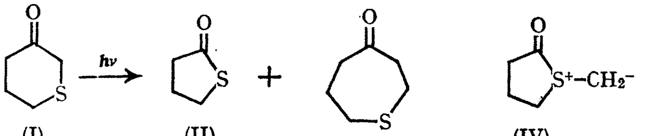
Photochemistry of Cyclic, Saturated β-Keto-sulphides

By K. K. MAHESHWARI and G. A. BERCHTOLD*

(*Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts* 02139)

PREVIOUS reports of the photochemistry of saturated β-keto-sulphides have not involved examples in which the sulphur atom was part of a ring containing the carbonyl chromophore.[1] In view of our results with cyclic, saturated γ-keto-sulphides,[2] and unsaturated β-keto-sulphides,[3] we have investigated the photochemistry of cyclic, saturated β-keto-sulphides.

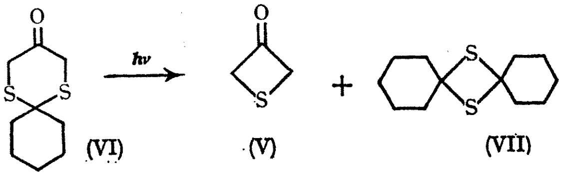
Irradiation (450 w mercury lamp, Pyrex 7740 filter, 0·5—1% solution w/v) of thiacyclohexan-3-one[4] (I) in t-butyl alcohol (19 hr.; 78% reaction) produced thiacyclohexan-3-ol (16%) and t-butyl 5-thiahexanoate (14%). Irradiation of (I) in Freon-113 (1,1,2-trichloro-1,2,2-trifluoroethane) for 8 hr. (90—95% reaction) produced tetrahydrothiophen-2-one (II) and thiacycloheptan-4-one (III) in yields of 6—8% each. Whether the methylene group insertion into (I) to form (III) occurs at position 2 or 3 [in (III)] is not yet established. The ylid (IV) appears to be a reasonable intermediate for this methylene transfer reaction. Treatment of (I) with trimethylsulphonium ylid[5] and trimethylsulphoxonium ylid[6] gave the expected oxiran (75—80%) and no (III). Irradiation of (I) in cyclohexene gave no detectable amounts of norcarane.



(I) (II) (III) (IV)

This ring-expansion–contraction reaction does not occur to any reasonable extent (0—3%) in the other examples studied. These include thiacyclopentan-3-one, thiacycloheptan-3-one, 6-methylthiacyclohexan-3-one, 2-methylthiacyclohexan-3-one and *trans*-3-thiabicyclo[4,4,0]decan-5-one. The photochemical products from these materials are complex mixtures in which thiophen and dihydrothiophen derivatives are major products.

Irradiation of 1,3-dithiacyclohexan-5-one in acetonitrile (3000 Å; 27 hr.; 100% reaction) produced thietan-3-one (V) in 21% yield. Similarly, (VI)† was converted into (V) (89%) and (VII) (67%) after irradiation for 40 hr. in Freon-113. This cleavage is identical to that previously observed in certain dithiaspiro-alkanes.[7]



(VI) (V) (VII)

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