# Photochemistry of β-Keto-sulphides: 1,2-Elimination of Thiol

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As part of a study of the photochemistry of β-keto-sulphides, we irradiated several compounds, (I), (IV), and (VIb), which contained the structural feature $ArCO{\cdot}CH(SR){\cdot}CH_2^-$. The predominant reaction was 1,2-elimination of the elements of thiol RSH to give an enone (or phenol), together with the formation of a disulphide (see Table).

With the exception of the *p*-nitrophenyl derivative (Id), which remained unchanged, the 2-substituted tetralones (I) gave α-naphthol on photolysis. The benzylthio-derivative (Ic) gave a polymeric material instead of disulphide, and α-naphthol was formed in lower yield. To some extent this decrease in yield may be due to a competing fission of the $PhCH_2$–S bond to give a stable benzyl species.† 1,2-Elimination also readily occurred with the chromanone (IV) to yield 6-methylchromone (V).

It was expected that the acyclic ketone (VIa) would similarly undergo elimination, but no change

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† The photolysis of the cyclic keto-sulphide isothiochroman-4-one, which also resulted in fission of an $ArCH_2$-S bond, was reported by W. C. Lumma, jun., and G. A. Berchtold, *J. Amer. Chem. Soc.*, 1967, **89**, 2761.

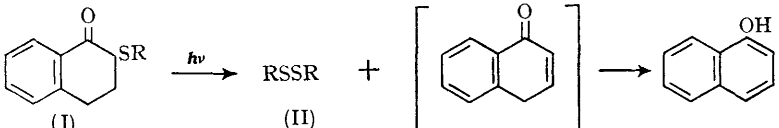
TABLE

| β-Keto-sulphide | Reaction time (hr.) | Yield (%)[a] Disulphide | Product of elimination | Other product |
|---|---|---|---|---|
| (Ia) | 11 | 52 (IIa) | 37 (III) | |
| (Ib) | 4·5 | 48 (IIb) | 53 (III) | |
| (Ic) | 11 | b | 17 (III) | |
| (IV) | 9 | 17 (IIa) | 42 (V) | |
| (VIb) | 13 | c | 33 (VIII) | 17 (VII) |

[a] Irradiation in methanol under an atmosphere of nitrogen, using a high-pressure mercury-vapour lamp as the light source.

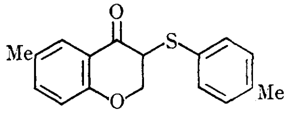
[b] Sulphur-containing polymeric material formed in high yield.

[c] Low yield of polymeric material isolated.

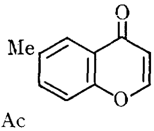


(I) (II) (III)

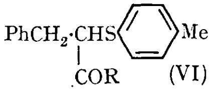
a: R = $p$-tolyl
b: R = 2,4,6-trimethylphenyl
c: R = benzyl
d: R = $p$-nitrophenyl



(IV)



(V)

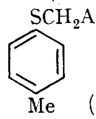


(VI)

a: R = Me
b: R = Ph

$PhCH_2{\cdot}CH_2{\cdot}COPh$ (VII)

$PhCH=CH{\cdot}COPh$ (VIII)



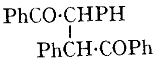
(IX)

$PhCO{\cdot}CH_2SEt$

(X)

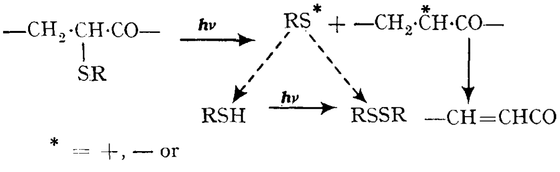
$PhCHSAr{\cdot}COPh$

(XI) Ar = Ph or cresyl



(XII) $\begin{array}{l} PhCO{\cdot}CHPH \\ \qquad | \\ \quad PhCH{\cdot}COPh \end{array}$

was observed after irradiating for several hours. This compound differs from ketones (I), (IV), and (VIb) in that its carbonyl group is not conjugated to a benzene ring. However, the apparent absence of reaction is surprising, since the related compound (IX) underwent photolysis in methanol to an appreciable extent.[1] Ketone (VIb) also behaved differently to the cyclic ketones, as the saturated ketone (VII) was formed together with the product of elimination (VIII), and no disulphide was obtained.



* = +, — or

The disulphide RSSR may be formed directly (radical combination) or through an intermediate, such as the thiol RSH. When toluene-$p$-thiol was irradiated in methanol, the disulphide (IIa) was formed in low yield (6%). To simulate more closely the conditions of the photo-elimination, toluene-$p$-thiol was irradiated in the presence of an aromatic ketone (acetophenone), and an increased yield (14%) of disulphide (IIa) was obtained.

Two photoreactions of β-keto-sulphides have been previously reported, and in neither case was 1,2-elimination possible. Photolysis of ω-ethylthioacetophenone (X) gave acetophenone,[2] and on prolonged exposure to sunlight of ketone (XI) in benzene, compound (XII) was formed.[3]

β-Ketosulphides (I), (IV), (VIa), and (VIb) were prepared by the action of the sodium or potassium salt of the thiol on the known halogeno-ketones, 2-bromo-1-tetralone,[4] 3-bromo-6-methylchroman-4-one,[5] α-benzyl-α-chloroacetone,[6] and 2-bromo-3-phenylpropiophenone[7] respectively. The structures of all photoproducts were confirmed by comparison (m.p. and i.r.) with authentic samples. Work is in progress on the nature of this photo-elimination, together with a study of the photochemistry of α-alkylthio- and α-arylthio-ketones which cannot undergo such an elimination.

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[1] J. R. Collier and J. Hill, to be published.
[2] H. Hogeveen and P. J. Smit, *Rec. Trav. chim.*, 1966, **85**, 489.
[3] A. Schönberg, A. K. Fateen, and S. M. A. R. Omran, *J. Amer. Chem. Soc.*, 1956, **78**, 1224.
[4] F. Straus, O. Bernoully, and P. Mautner, *Annalen*, 1925, **444**, 165.
[5] J. Colonge and A. Guyot, *Bull. Soc. chim. France*, 1958, 329.
[6] W. D. McPhee and E. Klingsberg, *J. Amer. Chem. Soc.*, 1944, **66**, 1132.
[7] R. V. Henley and E. E. Turner, *J. Chem. Soc.*, 1931, 1182.