

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 $\text{ArCO}\cdot\text{CH}(\text{SR})\cdot\text{CH}_2\cdot$. 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 $\text{PhCH}_2\text{-S}$ 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

[†] The photolysis of the cyclic keto-sulphide isothiochroman-4-one, which also resulted in fission of an $\text{ArCH}_2\text{-S}$ bond, was reported by W. C. Lumma, jun., and G. A. Berchtold, *J. Amer. Chem. Soc.*, 1967, **89**, 2761.

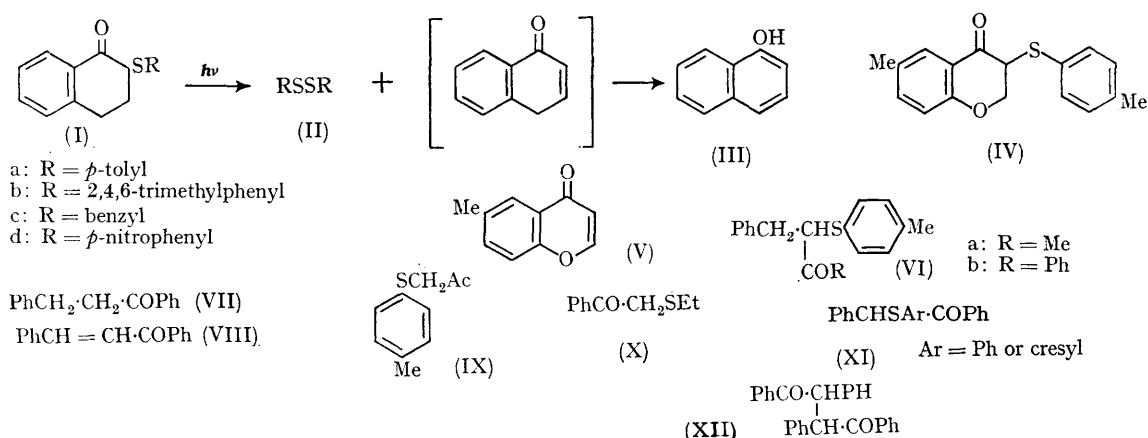
TABLE

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)

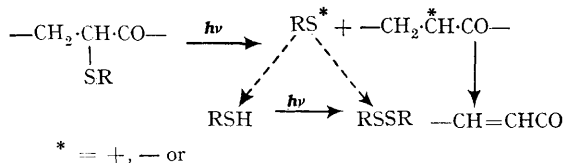
^a Irradiation in methanol under an atmosphere of nitrogen, using a high-pressure mercury-vapour lamp as the light source.

^b Sulphur-containing polymeric material formed in high yield.

^c Low yield of polymeric material isolated.



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.



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-phenylpropionophenone⁷ 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. Bernouilly, 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.