Photochemistry of Enethiol Esters

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Summary Enethiol esters are photolysed in cyclohexane to give enethio-radicals which dimerize to either the disulphide or the thiophen.

PREVIOUS studies[1,2] have implicated the involvement of 3*d*-orbitals in the molecular orbitals of aromatic enethiol esters. The object of this research is to establish what influence 3*d*-orbitals have on the photochemistry of enethiol esters.

The photolysis of *p*-tolyl thiolacetate (I) (0·5—1·0% solution in cyclohexane, 254 nm. light†) gave the disulphide (II) (77%) and the sulphide (III) (7%). Also, cyclohexen-1-yl thiolacetate under the same conditions gave the thiophen (IV) (15%) and *cis*- and *trans*-2-acetylcyclohexylthiolacetate (5% and 2%).

The sulphur–acyl bond of the excited enethiol ester cleaves homolytically to give the enethio-radical, which dimerizes at sulphur when the ester is aromatic (Scheme 1). This behaviour is consistent with the fact that the spin density of aryl thio-radicals is localized largely on sulphur.[3]

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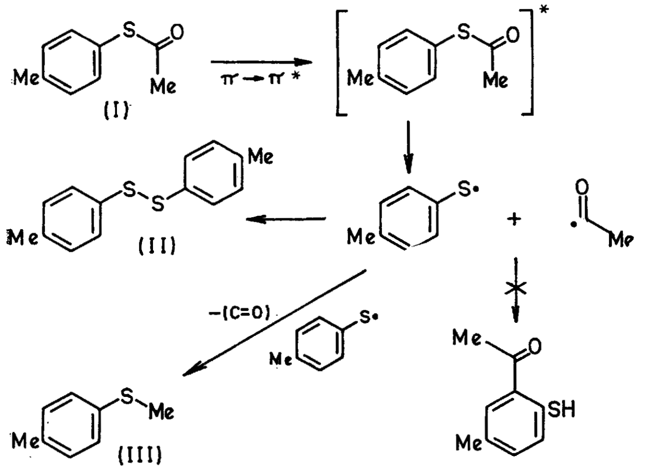
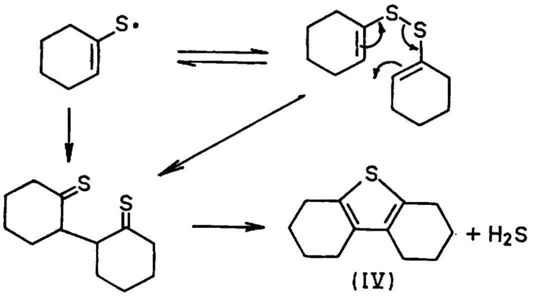
† Rayonet photochemical reactor.

It is not possible to distinguish between dimerization at carbon or at sulphur in the case of the cyclohexene-1-thio-radical (Scheme 2). In a related reaction, potassium cyclohexenyl-1-thiolate and N-bromosuccinimide give octahydrodibenzothiophen.[4] The postulated rearrangement of dicyclohexenyl 1,1-disulphide is being checked.



SCHEME 1

No photo-Fries products are found (Scheme 1). The probability of the acetyl radical coupling with the carbon atom of the enethio-radical is small because of the low spin density on the carbon atoms of the enethio-radical. Recently, the photo-Fries rearrangement for enol esters has been shown to be an intramolecular [1,3]-sigmatropic change of order.[5] This mechanism demands the sulphur–acyl bond be perpendicular to the plane of the benzene ring.



SCHEME 2

However, $3d^2p$ hybrid orbitals of sulphur would cause coplanarity of the benzene ring and the thioacetoxy-group and prevent an intimate contact photo-Fries rearrangement. Another consequence of $3d^2p_\pi$–$2p_\pi$ overlap in enethiol esters should be significant charge separation in the excited state.[2] The small red shift[6] in the u.v. maximum of a series of *para*-substituted phenyl thiolacetates with increasing solvent polarity tends to argue against $3d^2p_\pi$–$2p_\pi$ bonding.

An alternative explanation for the lack of photo-Fries rearrangement is the poor overlap between the σ-sulphur–acyl bond and the $2p$ orbitals of the benzene ring. Sulphur–carbon σ-bonds are significantly longer than oxygen–carbon σ-bonds.[7]

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[5] R. Sandner, E. Hedaya, and D. J. Trecker, *J. Amer. Chem. Soc.*, 1968, **90**, 7249.
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