp of this compound should read 60–61 °C and not as reported previously. The intermediate 3-methyl-3-phenylthiobutanoic acid has mp 68–69 °C and may be isolated in 58% yield by the method described (23).
[f]Arndt (27) reports mp 177–178 °C, but admits that his sulfoxide is likely contaminated with the sulfone, mp 191–192 °C.
[g]Recrystallized from *n*-hexane.

nmr ($CDCl_3$) δ 2.25 (3H, s), 3.35–4.05 (4H, A_2B_2 system), 6.77 (1H, t, J = 7.5 Hz), 7.32 (1H, dd, J = 1.5, 7.5 Hz), 7.53 (1H, dd, J = 2.0, 8.0 Hz), 12.23 (1H, s) ppm. *Anal.* calcd. for $C_{10}H_{11}ClO_2$: C 60.45, H 5.54, Cl 17.88; found: C 60.36, H 5.49, Cl 18.26.

Conversion of **6** *into the Disulfide,* **4**

Sodium disulfide was prepared by refluxing a mixture of sodium sulfide (90 mg) and sulfur (12 mg) in 95% ethyl alcohol (25 ml) until the sulfur had dissolved. The hot solution was then added slowly to a refluxing solution of **6** (85 mg) in 95% ethyl alcohol (12 ml). After a further 2.5 h refluxing the reaction mixture was cooled and filtered, and the filtrate made slightly acidic with dilute hydrochloric acid. After evaporation of the solvent the residue was sublimed to remove excess sulfur and the remaining solid was recrystallized from methanol to afford **4** (15 mg, 18%). The solid so obtained was identical (mp, mixture mp, ir, nmr) with the photoproduct obtained as described earlier.

8-Methylthiochroman-4-one 1-[^{18}O]-oxide

This compound was made by essentially the general method of Montanari and co-workers (12). A solution of iodobenzene dichloride (1.4 g) in anhydrous pyridine (3.0 ml) was added dropwise to a stirred solution of 8-methylthiochroman-4-one (0.9 g) in aqueous pyridine containing 0.8 ml $H_2{}^{18}O$ (20% enrichment) and 3.2 ml pyridine. After stirring for 30 min at 20 °C the mixture was diluted with chloroform (30 ml), washed with 10% sulfuric acid and water, and dried (Na_2SO_4). Evaporation and repeated recrystallization of the residue from benzene–hexane gave the labelled sulfoxide (0.7 g, 71%), mp 81–82 °C. The mass spectrum of the sulfoxide showed the expected enhancement in the intensity of the (M + 2) peak at m/e 196.

Irradiation of the labelled sulfoxide under the same conditions as described for the unlabelled 8-methylthiochroman-4-one 1-oxide gave the same crystalline disulfide, mp 133–134 °C. The relevant mass spectral data are reported below:

		Mass	
m/e	Formula	Calculated	Experimental
394(M+4)	$C_{20}H_{22}{}^{18}O_2{}^{16}O_2S_2$	394.1044	394.1048
392(M+2)	$C_{20}H_{22}{}^{18}O^{16}O_3S_2$	392.1001	392.0994
390(M)	$C_{20}H_{22}O_4S_2$	390.0959	390.0961
$165\left(\frac{M}{2}-S+2\right)$	$C_{10}H_{11}{}^{18}O^{16}O$	165.0801	165.0801
$163\left(\frac{M}{2}-S\right)$	$C_{10}H_{11}O_2$	163.0758	163.0756
$137\left(\frac{M}{2}-S,-C_2H_4,+2\right)$	$C_8H_7{}^{18}O^{16}O$	137.0488	137.0487
$135\left(\frac{M}{2}-S,-C_2H_4\right)$	$C_8H_7O_2$	135.0446	135.0443
$121\left(\frac{M}{2}-S,-C_2H_4,-O,+2\right)$	$C_8H_7{}^{18}O$	(Intensity too low for mass measurement)	
$119\left(\frac{M}{2}-S,-C_2H_4,-O\right)$	C_8H_7O	119.0497	119.0497
$91\left(\frac{M}{2}-S,-C_2H_4,-O,-CO\right)$	C_7H_7	91.0548	91.0548

Irradiation of 6-Methylthiochroman-4-one 1-Oxide

The sulfoxide (500 mg) was irradiated in dry, degassed benzene (80 ml) for 22 h under essentially the same conditions as those described for the 8-methyl analogue. Chromatography on silica gel afforded the starting material (75 mg, 15%) and the disulfide product **8***a* (30 mg, 6%). The disulfide had mp 128–129 °C; ir (Nujol) 1635, 1610 cm^{-1}; nmr ($CDCl_3$) δ 2.38 (6H, s), 3.33 (8H, A_2B_2 system), 6.9–7.6 (6H, m), 11.91 (2H, s) ppm. *Mol Wt.* calcd. for $C_{22}H_{22}O_4S_2$: 390.0959; found: 390.0959.

Irradiation of 6-Methoxythiochroman-4-one 1-Oxide

The sulfoxide (400 mg) was irradiated in dry, degassed benzene (150 ml) for 23 h. Chromatography on preparative tlc plates of silica gel afforded starting material (220 mg, 55%) and the disulfide product **8***b* (30 mg, 7.5%), mp 125–126 °C; ir (Nujol) 1640, 1610 cm^{-1}; nmr ($CDCl_3$) δ 3.09 (4H, t, J = 8 Hz), 3.44 (4H, t, J = 8 Hz), 3.82 (6H, s), 6.9–7.3 (6H, m), 11.79 (2H, s) ppm. *Mol. Wt.* calcd. for $C_{20}H_{22}O_6S_2$: 422.0856; found: 422.0857.

Irradiation of 3-Methylthiochroman-4-one 1-Oxide

The sulfoxide (2.0 g) was irradiated in degassed benzene (250 ml) under nitrogen in quartz for 35 h, by which time almost all of the sulfoxide band in the ir had disappeared. After evaporation of solvent, the residue was dissolved

in a mixture of methylene chloride – carbon tetrachloride (75:25) and chromatographed on silica gel.

A yellow liquid (136 mg, 10%) was eluted in 90% CH_2Cl_2–CCl_4; ir (neat) 1685 cm^{-1}; nmr ($CDCl_3$) δ 1.21 (3H, t, J = 7.5 Hz), 2.92 (2H, q, J = 7.5 Hz), 7.2–7.5 (3H, m), 7.8–8.0 (2H, m) ppm. Spectral comparison with propiophenone and a mp (174 °C) and mixture mp comparison of the semicarbazones showed this product to be identical with authentic propiophenone.

A second solid fraction (278 mg) was obtained on elution with 2% acetone in methylene chloride. This material proved to be rather impure and was rechromatographed on silica, affording a white solid (140 mg, 8%), mp 119–120 °C (cold crystallization from $CHCl_3$); ir ($CHCl_3$) 1724, 1680 cm^{-1}. *Anal.* calcd. for $C_{10}H_{10}O_2$: C 74.07, H 6.17; found: C 73.40, H 5.88.

Comparison of the ir and nmr spectra of an authentic sample of 2-benzoylpropanal, prepared by the base-catalyzed condensation of propiophenone with ethyl formate (29), with those of the photoproduct confirmed the identity of the photoproduct.

The third product isolated (110 mg, 9%) by elution with 2–5% acetone in methylene chloride was also a white solid, mp 121–122 °C, shown to be identical with benzoic acid by mp, mixture mp, and ir and nmr spectral comparisons.

Apart from considerable quantities of brown gummy, uncharacterizable material the only other compound recovered was the starting sulfoxide (294 mg, 15%), by elution with 30% acetone in methylene chloride.

Irradiation of 2-Benzoylpropanal

A solution of the keto-aldehyde (0.2 g) in degassed benzene (150 ml) was irradiated for 48 h in a quartz vessel, under nitrogen. Chromatography on silica gel led to the isolation of small quantities of benzoic acid, but no propiophenone. Starting material was also recovered. On repeating the irradiation in moist benzene after 12 h benzoic acid (67%) and propiophenone (13%) were recovered.

Irradiation of 3,6-Dimethylthiochroman-4-one 1-Oxide

The sulfoxide (0.9 g) was irradiated in degassed benzene (200 ml) with Vycor filtration for 24 h, under nitrogen. Chromatography of the crude product on silica gel gave, on elution with methylene chloride, a yellow oil (58 mg, 9%); ir (neat) 1685 cm^{-1}; nmr ($CDCl_3$) δ 1.20 (3H, t, J = 7 Hz), 2.38 (3H, s), 2.96 (2H, q, J = 7 Hz), 7.2–7.4 (2H, m), 7.65–7.8 (2H, m) ppm. The general similarity of the ir and nmr spectra to those of propiophenone led us to assign the 1-*m*-tolyl-1-propanone structure to this product.

A semisolid fraction obtained on elution with 2% acetone in methylene chloride was rechromatographed and afforded a white crystalline solid (50 mg, 7%) on elution with 2% acetone. After cold crystallization from chloroform a sample of this compound was further purified by recrystallization from cyclohexane; mp 122–123 °C; ir 1725, 1685 cm^{-1}; nmr (acetone-d_6) δ 1.35 (3H, m), 1.83 (3H, s), 3.05 (1H, m), 7.3–7.7 (3H, m), 8.09 (1H, dd, J = 2.0, 7.5 Hz), 9.86 (1H, s) ppm. *Anal.* calcd. for $C_{11}H_{12}O_2$: C 75.00, H 6.82; found: C 74.42, H 6.65.

Apart from considerable amounts of brown gummy material, some starting sulfoxide (121 mg, 13%) was recovered by elution with 50% acetone–methylene chloride.

Irradiation of 3,3-Dimethylthiochroman-4-one 1-Oxide

The sulfoxide (1.0 g) dissolved in 200 ml degassed benzene was irradiated under nitrogen in a quartz vessel with Vycor filtration for 10 h. The residue obtained on evaporation was chromatographed on silica gel.

A liquid product (106 mg, 15%) obtained on elution with 90% methylene chloride – carbon tetrachloride showed ir 1685 cm^{-1}; nmr ($CDCl_3$) δ 1.21 (6H, d, J = 7 Hz), 3.55 (1H, septet, J = 7 Hz), 7.3–7.6 (3H, m), 7.8–8.05 (2H, m) ppm. These spectra were identical with those of an authentic sample of isobutyrophenone and the semicarbazone of the photoproduct (mp 180–181 °C) was undepressed on admixture with that of isobutyrophenone.

Elution with 2% acetone in methylene chloride gave a semicrystalline product (314 mg, 37%) which showed two carbonyl peaks (1720, 1675 cm^{-1}) in the ir. The material was rechromatographed on silica gel affording a colorless oil (131 mg, 15%), bp 85–90 °C/1 Torr; nmr ($CDCl_3$) δ 1.47 (6H, s), 7.4–7.9 (5H, m), 9.73 (1H, s) ppm. This product was identical (ir, nmr) with an authentic sample of 2-methyl-2-benzoylpropanal prepared by benzoylation of isobutyraldehyde (morpholine) enamine by the method of Inukai and Yoshizawa (13). The (mono) 2,4-dinitrophenylhydrazone, mp 149–50 °C (ethanol) showed no depression of mp on admixture with a sample prepared from the known compound.

Elution with 5% acetone in methylene chloride afforded a crystalline product (151 mg, 25%) shown to be identical (mp, mixture mp) with benzoic acid.

The final fraction (81 mg, 8%), eluted with 50% acetone in methylene chloride, was shown to consist of the starting sulfoxide.

Irradiation of 2-Benzoyl-2-methylpropanal

A solution of the keto-aldehyde (0.3 g) in degassed benzene was irradiated under nitrogen in a quartz vessel, with a Vycor filter. After 1 h, the solution was evaporated and the product chromatographed on silica. Isobutyrophenone (180 mg, 71%) and benzoic acid (30 mg, 14%) were isolated as described in the original photolysis.

2,2-Dideuterio-3,3-dimethylthiochroman-4-one 1-Oxide

3,3-Dimethylthiochroman-4-one 1-oxide (0.33 g) in dioxan (10 ml) containing deuterium oxide (2 ml) and potassium *tert*-butoxide (0.25 g) was refluxed with stirring for 4 h. After acidification (20% deuterium chloride) the solution was evaporated under vacuum to remove most of the dioxan and a further 5–10 ml of deuterium oxide was added. Extraction with methylene chloride, washing (D_2O), and drying ($MgSO_4$) gave, on evaporation and distillation, (140 °C/0.5 Torr) a viscous liquid (0.23 g, 69%). Unlike the protonated precursor, this sulfoxide showed complete absence of the AB quartet at δ 3.45 ppm, indicating that exchange at the 2-position was complete.

Irradiation of 2,2-Dideuterio-3,3-dimethylthiochroman-4-one 1-Oxide

Irradiation in benzene and the subsequent column chromatography and isolation of the products were conducted exactly as described for the undeuterated 3,3-dimethylthiochroman-4-one 1-oxide. The isobutyrophe-

none thus isolated showed a molecular ion at *m/e* 150 showing that it retained two deuterium atoms. In the nmr of this product the methyl groups appeared as a *singlet* at δ 1.43 while the septet at δ 3.49 due to the methine proton had completely disappeared. Furthermore, the integrated intensities of the two groups of aromatic protons were now in the ratio 3:1 instead of 3:2, indicating that the other deuterium atom had replaced a hydrogen *ortho-* to the carbonyl group.

The keto-aldehyde (2-benzoyl-2-methylpropanal) also showed a molecular ion two units higher than the undeuterated analogue, at *m/e* 178, confirming that it was also doubly labelled. In the nmr the characteristic aldehyde proton signal at δ 9.70 ppm had disappeared and the integrated intensities of the two groups of aromatic protons had again become 3:1, instead of 3:2, thus confirming the presence of a deuterium atom in the formyl group and *ortho-* to the aromatic carbonyl group.

The benzoic acid isolated showed a molecular ion at *m/e* 123, indicating a singly-labelled compound. The 3:1 ratio for the aromatic protons and the presence of the characteristic acidic proton as a broad singlet at δ 12.6 ppm confirmed the C-2 position as the location of the deuterium atom.

Irradiation of 3-Methyl-2-phenylthiochroman-4-one 1-Oxide

A solution of the sulfoxide (1.0 g) in degassed benzene was irradiated under the usual conditions for 48 h. Chromatography on silica gel produced a rather impure product, which, after being rechromatographed and eluted with 1% acetone in methylene chloride, afforded white crystals (347 mg, 39%), mp 83–84 °C (cyclohexane); ir (Nujol) 1695, 1678 cm^{-1}; nmr ($CDCl_3$) δ 1.60 (3H, d, J = 7.5 Hz), 5.30 (1H, q, J = 7.5 Hz), 7.3–7.6 (6H, m), 7.8–8.1 (4H, m) ppm. *Anal.* calcd. for $C_{16}H_{14}O_2$: C 80.67, H 5.88; found: C 80.85, H 5.79.

The results suggest that this compound is 1,1-dibenzoylethane and this was confirmed by comparison (mp, mixture mp, ir, nmr) with an authentic sample prepared by methylation of dibenzoylmethane with methyl iodide and silver oxide (14).

Further fractions from the original chromatography produced only traces (<0.5%) of benzoic acid and some starting sulfoxide (117 mg, 12%).

Irradiation of 2,2-Dimethylthiochroman-4-one 1-Oxide

Method A

A solution of the sulfoxide (0.5 g) in degassed benzene (200 ml) was irradiated under nitrogen, with a Vycor filter, for 4 h. The residue was chromatographed on silica.

Elution with 1% acetone in methylene chloride gave a product (14 mg, 3%) which crystallized on standing; ir (Nujol) 1675 cm^{-1}; nmr ($CDCl_3$) δ 2.15 (3H, s), 2.52 (3H, s), 7.1–7.6 (3H, m), 7.87 (1H, dd, J = 1.5, 7.5 Hz) ppm. The spectral data and the mp (102–103 °C) for this compound are in accord with those reported for 2-isopropylidene-3-thiaindanone, mp 103–105 °C (30). Comparison with an authentic sample synthesized by the procedure of Morin *et al.* confirmed this conclusion.

A further solid product (38 mg, 8%) was obtained with the same eluent. This compound was shown by mp, mixture mp and spectral comparison to be identical with 2,2-dimethylthiochroman-4-one.

The starting sulfoxide (230 mg, 46%) was also recovered by elution with 50% acetone-methylene chloride.

Method B

Irradiation of the sulfoxide (0.5 g) in methanol (200 ml) with a Vycor filter, for 2 h and chromatography on silica gel led to the recovery of a new product (27 mg, 6%) by elution with benzene and 2% ether in benzene. This product was obtained as a white crystalline solid, mp 110–111 °C (benzene–petroleum ether); ir ($CHCl_3$) 2450 (w) and 1685(s) cm^{-1}; nmr ($CDCl_3$) δ 1.58 (1H, s, exchanges with D_2O), 1.85 (3H, s), 3.71 (2H, s), 4.91 (2H, br d, J_{gem} = 8 Hz), 7.1–7.35 (2H, m), 7.7–7.95 (2H, m) ppm; *m/e* 192 (M^+), 190, 177, 158, 145, 136 (100). *Anal.* calcd. for $C_{11}H_{12}OS$: C 68.75, H 6.25, S 16.66; found: C 68.84, H 5.84, S 16.88. This evidence is in accord with the thiol structure **47**. Starting material (180 mg, 36%) was also recovered on elution with ether.

Irradiation of the sulfoxide in mixtures of benzene and methanol containing 10–50% methanol gave essentially the same results. Use of a low-pressure (2 W Hanovia) mercury lamp gave a slightly improved conversion to thiol product (11%) after 4 h, but much less starting material was recovered in this experiment.

Method C

Irradiation of the sulfoxide (0.5 g) in a degassed mixture of benzene (100 ml) and isopropyl alcohol (100 ml) after 4 h, followed by the usual isolation procedure, indicated that no thiol was formed. The only identifiable compounds isolated from this experiment were 2,2-dimethylthiochroman-4-one (20 mg, 4%) and starting sulfoxide (150 mg, 30%).

Irradiation of 6-Methyl-2-phenylthiochroman-4-one 1-Oxide

A solution of the sulfoxide (1.0 g) in degassed benzene (200 ml) was irradiated under nitrogen for 24 h. Chromatography on silica gel gave among the early fractions an impure crystalline material which was rechromatographed and eluted with 1% ether in benzene as orange needles (125 mg, 14%) ir (Nujol) 1672 cm^{-1}; nmr ($CDCl_3$) δ 2.35 (3H, s), 7.3–7.9 (9H, m) ppm. The mp (144–145 °C; ethanol) of the photoproduct and the spectral data indicated the structure 5-methyl-2-benzylidene-3-thiaindanone (lit. (31) mp 145.5 °C). A sample of this compound was prepared by the alkaline condensation of benzaldehyde and 5-methylthiaindanone, synthesized by the method of Auwers and Arndt (31). The ir and nmr spectra of the samples were identical and the mp of the photoproduct remained undepressed on admixture with the authentic sample.

Further confirmation of the identity of the photoproduct was established by direct comparison of its dibromide, mp 111–113 °C, prepared on addition of bromine in chloroform, with the corresponding dibromide of 5-methyl-2-benzylidene-3-thiaindanone, lit (31) mp 116 °C.

The only other identifiable compound obtained on chromatography was the starting sulfoxide (441 mg, 44%) on elution with 30% acetone in methylene chloride.

Irradiation of 2,2,3,3-Tetramethylthiochroman-4-one 1-Oxide

Method A

Irradiation of the sulfoxide (200 mg) in dry benzene

(200 ml) in Pyrex for 6 h under nitrogen afforded on evaporation a yellow oil. Chromatography on silica gel and elution with 70–90% methylene chloride – carbon tetrachloride afforded an essentially colorless oil (62 mg, 33%), shown by ir and nmr spectral comparison to be identical with 2,2,3,3-tetramethylthiochroman-4-one. Starting sulfoxide (19 mg, 10%), eluted with 15% acetone in methylene chloride, and dark viscous oils were the only other materials obtained.

Method B

Irradiation of the sulfoxide (200 mg) in degassed acetone (150 ml) in Pyrex for 6 h under nitrogen, followed by a similar chromatographic separation afforded 2,2,3,3-tetramethylthiochroman-4-one (70 mg, 38%) and the starting sulfoxide (24 mg, 12%) as the sole identifiable products.

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