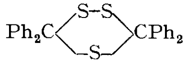
# **72.** *Photo-reactions. Part V. Photo-oxidation of Non-ionisable Thioketones in Sunlight.*

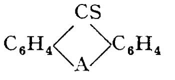
By A. Schönberg and Ahmed Mostafa.

Thiobenzophenone, a number of its derivatives, and 4-thiopyrones have been investigated with regard to their behaviour in benzene solution towards oxygen in the presence and in the absence of sunlight. Thiobenzophenone is oxidised even in the dark, yielding benzophenone.

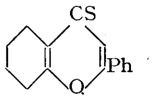
It is well known that solid thiobenzophenone is extremely sensitive to oxygen under normal laboratory conditions (Gattermann and Schulze, *Ber.*, 1896, **29**, 2944), being converted into benzophenone and the trisulphide (I) (Schönberg, Schütz, and Nickel, *Ber.*, 1928, **61**, 1380, 2175; Staudinger and Freudenberger, *ibid.*, p. 1836). We have now found that thiobenzophenone is converted into benzophenone even in the absence of light. On the other hand, 4 : 4′-dimethoxythiobenzophenone, 4 : 4′-bisdimethylaminothiobenzophenone, xanthione (II), and thioxanthione (III) in benzene solution (thiophen-free) are stable or almost completely stable to oxygen in the dark, but are readily converted into the corresponding ketones in sunlight,* sulphur and sulphur dioxide being formed; *N*-phenylthioacridone (IV), 4-thioflavone (V), and 2 : 6-diphenyldithiopyrone (VI) are stable or almost completely stable both in the dark and in sunlight.



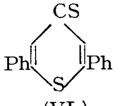
(I.)



(II.) A = O. (III.) A = S. (IV.) A = NPh.



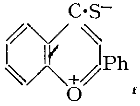
(V.)

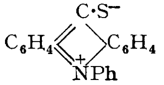


(VI.)

In order to explain the fact that the last three substances are not affected by oxygen in sunlight, it may be pointed out that they are not thioketones proper, but have the structure of zwitterions (compare VII and VIII in the case of 4-thioflavone and *N*-phenylthioacridone respectively) or that the zwitterion structure makes a great contribution to their resonance structure.

(VII.)





(VIII.)

The zwitterion structure of some of these thioketones and of related thioketones has been discussed by Arndt, Scholz, and Nachtwey (*Ber.*, 1924, **57**, 1903), who connect it with their colour, and by Weizmann (*Trans. Faraday Soc.*, 1940, **36**, 978), who draws her conclusions from the high dipole moment of some heterocyclic thioketones, *e.g.*, *N*-methylthioacridone.

## Experimental.

*Action of Oxygen on Thiobenzophenone in the Dark.*—Oxygen was passed for 5 hours through sodium hydroxide solution, concentrated sulphuric acid, a safety tube, a dry benzene solution of thiobenzophenone (0·5 g.), a second safety tube, a tube containing wet potassium chromate paper, a tube containing mercuric sulphate solution, and finally a calcium chloride tube, the tubes being completely covered with dark paper. (All the tubes used in this and the following experiments were of Pyrex glass.) The intense blue colour of the thiobenzophenone solution faded gradually, and a colourless crystalline substance separated, which was proved to be sulphur by means of benzyliminodi-(4-methoxyphenyl)-methane (micro-method for the detection of elementary sulphur; Schönberg and Urban, *Ber.*, 1934, **67**, 1999). After removal of the solid the benzene filtrate was evaporated in a vacuum, and the residual oil inoculated with a crystal of benzophenone. The product, after recrystallisation from benzene, did not depress the m. p. of benzophenone. During the experiment the potassium chromate paper became green and a crystalline precipitate appeared in the mercuric sulphate solution, indicating the evolution of sulphur dioxide (compare Tables of Reagents for Inorganic Analysis, Leipzig, 1938, Akademische Verlagsgesellschaft M.B.H.).

*Action of Oxygen on Thioketones.*—(a) *In the dark.* 4 : 4′-Dimethoxythiobenzophenone, 4 : 4′-bisdimethylaminothiobenzophenone, xanthione (II), thioxanthione (III), *N*-phenylthioacridone (IV), 4-thioflavone (V), and 2 : 6-diphenyldithiopyrone (VI), dissolved in dry benzene, were treated for a week in darkness with oxygen under the conditions described above. They all remained unchanged or almost completely unchanged and no sulphur dioxide could be detected.

(b) *In sunlight.* Parallel experiments were carried out with the same thioketones.

The intense blue colour of the 4 : 4′-dimethoxythiobenzophenone solution changed to reddish and then orange-yellow. After evaporation of the benzene in a vacuum the yellow residue was proved to contain elementary sulphur and 4 : 4′-dimethoxybenzophenone, which was obtained pure after crystallisation from absolute ethyl alcohol. The presence of sulphur dioxide was shown as before.

The colours of the solutions of 4 : 4′-bisdimethylaminothiobenzophenone, xanthione, and thioxanthione faded. The products, isolated as before and crystallised from absolute ethyl alcohol, did not depress the m. p.'s of authentic 4 : 4′-bisdimethylaminobenzophenone, xanthone, and thioxanthone respectively.

4-Thioflavone, *N*-phenylthioacridone, and 2 : 6-diphenyldithiopyrone, after a week's treatment, were recovered unchanged or nearly unchanged.

*Comparative Rates of Oxidation of Thioketones and 4 : 4′-Dimethoxythiobenzophenone.*—(1) 4 : 4′-Dimethoxythiobenzophenone and 4 : 4′-bisdimethylaminothiobenzophenone in molecular proportion were each dissolved in 10 c.c. of dry benzene (thiophen-free). Oxygen was passed through sodium hydroxide solution, concentrated sulphuric acid,

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* The different m. p.'s reported for various thioketones may be due to partial conversion into the corresponding ketones by the action of air in the presence of light during crystallisation. These thioketones should be crystallised in the dark.

a safety tube, the benzene solution of 4 : 4′-bisdimethylaminobenzophenone, the benzene solution of 4 : 4′-dimethoxythiobenzophenone, a third safety tube, and finally a calcium chloride tube. After 3 hours the solution of 4 : 4′-dimethoxythiobenzophenone had lost its blue colour and become slightly orange and when it was shaken with water the aqueous layer became colourless and the benzene layer faintly yellow (formation of a small amount of a red by-product or perhaps due to a small amount of impurity in the original material). When the 4 : 4′-dimethoxythiobenzophenone had been almost completely oxidised, a large amount of 4 : 4′-bisdimethylaminothiobenzophenone could still be recovered from its solution.

(2) The experiment was repeated, xanthione being used instead of 4 : 4′-bisdimethylaminobenzophenone. When the 4 : 4′-dimethoxythiobenzophenone had been almost completely converted into the corresponding ketone, a large amount of xanthione could be recovered.

(3) 4 : 4′-Dimethoxythiobenzophenone was oxidised before thioxanthione under the same conditions.

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