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A ONE-STEP SYNTHESIS OF THIIRANES FROM KETOHYDRAZONES.

N. Latif, I. Fathy, and B. Haggag.
(National Research Centre, Dokki, Cairo, U.A.R.)

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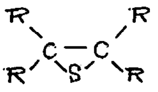
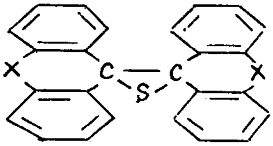
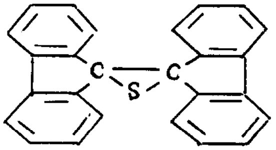
The successful use of thiiranes as synthetic intermediates prompted various investigators to study the chemistry of this group of compounds in more detail. It has been shown recently[1] that symmetrical ethylene sulphides of the general formula (I) can be produced by the interaction of elemental sulphur and diazoalkanes. However, the inaccessibility and the difficulty of preparation of some diazoalkanes limits the usefulness of this reaction.



(I)



(IIa); X=O
(IIb); X=S



(III)

In the present study, it is found that thiiranes (I) are directly synthesized from the readily available ketohydrazones when the latter compounds are allowed to react with elemental

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1) N. Latif and I. Fathy; J. Org. Chem., **27**, 1633 (1962).

sulphur in presence of mercuric oxide and alkali. Thus, for example, when an ethereal solution of xanthone hydrazone containing a few drops of ethanolic potassium hydroxide is boiled under reflux with yellow mercuric oxide for a few hours, dispiro(xanthene-9,2'-thiirane-3',9"-xanthene) (IIa) is produced, in good yield, together with xanthone azine. The analogous sulphides (I; R=Ph), (IIb), and (III) are obtained in a similar manner from benzophenone, thiaxanthone, and fluorenone hydrazones respectively. However, when the reaction is carried out in absence of mercuric oxide, the ketohydrazones are recovered unchanged.

It is assumed that the hydrazone is first dehydrogenated by mercuric oxide to give the corresponding diazoalkane which reacts with sulphur to give the cyclic sulphide. The production of the cyclic sulphide might proceed through the intermediate formation of a carbene[1]. However, an ionic mechanism involving the heterolytic fission of the eight membered sulphur ring is quite possible[2].

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2) Cf. P. D. Bartlett and G. Meguerian; J. Am. Chem. Soc., **78**, 3710 (1956).