Tetrahedron Vol. 27, pp 5163 to 5176. Pergamon Press 1971. Printed in Great Britain

PHOTOCHEMISTRY—II*

THE PHOTOCHEMISTRY OF THE 4-THIOISOCHROMAN-1-ONE-4-OXIDE SYSTEM†

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(*Received in the UK* 24 *August* 1970: *Accepted for publication* 24 *April* 1971)

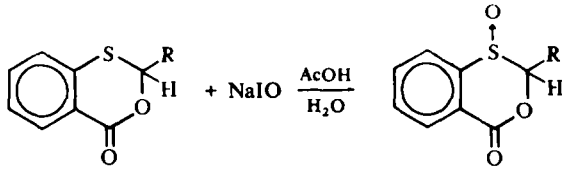
Abstract—Three different 3-substituted 4-thioisochroman-1-one-4-oxides have been prepared and the configuration of the 3-phenyl sulphoxides determined by NMR spectroscopy. The photochemistry of the system was studied by means of O^{18}-labelling of the sulphoxide oxygen and triplet sensitizers.

THE research on the photochemistry of sulphoxides has in general been very scattered.[1-13] A study of the pyramidal inversion in the sulphoxide group has been reported.[2-4] but only one general photochemical investigation of a series of simple sulphoxides has been submitted (as part of a Ph.D. Thesis[11]). On the other hand the spectroscopy of the sulphoxide group has attracted much attention.[17-28] We have extended our recent investigation of the photochemistry of the 3-substituted 4-thioisochroman-1-ones[1] to include the photolysis of the corresponding sulphoxides. In addition to the photochemistry of sulphoxides, measurements on the variations in chemical shifts due to changes of solvent are reported in this paper and are related to the configuration of the 3-phenyl compounds.

Preparation of the sulphoxides

Three different sulphoxides (IV–VI) were prepared. The oxidation of the 4-thioisochromanone system was not straightforward. Attempts to oxidize with H_2O_2[14]

SCHEME 1



R = H (I)
R = CH_3 (II)
R = Ph (III)

R = H (IV)
R = CH_3 (Va and Vb)
R = Ph (VIa and VIb)

* Part I, see ref.[1]

† Presented in part at the 2nd International Congress of Heterocyclic Chemistry, July 1969 in Montpellier, France.

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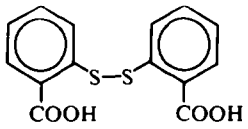


(VII)

in AcOH and AcOH–Ac_2O mixtures were unsuccessful. Instead of the desired sulphoxide we isolated 2,2'-dithiodibenzoic acid (VII). Also oxidation with $NaIO_4$[14a] in EtOH and EtOH–H_2O mixtures failed.

However. when a solution of the thioisochromanone in AcOH was treated by adding dropwise a solution of $NaIO_4$ in AcOH H_2O mixture (2:1). the oxidation was successful (Scheme 1). The product was a mixture of the two geometrical isomers where the sulphoxide oxygen was *cis* and *trans* to the 3-R group (R ≠ H). respectively. When R = Ph. the ratio *cis/trans* equals $\frac{1}{2}$. This was determined by NMR and by PLC (silica gel). It was not possible to determine the ratio of the methyl compounds (R = CH_3) exactly either by separation or by NMR. but it was close to 1:1 (with the *trans* isomer slightly prevailing).

When R = Ph, it was possible to get the *cis* isomer from the product mixture in pure form by fractional recrystallization from $CHCl_3$. The method of choice to prepare nearly pure *trans* sulphoxide (R = Ph) was to oxidize the isothiochromanone in $CHCl_3$ by *m*-Cl-perbenzoic acid.[15] Here the stereoselectivity was over 95% in favour of the *trans* sulphoxide. When the same method was applied to the 3-methyl isothiochromanone, it gave no greater stereospecificity than the periodate oxidation.

Finally. the 3-phenyl compound was oxidized with iodobenzene-α,α-dichloride in aqueous pyridine.[16] In this case the product was again almost pure *trans* sulphoxide. The yield was lower than in the procedures earlier described. However. the advantage of this method was that it was now possible to get isotopic enrichment of the sulphoxide oxygen.

Spectroscopic studies

Ultraviolet spectra. The absorptions (EtOH) appear in Table 1.

TABLE 1. UV ABSORPTIONS OF THE THIOISOCHROMANONE-4-OXIDES IN ETHANOL

	λ (in nm)	ε
IV	283	1905
	289 (sh)	1770
Va	282	1855
Vb	288 (sh)	1810
VIa	290 (sh)	2370
VIb	284	2640
	290	2600

Infrared spectra. In all cases the sulphoxides prepared showed strong absorption near 1050 cm^{-1} (Table 2), characteristic of the sulphoxide group.

TABLE 2. IR STRETCHING FREQUENCIES OF THE SULPHOXIDE GROUP

Compound	ν cm^{-1}	Phase
IV	1045 and 1050 (sh)	KBr
Va. b	1037 and 1050	KBr
VIa	1066 (broad)	KBr
VIb	1050 and 1063	KBr
VIa	1060 and 1065	$CHCl_3$
VIb	1063	$CHCl_3$

All the spectra with the exception of VIb exhibited a doublet or a broad singlet in the region of the sulphoxide stretching frequency. Only the solution spectrum of the *cis* isomer (VIb) displayed a singlet absorption.

The reason for the appearance of the doublets may be due to the existence of conformational isomers. This question has been examined earlier in the literature.[17–19] and it has been stated[17, 18] that in cyclic sulphoxides the most stable conformation is the one with the sulphoxide oxygen axial. In non-cyclic sulphoxides the occurrence of more bands near 1050 cm^{-1} has been claimed to be caused by the presence of more rotamers.[19] In the system examined here the ring containing the sulphoxide group is very rigid because of its fusion to the benzene ring, and the angle of the sulphur-oxygen bond to the plane of the benzene ring remains almost constant, independent of the conformations of the other atoms in the ring. This can be seen by the inspection of Dreiding models. The inspection also gives a possible explanation for the differences in the multiplicity of the various sulphoxide absorptions. Adopting the idea of different absorptions due to different rotamers having the sulphoxide oxygen situated between various groups, it can be seen that for the *trans* isomer the 3-phenyl group has the possibility of being either equatorial with the sulphoxide oxygen between the phenyl group and hydrogen (Fig 1) or axial with

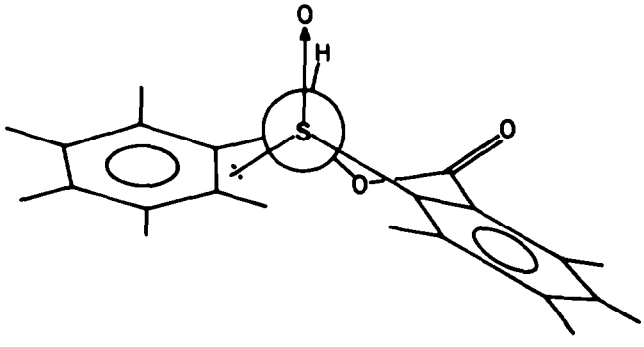


FIG 1

the oxygen outside the angle between phenyl and hydrogen (Fig 2). In both cases the interaction between the phenyl group and the sulphoxide oxygen is not very important.

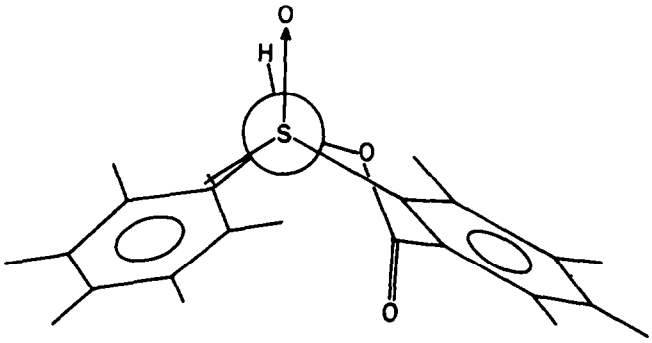


FIG 2

Concerning the *cis* sulphoxide (VIb) it can be seen that when the phenyl group is equatorial (Fig 3), its interaction with the oxygen is stronger than in VIa, but not so strong as when the phenyl group is axial (Fig 4, eclipsing interaction is greater). Evidently this has no influence on the doublet in the solid state (KBr), but when the spectrum is recorded in $CHCl_3$, the solvation of the sulphoxide will exclude the existence of the conformer with axial phenyl group and only one sulphoxide absorption band will appear.

Also in IV the reason for the occurrence of the doublet may be caused by different conformers, whereas in V it might as well be due to the presence of the two stereoisomers. From the present data it would be hazardous to correlate any of the absorption bands to a specific conformation.

NMR spectra. The NMR spectra displayed evident effects of the chemical shifts when going from the sulphide to the corresponding sulphoxide (Table 3). The protons

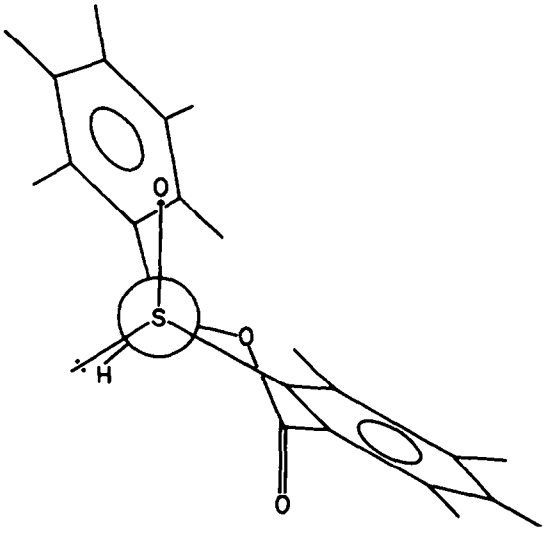


FIG 3

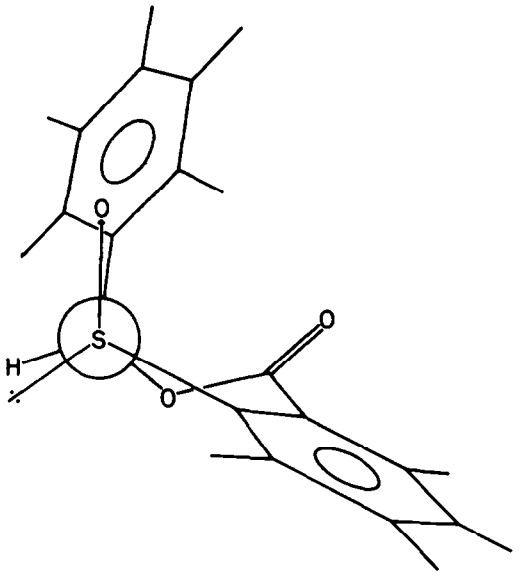


FIG 4

TABLE 3. NMR SPECTRA ($CDCl_3$) OF THE THIOISOCHROMANONES AND THE CORRESPONDING 4-OXIDES

Compound	Protons	σ (ppm)	J cps
I	CH_2	5·42	
	Aromatic	7·1–7·7	
		8·0–8·3	
IV	C–H′	5·34	11·5 d
	C–H″	5·45	11·5 d
	Aromatic	7·6–8·0	
		8·1–8·3	
II	CH	5·68	6·5 q
	CH_3	1·78	6·5 d
	Aromatic	7·1–7·7	
		8·0–8·3	
Va	CH	5·25	6·5 q
	CH_3	1·67	6·5 d
	Aromatic	7·4–8·0	
Vb	CH	5·31	7·0 q
	CH_3	1·83	7·0 d
	Aromatic	7·4–8·0	
III	CH	6·55	
	Aromatic	7·1–7·7	
		8·1–8·3	
VIa	CH	6·01	
	Aromatic	7·4–8·4	
VIb	CH	6·14	
	Aromatic	7·4–7·6	
		7·8–8·0	

α to the sulphoxide group were especially affected. In all cases the signals from the sulphoxide α-protons occurred at higher field relative to the sulphides. This effect was most pronounced in the spectra of the 3-phenyl substituted sulphoxides (VIa and b). As to the difference in the α-protons absorption of VIa and b we made a preliminary assignment where the phenyl group in VIa is *trans* and in VIb where it is *cis* to the sulphoxide oxygen in accordance with recent investigation.[24] Considering the anisotropic effects from the sulphur-oxygen bond will be of little help because the nature of this effect has not yet been definitely settled. both acetylenic[26] and carbonyl type[28] anisotropy having been postulated.

However. the difference in anisotropic effects exerted by the α-phenyl group will give information consistent with solvent experiments (*vide infra*). In the *trans* configuration the phenyl group can rotate almost freely, whereas in the *cis* isomer the rotation of this group is hindered to some degree. Therefore. the α-proton will be on the average more in the plane of the phenyl group in the *cis* isomer than in the *trans* isomer and will be subjected to a larger deshielding effect than in the *trans* isomer. The chemical shift of the α-proton at 6·14 ppm will therefore represent the *cis* isomer and $\sigma = 6{\cdot}01$ the *trans* isomer.

The question of configuration was examined more closely in a series of papers by Nishio.[20–23] The measurement of the solvent effects on the signal of the α-protons proved to be an elegant way of determining the configuration of the sulphoxides. The most significant effect was obtained when going from $CDCl_3$ to trifluoro acetic acid (TFA). The ranges of variations for the chemical shifts were:

$$\Delta\sigma = -0{\cdot}22 \text{ to } -0{\cdot}31 \text{ ppm for the } cis \text{ isomer}$$
$$\Delta\sigma = -0{\cdot}47 \text{ to } -0{\cdot}60 \text{ ppm for the } trans \text{ isomer}$$
$$\Delta\sigma = \sigma(CDCl_3) - \sigma(TFA)$$

In our case the variations were somewhat greater (Table 4).

TABLE 4. EFFECT EXERTED BY SOLVENT SHIFT ON THE SIGNAL CORRESPONDING TO THE METHINE PROTON

Compound	Solvent	σ (ppm)	$\Delta\sigma$
VIa	$CDCl_3$	6·01	−0·72
VIa	TFA	6·73	
VIb	$CDCl_3$	6·14	-0·53
VIb	TFA	6·67	

We suggest that VIa has the *trans* configuration and VIb the *cis* configuration. despite our higher numerical values for the difference ($\Delta\sigma$) in comparison to other sulphoxides.[22] From these results it is seen that if the anisotropic effect was to account for the difference in chemical shifts of the α-protons in VIa and VIb. this would have to be a carbonyl rather than an acetylenic type of anisotropy.

Because of lack of pure Va and Vb it was not possible to make the same measurements on these compounds.

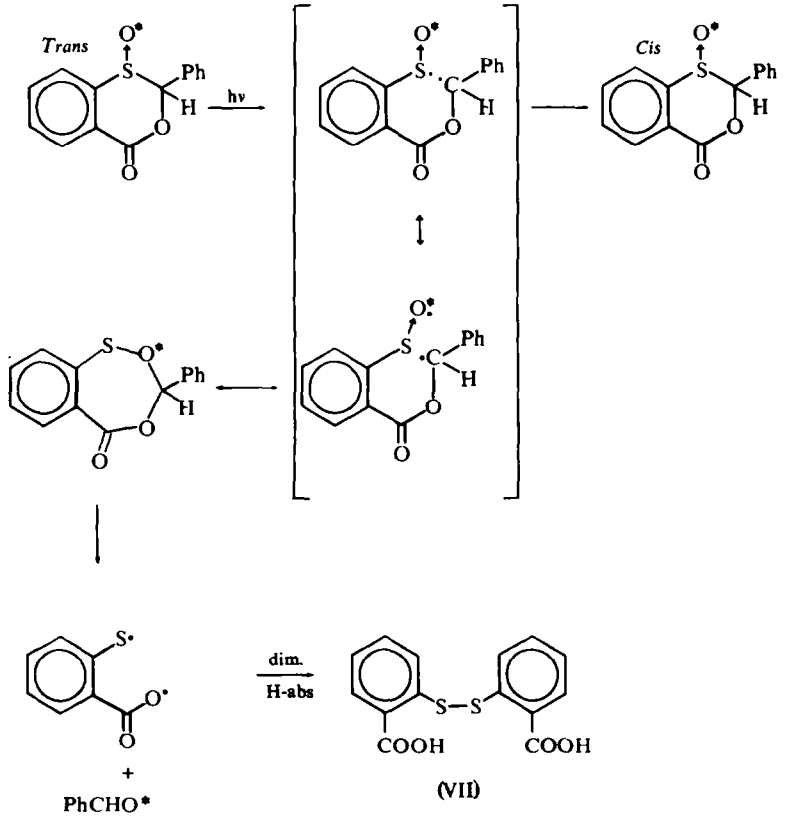
The photolysis of the trans *3-phenyl-4-thioisochroman-1-one-4-oxide* (VIa)

VIa was irradiated in a Rayonet photoreactor equipped with RUL 3500 Å lamps. The reaction medium was $CHCl_3$ purified from EtOH stabilizer.

The products isolated in addition to the recovered starting material were (Table 5) 2.2′-dithiodibenzoic acid (VII), *cis*-3-phenyl-4-thioisochroman-1-one-4-oxide (VIb), 3-phenyl-4-thioisochroman-1-one-4,4-dioxide (VIII), and benzaldehyde (IX), furthermore varying amounts of unidentified polymer were formed. No other products could be detected by TLC. The percent yields were taken relative to the consumed amount of starting material.

To explain the products formed we suggested three different mechanisms (Schemes 2–5).

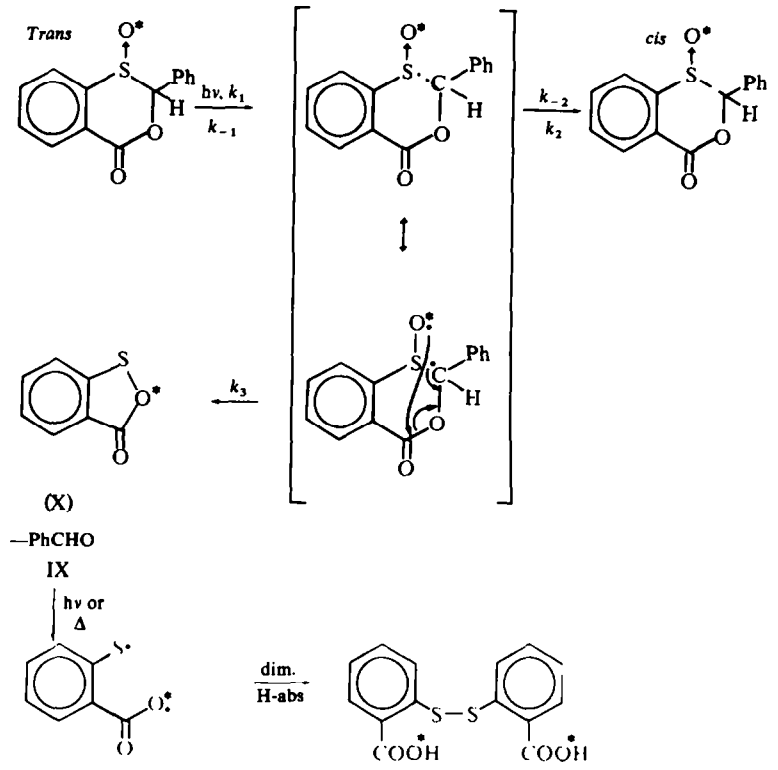
SCHEME 2



At first glance the mechanism shown in Scheme 2 seems most likely since rearrangement from sulphoxides to sulphenate esters are known in the ground state chemistry[34] as well as in photochemistry.[11] Elimination of benzaldehyde yields a phenyl thio-2-carboxyl-di-radical which gives VII by dimerisation and abstraction of hydrogen from the solvent or from the traces of water in the solvent.

In Scheme 3 the presence of the same diradical is postulated. The necessity of abstracting a hydrogen radical leads us to use C_6H_6 in which hydrogen abstraction is difficult, and which could be more carefully dried as a solvent.

SCHEME 3



A way to diminish the possible importance of water as the hydrogen source when $CHCl_3$ was the solvent was to raise the concentration of VIa in the $CHCl_3$ solution. From Table 5 is seen that the relative yield of VII was considerably lowered in benzene but not in the concentrated $CHCl_3$ solution, hydrogen must therefore be abstracted from the solvent. Also from IR it was furthermore seen that the compound was not pure but mixed with another compound which could be the corresponding anhydride (XII) of VII: $\nu = 1780$ and $1715\ cm^{-1}$. Hydrolysis of the mixture only gave compound VII.

Another feature of the experiments with VIa is the markedly increased amount of sulphone VIII. In the C_6H_6 case this may be due to oxygen in the solution. But in $CHCl_3$ the high concentration of the sulphoxide makes this unlikely although some of the sulphone may have this origin, and the disproportionation reaction shown in Scheme 4 may be participating.[13] This leads to the idea of the mechanism shown in Scheme 5, the oxidant being the sulphoxide. The step corresopnding to the step

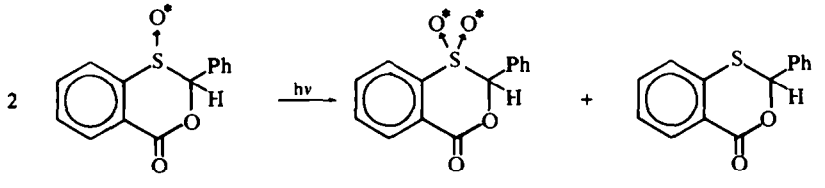
XI → XII has not been observed or described in the literature, only similar α-diketone cases.[35–37] When a $CHCl_3$ solution of the α-diketone XI (prepared from photolysis of III in light petroleum) was irradiated with simultaneous bubbling of oxygen through the solution, only traces of the acid VII were isolated after hydrolysis of the photolyses mixture, thus making the mechanism depicted in Scheme 5 unlikely.

TABLE 5. PRODUCT DISTRIBUTION FROM THE PHOTOLYSIS OF VIa AND VIb

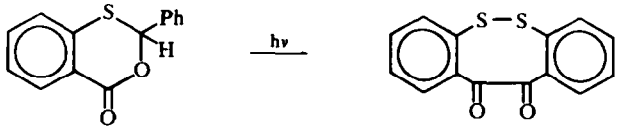
Compounds/Amounts	VIa			VIb	
Starting material (g)	0·5	1·0	22·0	1·0	1·0
Recovered VIa (VIb) (g)	0·130	0·330	5·3	0·579	0·440
Inversion to VIb (VIa) (%)	~5	17	13	30	0
VII (%)	35	31	29	12	25
VIII (%)	11	5	25	23	0
IX (%)	27	20	20	19	16
Unidentified products (%)	21	27	13	16	59
Solvent	$CHCl_3$	$CHCl_3$	$CHCl_3$	C_6H_6	C_6H_6
ml	250	250	250	250	250
Reaction time (h)	4	18	110	4	4

To rigorously determine the right mechanism, we repeated the photolysis of VIa with 20% O^{18}-enrichment in the sulphoxide group. If the mechanism of Scheme 2 is followed, the O^{18}-enrichment will appear in the benzaldehyde part of the molecule. On the other hand, if the mechanism of Scheme 3 is involved, the enrichment will be found in both carboxyl groups of VII. Finally, if the third mechanism (Scheme 5) is right, and the oxidant is the sulphoxide itself, only one of the carboxylic groups will be enriched.

SCHEME 4

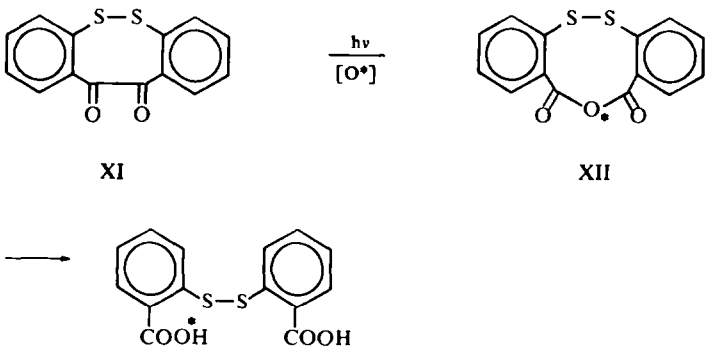


VIII III



III XI

SCHEME 5



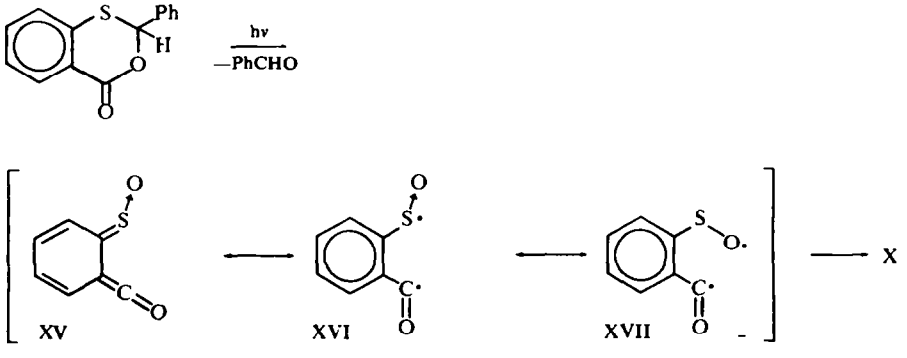
XI XII VII

The enrichment in the photoproducts were analysed by mass spectrometry. The molar peak $m/e = 306$ in VII showed to be too weak to give any information of the enrichment. The peak $m/e = 152$ represented by the structure XIII, and $m/e = 136$ (base peak), structure XIV, were used instead for the measurement of the isotope-enrichment.

XIII XIV

The result of the measurement was that the peak $m/e = 154$ was enriched $20 \pm 1\%$ and $m/e = 138$ $10 \pm 1\%$, whereas no enrichment was found in the benzaldehyde. Thus the mechanism of Scheme 3 is likely to be responsible for the photofragmentation.

SCHEME 6



XV XVI XVII

In Scheme 3 (and 2) a scission of the sulphur-α-carbon bond occurs after the initial excitation, the diradical formed being stabilized by the arenesulphinyl group and the benzylic group. This diradical probably is the intermediate for the stereomutation yielding the *cis* isomer[38] whereas the other resonance form, the thioperoxyform, is responsible for the further fragmentation of the molecule.

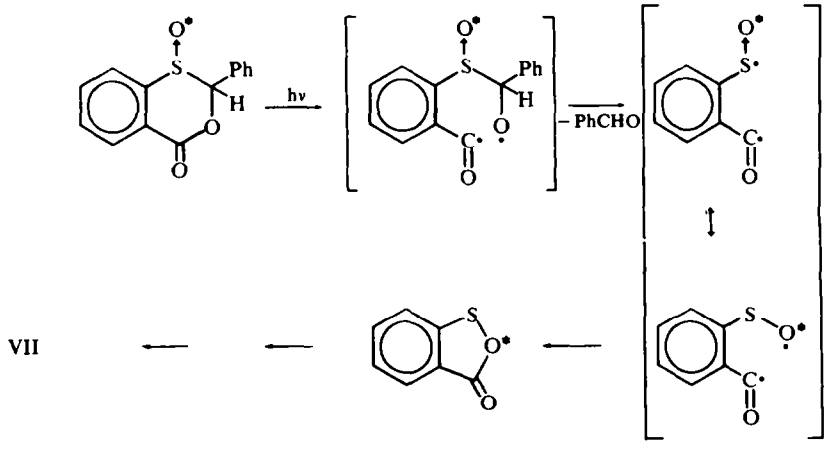
It is not unlikely that the benzaldehyde is detached prior to the formation of X, thus involving the sequence of Scheme 6 as a part of the Scheme 3. Here the sulphine structure (XV) is stabilizing the diradicals (XVI) and (XVII) via resonance. Literature records precedence for the formation of sulphines from sulphoxides.[9] Compound X was never isolated from the photolysis mixture, but the corresponding Se- and Te-compounds are known to exist.[39]

Photolysis in rigid matrices (EPA and 2-Me-THF at 77°K) did not help to decide the question of specific participation of photochemical and thermal processes in the whole reaction sequence. It proceeded very slowly when compared to the matrix photolysis of the corresponding sulphide III.[1] The lack of long wavelength absorption of the primarily formed photoproducts is supporting the suggested carbonyl attack by the thioperoxyradical (Scheme 3). Another piece of contributing evidence may be the observed difference in low-temperature matrix photolysis of sulphoxides Ph—S(O)—CH_2—Ph[6] (greenish-yellow coloured intermediate) and VI (no coloured intermediate).

The question of spin multiplicity in the excited state was examined by various triplet sensitizers. In Table 6 it is seen that the degree of decomposition is fairly constant for sensitizers having triplet energy > 59 kcal/mol. When using 2-acetonaphtone as sensitizer the fragmentation was partly quenched, whereas the amount of sulphone was raised considerably. Also the relative yield of the *cis* isomer was depressed, thus supporting the suggestion that this compound is formed *via* the same homolytic bond scission involved in the fragmentation.

This also rules out the possibility of initial bond scission between the carbonyl group and the ring oxygen (Scheme 7) even if the prediction of the 20% O^{18}-enrichment is correct because in this case there will be no stereomutation of the sulphoxide group.

SCHEME 7



The *cis* sulphoxide VIb was much more stable to irradiation in $CHCl_3$ than VIa. Thus the photolysis of VIb gave only traces of the fragmentation products. No inversion to VIa or formation of VIII was observed either.

However, in C_6H_6, the disulphide VII as well as benzaldehyde were isolated (Table 6), whereas no inversion was observed in this case either. Although we have made no measurements of the rate constants, this may be due to differences in reaction rates (Scheme 3), $k_{-1} \ll k_{-2} \approx k_3$ would explain these observations. In summary, the mechanism of the Scheme 3 seems to be responsible for the photochemical products obtained from the sulphoxide VI, together with a participation of the disproportionation (as given in Scheme 5).

TABLE 6. PRODUCT DISTRIBUTION FROM SENSITIZER EXPERIMENT OF VIa IN BENZENE

Amounts	VIa				
Starting material (g)	1·0	1·0	1·0	1·0	1·0
Recovered VIa (g)	0·579	0·520	0·409	0·450	0·485
Inversion to VIb %	30	22	28	23	13
VII %	12	10	12	5	~1
VIII %	23	24	31	25	60*
IX %	19	22	17	21	11
Unidentified products %	16	22	12	26	15
Solvent	C_6H_6	C_6H_6	C_6H_6	C_6H_6	C_6H_6
ml	250	250	250	250	250
Reaction time (h)	4	4	4	4	4
Sensitizer	none	aceto-phenone	benzo-phenone	thioxanthen-9-one	2-aceto-naphtone
E_T kcal/mole		74	69	65	59

* In disproportionation initiated by irradiation it is not possible to get a 60% yield of the sulphone. Therefore, there must be an alternative way of oxidizing the sulphoxide.

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were determined on either a Perkin–Elmer Infracord or Beckman IR-18A spectrometer and UV spectra on a Bausch and Lomb Spectronic 505 spectrometer. NMR spectra were recorded on a Varian A-60 spectrometer using TMS as an internal standard. The mass spectra were recorded on an AEI M.S. 902 mass spectrometer.

In low-temperature absorption work quartz cells and quartz dewar equipped with flat windows and containing liquid N_2 were used.

The preparation of compounds I–III is described by Senning and Lawesson.[40, 41]

The preparation of the sulphoxides. The thioisochromanone (0·01 mole) was dissolved in 30 ml of glacial AcOH. Under magnetic stirring a solution of 0·011 mole $NaIO_4$ in AcOH H_2O (40 ml/20 ml) was added dropwise. After 15 hr, stirring at room temperature, the red coloured solution (I_2) was poured into *ca.* 0·5 l H_2O, extracted with $CHCl_3$ and the $CHCl_3$ solution washed with $NaHSO_3$ (to remove the I_2), and finally with Na_2CO_3 aq to remove acidic by-products. Recrystallized from $CHCl_3$ or $CHCl_3$-petroleum, or purified by chromatography on silica gel using a mixture of 10% acetone, 45% C_6H_6, and 45% petr. ether as eluent. The yields were 60–70%. M.ps: IV: 112–114°, Va, Vb: 95–105° (mixture of two isomers), VIa: 130–132°, and VIb: 134–135°.

IV (Found: C, 52·82; H, 3·43; S, 17·79. Calc.: C, 52·75; H, 3·22; S, 17·56%). Va, b (Found: C, 55·07; H, 4·38; S, 16·35. Calc.: C, 55·10; H, 4·11; S, 16·31%). VIa (Found: C, 64·45; H, 3·88; S, 12·26. Calc.: C, 65·12; H, 3·90; S, 16·35%). VIb (Found: C, 64·76; H, 3·84; S, 12·58. Calc.: C, 65·12; H, 3·90; S, 12·39%).

The photolysis of 3-phenyl-4-thioisochroman-1-one-4-oxide in $CHCl_3$. The sulphoxide. VIa. dissolved in 250 ml $CHCl_3$ and stirred by N_2-flow. was irradiated in a Rayonet photoreactor at 3500 Å. The precipitate formed was filtered. and the filtrate evaporated under red. press.. This enriched mixture was fractionated by PLC using 10% acetone. 45% C_6H_6. and 45% petr.ether as eluent. The isolated compounds were identified by their IR and NMR spectra. The sulphone (VIII) was identified by the spectra IR: ν = 1155 and 1320 cm^{-1}. NMR ($CDCl_3$) 6·39 σ ppm and 7·3–8·5 σ ppm. m.p. 130–160 (decomp.). (Found: C. 61·55; H. 3·63; S. 11·55. $C_{14}H_{10}O_4S$ requires: C. 61·32: H. 3·68; S. 11·67%).

The sensitizer experiments. In the sensitizer experiments the solvent was C_6H_6. other conditions identical with previous photolysis. The concentration of the sensitizer was twice of the concentration of the sulphoxide. After filtration of the photolysis mixture the solvent was removed under red. press. and the amounts determined by NMR.

All the solvents used for chromatography were distilled before use. $CHCl_3$: The EtOH stabilizer was removed by extraction with conc. H_2SO_4 followed by washing five times with H_2O. dried over $CaCl_2$. and distilled.

Benzene Analar. BDH Chemical Ltd.. U.K.. was dried over Na and used without any further purification.

Acknowledgements—This work was supported by grants from Statens almindelige Videnskabsfond and Carlsberg-fondet. Thanks are expressed to Dr. G. Schroll for the mass spectra. We are grateful to Prom's kemiske Fabrik for supply of thiosalicylic acid.

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