

# Photochemistry of Organic Sulphur Compounds

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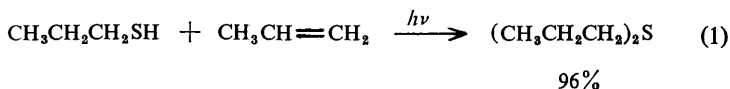
## 1 Introduction

This review forms part of an attempt to give a systematic description of the characteristic photochemical reactions of organic compounds on the basis of their functional groups. Introductory surveys have been presented previously for carbonyl<sup>1</sup> and for olefinic<sup>2</sup> chromophore systems. Here are described the photoreactions of several groups of compounds with sulphur-containing chromophores.

## 2 $\sigma$ -Bonded Compounds

Although there are similarities between the photochemistry of thiols, sulphides, and disulphides and that of their oxygen analogues (alcohols, ethers, and peroxides), differences arise (i) because the C—S bond is weaker than the C—O bond, (ii) because alkoxy ( $R_3C—O\cdot$ ) and thiyl ( $R_3C—S\cdot$ ) radicals behave differently in the secondary reactions, and (iii) because the excited states are different in energy. The sulphur compounds have lower-energy  $n \rightarrow \sigma^*$  electronic transitions because of the higher energy of the sulphur non-bonded electrons ( $\lambda_{\max}$  for MeSH, MeSMe, and MeSSMe is at 228, 212, and 255 nm respectively; *cf.* values of 184, 184, and 215 nm for MeOH, MeOMe, and MeOOME).

Thiols undergo homolytic S—H bond cleavage on irradiation (254 nm), despite the fact that the C—S bond is much weaker than the S—H bond. This is often encountered in excited-state reactions, that a bond to hydrogen cleaves in preference to a weaker bond, and it implies that dissociation is faster than randomization of energy. Methanethiol (MeSH) yields hydrogen ( $\Phi = 0.83$ ), dimethyl disulphide ( $\Phi = 0.99$ ), and methane ( $\Phi = 0.16$ ) from the radicals obtained on cleavage.<sup>3</sup> Anti-Markovnikov addition of thiols to alkenes<sup>4</sup> can be of value in the preparation of sulphides (1), and ultraviolet radiation is often the



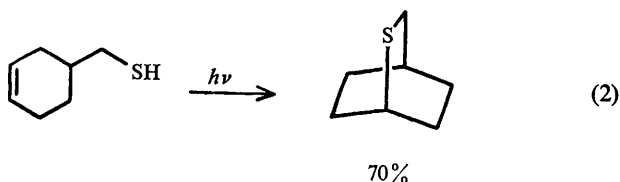
<sup>1</sup> J. D. Coyle and H. A. J. Carless, *Chem. Soc. Rev.*, 1972, 1, 465.

<sup>2</sup> J. D. Coyle, *Chem. Soc. Rev.*, 1974, 3, 329.

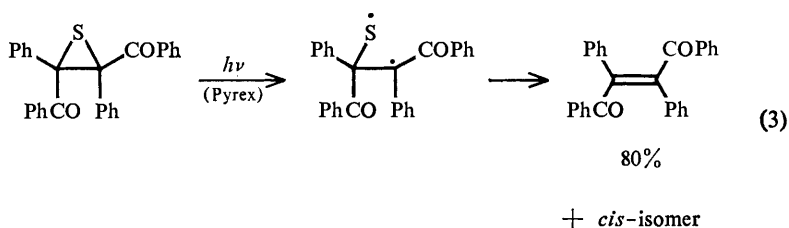
<sup>3</sup> L. Bridges and J. M. White, *J. Phys. Chem.*, 1973, 77, 295.

<sup>4</sup> R. M. Kellogg, in 'Methods in Free Radical Chemistry', ed. E. S. Huyser, Marcel Dekker, New York, 1969, Vol. 2, p. 17; F. W. Stacey and J. F. Harris, *Org. Reactions*, 1963, 13, 150.

most convenient initiator. Heterocyclic sulphur compounds can be formed by an analogous intramolecular reaction (2).<sup>5</sup>

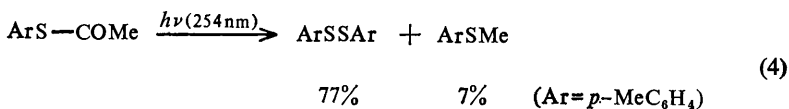


Dialkyl sulphides undergo primary C—S cleavage on direct or sensitized irradiation. Dimethyl sulphide (MeSMe) gives ethane ( $\Phi = 0.47$ ) and dimethyl disulphide ( $\Phi = 0.37$ ) by dimerization of Me· and MeS· radicals.<sup>6</sup> With thiirans<sup>7</sup> extrusion of sulphur often occurs (3), and in a few simple cases the



relatively long-lived intermediate biradical (*e.g.*  $\cdot\text{CH}_2\text{CH}_2\text{S}\cdot$ ) has been trapped by added alkene.

*S*-Aryl or *S*-alkyl thiocarboxylates give fragmentation products<sup>8</sup> by C—S cleavage (4); no photo-Fries rearrangement occurs (*cf.* aryl carboxylates).



Both C—S and S—S homolytic cleavage occur on irradiation of dialkyl disulphides with short-wavelength u.v. radiation, but with lower-energy radiation C—S cleavage is important only if stabilized carbon radicals are produced. Hence primary and secondary dialkyl disulphides are relatively photostable in solution towards 254 nm radiation because S—S cleavage leads to radicals which recombine. Tertiary dialkyl disulphides give products by C—S cleavage (5), and the alkyl radicals can be trapped (6).<sup>9</sup>

<sup>5</sup> J.-M. Surzur, R. Nougier, M.-P. Crozet, and C. Dupuy, *Tetrahedron Letters*, 1971, 2035.

<sup>6</sup> D. R. Tycholiz and A. R. Knight, *J. Amer. Chem. Soc.*, 1973, **95**, 1726.

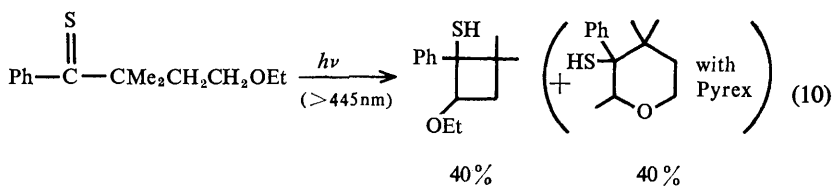
<sup>7</sup> A. Padwa, *Internat. J. Sulfur Chem. (B)*, 1972, **7**, 331.

<sup>8</sup> J. R. Grunwell, N. A. Marron, and S. I. Hanhan, *J. Org. Chem.*, 1973, **38**, 1559.

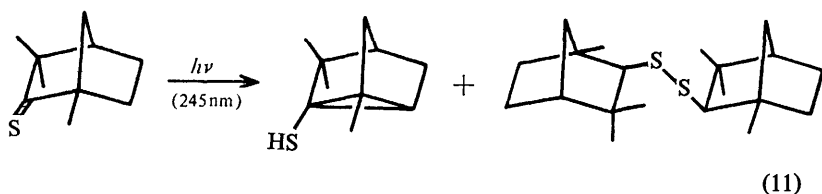
<sup>9</sup> G. W. Byers, H. Gruen, H. G. Giles, H. N. Schott, and J. A. Kampmeier, *J. Amer. Chem. Soc.*, 1972, **94**, 1016.



no reaction takes place unless the C—H bond in the  $\gamma$ - or  $\epsilon$ -position is weaker than normal. The ( $n, \pi^*$ ) state then undergoes  $\gamma$ -hydrogen abstraction, and this can be accompanied by  $\epsilon$ -abstraction with higher-energy radiation (10).

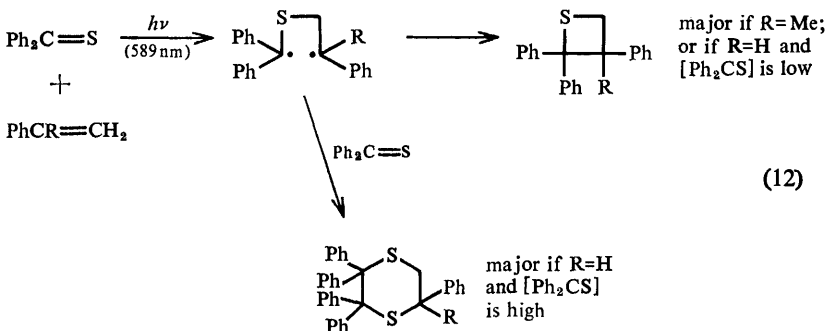


Thiocamphor and similar rigid compounds undergo intramolecular  $\beta$ -hydrogen abstraction (11),<sup>13</sup> and this emphasizes the wide range of internal abstractions which are commonly encountered with thioketones.



Photocycloaddition of thiocarbonyls with alkenes gives thietans and 1,4-dithians.<sup>14</sup> The ( $n, \pi^*$ ) thiocarbonyl excited state reacts with electron-rich alkenes to give both products, and the ratio depends on steric factors and on the concentration of thioketone, as expected for a reaction through a biradical intermediate which can be trapped by ground-state thioketone (12).

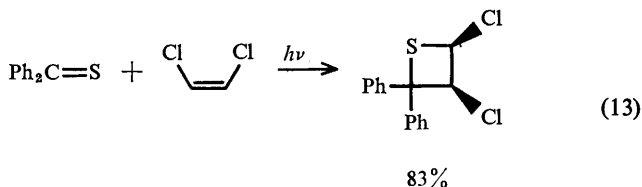
The reactions with electron-deficient alkenes are more complex. A higher-energy excited state of thiobenzophenone is reactive, and a thietan is formed



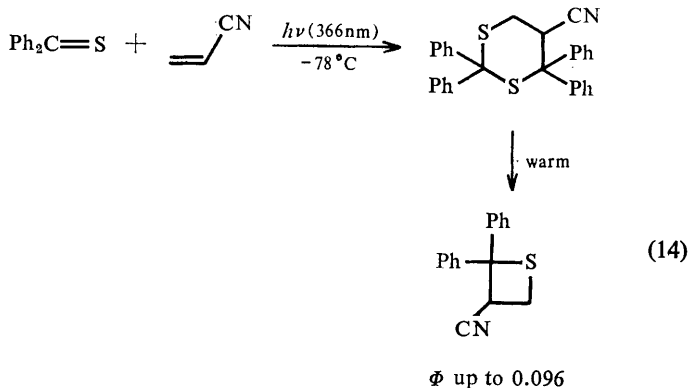
<sup>13</sup> D. S. L. Blackwell and P. de Mayo, *J.C.S. Chem. Comm.*, 1973, 130.

<sup>14</sup> A. Ohno, *Internat. J. Sulfur Chem. (B)*, 1971, 6, 183.

stereospecifically (13).<sup>15</sup> Sometimes, as with thiobenzophenone and dichloroethylene, the ( $n, \pi^*$ ) state is unreactive; sometimes, as with thiobenzophenone



and dimethyl maleate,<sup>16</sup> both states are reactive but the ( $n, \pi^*$ ) gives thietan non-stereospecifically. With acrylonitrile,<sup>17</sup> the thietan formed with shorter-wavelength radiation arises from thermal decomposition of a 1,3-dithian (14), of a



type which has been isolated at room temperature in other systems. With longer-wavelength radiation the expected thietan and 1,4-dithian are produced, together with a product arising from intramolecular attack on a phenyl ring in the biradical intermediate [similar to that obtained with alkynes; see (15)].

1,3-Dienes react with thiobenzophenone to give 3-vinylthietans, which predominate over the thermal Diels-Alder adducts (4-thiacyclohexenes) if the irradiation is carried out at low temperature.<sup>16</sup> Alkynes lead to isothiochromenes (15) by internal attack in the biradical intermediate.<sup>18</sup>

The cyclodimerization of alkyl thiocarbonyl compounds to 1,3-dithietans is brought about by irradiation (16);<sup>19</sup> it also occurs in an acid-catalysed thermal reaction.

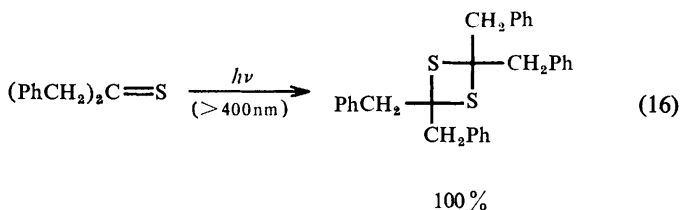
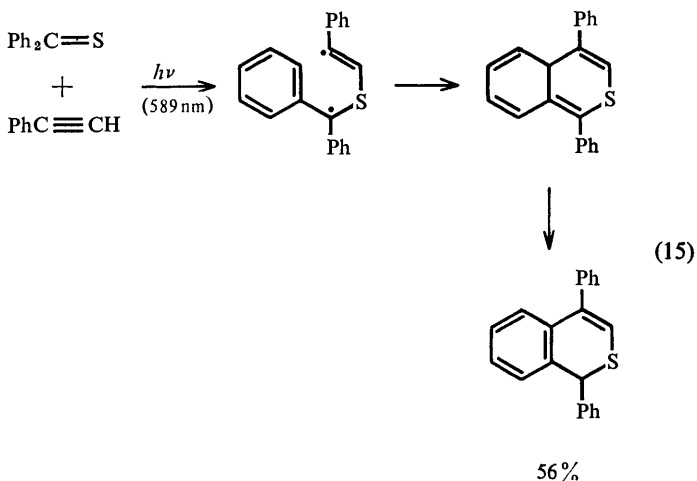
<sup>15</sup> A. Ohno, Y. Ohnishi, and G. Tsuchihashi, *Tetrahedron Letters*, 1969, 161.

<sup>16</sup> H. Gotthard, *Chem. Ber.*, 1972, **105**, 2008.

<sup>17</sup> P. de Mayo and H. Shizuka, *J. Amer. Chem. Soc.*, 1973, **95**, 3942.

<sup>18</sup> A. Ohno, T. Koizumi, and Y. Ohnishi, *Bull. Chem. Soc. Japan*, 1971, **44**, 2511.

<sup>19</sup> J. J. Worman, M. Shen, and P. C. Nichols, *Canad. J. Chem.*, 1972, **50**, 3923.



#### 4 Five-membered Aromatic Heterocycles

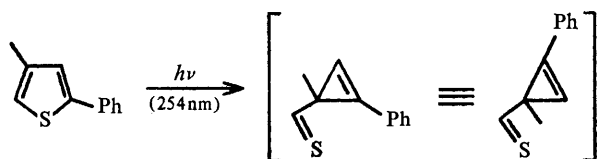
Five-membered heteroaromatic sulphur compounds give products on irradiation in which the atoms of the ring are transposed. One main group of isomerizations, typical of 2-aryl- or 2-alkyl-thiophens (17),<sup>20</sup> involves a transposition of positions 2 and 3 of the ring ( $2 \rightleftharpoons 3$  interchange). An intermediate cyclopropenyl thio-carbonyl compound can be envisaged, analogous to the aldehyde or ketone isolated from irradiation of some furans. The fact that pyrroles are formed if the reaction is carried out in the presence of amines supports this view.<sup>20b</sup>

A second main group of isomerizations involves a shift of the sulphur atom around the ring (equivalent to  $2 \rightleftharpoons 4$  or  $2 \rightleftharpoons 4/3 \rightleftharpoons 5$  transpositions), and these are often encountered with thiazoles (18)<sup>21</sup> or isothiazoles, as well as with 3-arylthiophens. Electrocyclic ring-closure followed by one or two 1,3-shifts of the sulphur atom and ring-opening could account for these changes, and a bicyclic compound of this kind has been isolated after irradiation of tetrakis(trifluoromethyl)thiophen.<sup>22</sup>

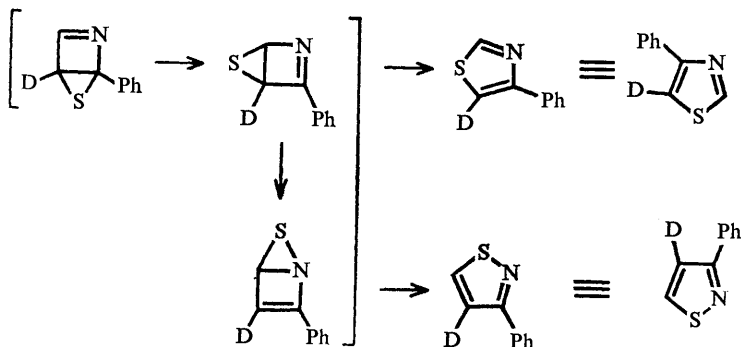
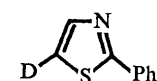
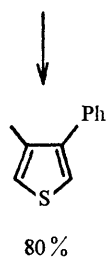
<sup>20</sup> (a) H. Wynberg, R. M. Kellogg, H. van Driel, and G. E. Beekhuis, *J. Amer. Chem. Soc.*, 1967, **89**, 3498, 3501; (b) A. Couture, A. Delevallee, and A. Lablache-Combiere, *Tetrahedron*, 1975, **31**, 785.

<sup>21</sup> C. Riou, G. Vernim, J. J. M. Dou, and J. Metzger, *Bull. Soc. chim. France*, 1972, 2673.

<sup>22</sup> H. A. Wiebe, S. Braslavsky, and J. Heicklen, *Canad. J. Chem.*, 1972, **50**, 2721.

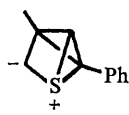


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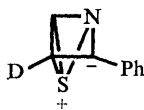


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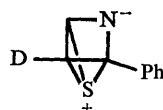
Other types of intermediate have been proposed, particularly those incorporating a bicyclobutane unit (as in the benzvalene bond-isomer of benzene). An ylide such as (19) can account simply for a  $2 \rightleftharpoons 3$  transposition, whilst a zwitterion of type (20) can lead to migration of the sulphur atom. A second type of ylide (21)



(19)



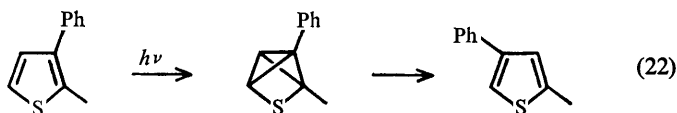
(20)



(21)

allows a direct double interchange  $2 \rightleftharpoons 4/3 \rightleftharpoons 5$ , and it could also lead to a transformation in which only one atom (adjacent to the sulphur) remains in the same position after rearrangement.

A neutral bond-isomer of the benzvalene type can explain the  $3 \rightleftharpoons 4$  transition which is sometimes observed with 3-arylthiophens (22).<sup>20</sup>

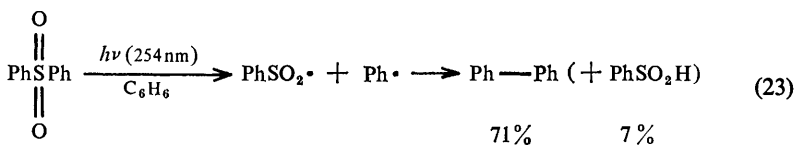


Evidence that carbanionic carbon is present in the intermediate(s) in thiazole transformations comes from the incorporation of deuterium from  $D_2O$ ,<sup>23</sup> but overall it seems that either several mechanisms operate for thiophens and related compounds or the various types of intermediate are readily interconverted.

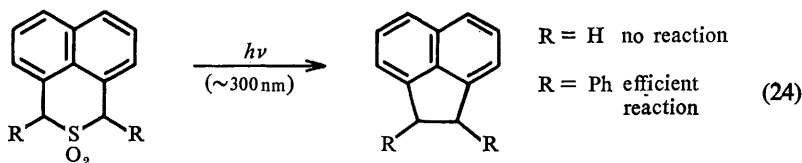
### 5 Sulphur–Oxygen Compounds

Compounds containing the  $O=S=O$  unit, such as sulphonyl halides (*e.g.*

$PhCH_2SO_2I$ ) or sulphones (23),<sup>24</sup> lose sulphur dioxide on photolysis. An  $\alpha$ -cleavage



mechanism seems reasonable, since elimination of  $SO_2$  is much more efficient when stabilized radicals are formed (24).<sup>25</sup>



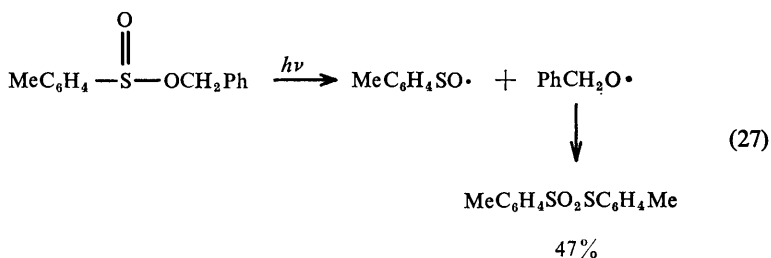
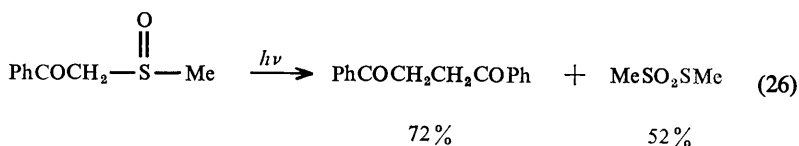
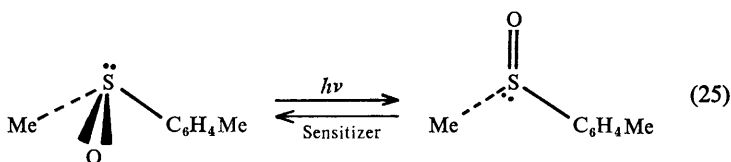
<sup>23</sup> M. Maeda and M. Kojima, *Tetrahedron Letters*, 1973, 3523.

<sup>24</sup> M. Nakai, N. Furukawa, S. Oae, and T. Nakabayashi, *Bull. Chem. Soc. Japan*, 1972, **45**, 1117.

<sup>25</sup> P. M. Weintraub, *Chem. and Ind.*, 1970, 1296.



The S=O unit similarly gives rise to  $\alpha$ -cleavage on irradiation. Sulphur monoxide is not eliminated, but  $\alpha$ -cleavage can account for the photoracemization of sulphoxides (25),<sup>26</sup> for their breakdown (26),<sup>27</sup> and for reactions of sulphinate esters (27).<sup>28</sup>



Some cyclic sulphoxides undergo photochemical desulphuration. Sensitized irradiation leads to a ring-opened ketone (28), whilst direct irradiation gives a cyclic ether (29) as well.<sup>29</sup> In both instances initial C—S(=O) cleavage probably occurs.

<sup>26</sup> R. S. Cooke and G. S. Hammond, *J. Amer. Chem. Soc.*, 1968, **90**, 2958.

<sup>27</sup> H. Nozaki, T. Shirafugi, K. Kuno, and Y. Yamamoto, *Bull. Chem. Soc. Japan*, 1972, **45**, 856.

<sup>28</sup> M. Kobayashi, H. Minato, Y. Miyaji, T. Yoshioka, K. Tanaka, and K. Honda, *Bull. Chem. Soc. Japan*, 1972, **45**, 2817.

<sup>29</sup> A. G. Schultz and R. H. Schlessinger, *Tetrahedron Letters*, 1973, 3605.

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