Photolysis of Mesoionic 2,5-Diphenyl-1,3-dithiol-4-one: a Probable 4π-Antiaromatic Intermediate

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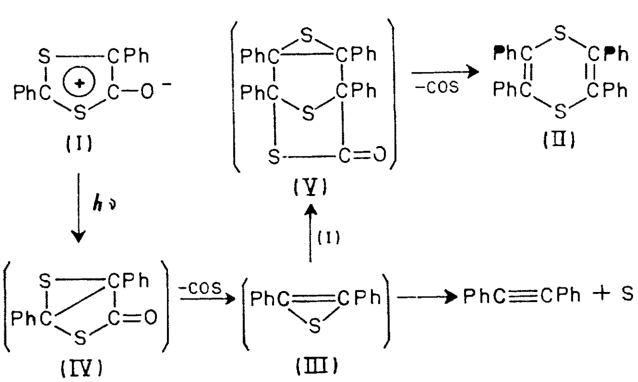
Summary The photolysis of mesoionic 2,5-diphenyl-1,3-dithiol-4-one gave tetraphenyl-1,4-dithiin, diphenylacetylene, and sulphur, probably *via* an antiaromatic thiiren intermediate.

ALTHOUGH much work has been accumulated concerning the preparation and reactions of mesoionic compounds,[1] their photolytic behaviour has attracted only little attention.[2,3] We report here our findings on the photolysis of mesoionic 2,5-diphenyl-1,3-dithiol-4-one (I).[4] The irradiation through Pyrex of a benzene solution of (I) afforded tetraphenyl-1,4-dithiin[5] (II, 19% yield), diphenylacetylene (16% yield), and sulphur (15% yield).

Attention should be focussed upon the formation of diphenylacetylene, because it suggests the possible intermediacy of diphenylthiiren (III),[6] a theoretically interesting 4π-antiaromatic heterocyclic system, in the photolytic path. Thus, the dithiolone (I) is first photolysed [probably *via* a bicyclic intermediate (IV)] into carbon oxysulphide and (III), the latter either decomposes into sulphur and diphenylacetylene, or undergoes cycloaddition to dithiolone (I) to give an intermediate cycloadduct (V), which in turn decomposes photolytically or thermally into (II).



Such a 4π-antiaromatic system has been suggested before as an intermediate in an interpretation of the photo-rearrangement of 3-phenylsydnone.[2] The intermediacy of such a species in the decomposition of mesoionic compounds may be considered to be general. The pyrolyses of mesoionic oxathiazolone[7] and oxatriazolone[8] can be explained in terms of a thiazirine and a triazirine intermediate respectively. Our unpublished results on the formation of benzonitrile by the pyrolysis of 3,4-diphenylsydnone indicate that this also is a reaction involving a diazirine intermediate.

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