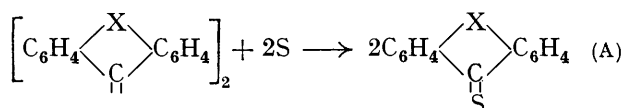


## 52. Cleavage of the Ethylene Linkage by the Action of Sulphur.

By ALEXANDER SCHÖNBERG and (MISS) WAFFIA ASKER.

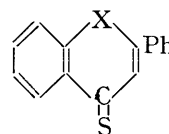
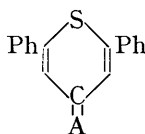
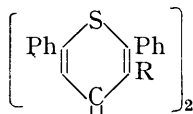
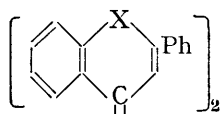
Dithioxanthylene (III), diflavylene (VI), and dithioflavylene (VII) react with sulphur at about 280° with the formation of the corresponding thioketones; for example, dithioflavone (XII) is formed from (VII), and thioxanthione (V) from (III) (compare scheme A). A theory based on resonance is proposed to explain these reactions. Dixanthylene (I), dithioxanthylene (III), dithioflavylene (VII),  $\alpha\alpha'\alpha''\alpha'''$ -tetraphenyl- $\gamma\gamma'$ -dithiopyrylene (VIII) and its chloro-derivative (IX) were obtained by treating the corresponding ketones (example, xanthone in the case of dixanthylene) with thionyl chloride, followed by the action of copper bronze. In the case of dithioflavylene (VII) an intermediate compound was obtained for which formula (XVI) or (XVII) is proposed.

FISSION of the ethylene linkage in dixanthylene (I) by the action of sulphur with the formation of xanthione (IV) (Schönberg, *Ber.*, 1925, **58**, 1796) takes place quickly at 280°. Gleu and Schaarschmidt (*Ber.*, 1939, **72**, 1246) reported on a similar reaction of (II). The present paper deals with the substances (III), (VI),



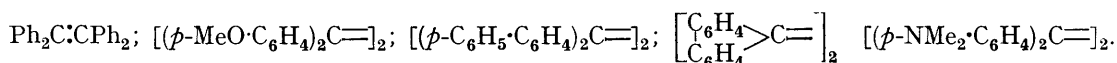
(I, X = O; II, X = NMe; III, X = S.) (IV, X = O; V, X = S.)

(VII), and (VIII), of which (III), (VI), and (VII) reacted with sulphur at about 280° according to scheme (A).

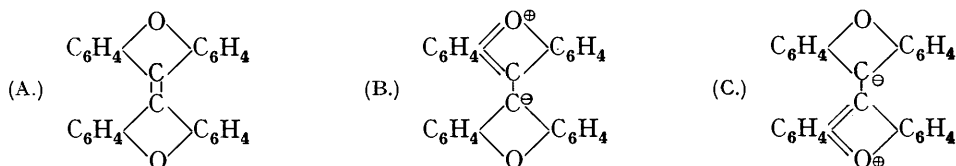


(VI, X = O; VII, X = S.) (VIII, R = H; IX, R = Cl.) (X, A = S; XI, A = O.) (XII, X = S; XIII, X = O.)

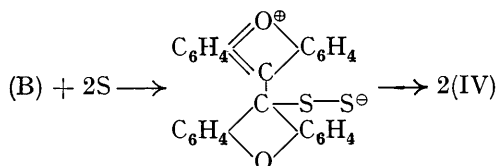
*Explanation of the Sulphur Cleavage Reaction.*—As the substances listed below do not form thioketones when acted upon by sulphur [Schönberg: "Thioketone, Thioacetale und Aethylensulphide," *Sammlung chemischer und chemisch technischer Vorträge*, Verlag Ferdinand Enke, p. 29 (1933)], it is reasonable to attribute the sensitivity of the central ethylene linkage in the substances (I), (II), (III), (VI), and (VII) to their hetero-ring atoms.



The actual ground state of the dixanthylen molecule above 280° is possibly a resonance hybrid involving the forms A, B, and C :



and the cleavage of dixanthylen by sulphur can be illustrated according to the scheme :



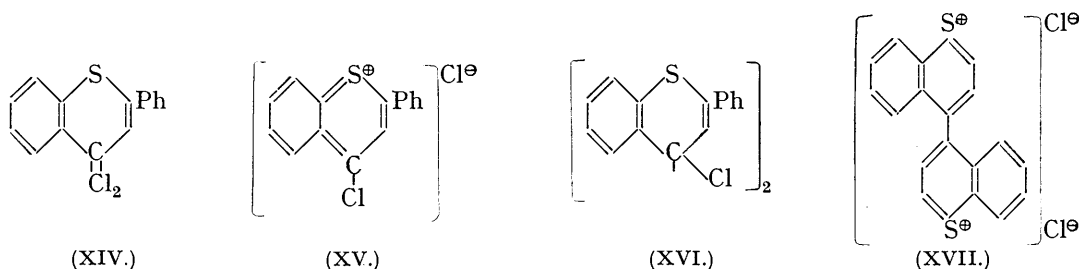
For another possible explanation, see Schönberg and Nickel (*Ber.*, 1931, **64**, 2323). Our failure to perform the sulphur cleavage reaction on (VIII) is explained by the fact that (X), which should be the product, loses sulphur easily at 145° with the formation of (VIII) (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, **58**, 1646).

Dithioxanthylen (III) and dithioflavylen (VII) were changed only very slightly or not at all when air was passed through their solutions in benzene (thiophen-free) for 10 hours at room temperature.

The yellow crystals of diflavylen (VI), but not those of dithioflavylen (VII), when pressed in a mortar, gave a dark red colour which changed to yellow again on the addition of a drop of ether. We cannot suggest an explanation for this phenomenon.

*Preparation of Dichromylen, Dipyrylen, Dixanthylen, their Derivatives, and their Sulphur Analogues.*—The compounds (I), (III), (VII), and (IX) were prepared by the action of copper bronze on the keto-chlorides formed when the corresponding ketones were treated with thionyl chloride (Schönberg and Nickel, *Ber.*, 1934, **67**, 1795).

It may be more correct to formulate the products obtained by the action of thionyl chloride on these ketones as salts; *e.g.*, formula (XV) instead of (XIV) should be given to the product of the action of thionyl chloride on 1-thioflavone. By the action of copper bronze on a dilute benzene solution of (XIV)



or (XV) a compound (XVI or XVII) was obtained which must be regarded as an intermediate product in the preparation of dithioflavylen (VII), since it yields (VII) on further treatment with copper bronze.

The yield obtained by the thionyl chloride method is often better than that from earlier methods. For example, dixanthylen (I), previously obtainable only in poor yield by the reduction of xanthone (Gurgenjanz and Kostanecki, *Ber.*, 1895, **28**, 2310, stated no yield), is produced in about 75% yield from xanthone.

#### EXPERIMENTAL.

*Dithioflavylen (2 : 2'-Diphenyldithiochromylen) (VII).*—1-Thioflavone (Arndt, *Ber.*, 1925, **58**, 1620) (1 g.) was treated with thionyl chloride (15 c.c.) on a water-bath for 10 hours, the excess of thionyl chloride distilled by means of the pump, and the residual dark red oil dissolved in dry benzene (50 c.c.) and refluxed for 6 hours with copper bronze (8 g.) with occasional shaking or stirring. The benzene solution was filtered hot and concentrated. Addition of light petroleum (b. p. 60—70°) precipitated dithioflavylen in yellow crystals, m. p. 285°, difficultly soluble in boiling benzene and carbon tetrachloride (giving an orange colour), and very sparingly soluble in boiling absolute alcohol. With concentrated sulphuric acid it gave a yellow solution (Found : S, 14.3. Calc. for C<sub>30</sub>H<sub>20</sub>S<sub>2</sub> : S, 14.4%).

Dithioflavylen in glacial acetic acid was recovered unchanged after 6 hours' refluxing with water and concentrated hydrochloric acid (equal vols.).

*Formation of (XVI) or (XVII).*—The dark red oil obtained by the procedure described above (1-thioflavone, 0.5 g.; thionyl chloride, 15 c.c.) was dissolved in dry benzene (60 c.c.) and refluxed with copper bronze (4 g.) for about 6 hours, the time depending on the size of the copper bronze particles. The reddish-brown benzene solution was filtered hot and evaporated to dryness. The pink residue was crystallised from light petroleum (b. p. 100—110°), giving pale brown, feather-shaped needles, m. p. 120°, soluble in hot benzene and acetone. The substance was not obtained in a pure state (Found: S, 11.2; Cl, 12.1. Calc. for  $C_{30}H_{20}Cl_2S_2$ : S, 12.4; Cl, 13.5%).

A solution of this substance (0.2 g.) in dry benzene (10 c.c.) was refluxed for 3 hours with copper bronze (2 g.). On concentration of the hot filtered solution dithioflavylen (VII) was obtained.

*Action of Sulphur on Dithioflavylen (VII).*—Dithioflavylen (0.5 g.) was ground with sulphur (0.5 g.) and heated. The colour changed from bright yellow to deep red as soon as melting occurred. The melt was kept at 270—280° (bath temp.), allowed to cool, powdered, and extracted repeatedly with petroleum (b. p. 100—110°). The extract was concentrated, cooled, filtered from precipitated sulphur, further concentrated, and cooled. Dithioflavone (XII) crystallised in reddish-brown needles, m. p. 110°, not depressed by an authentic specimen (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, 58, 1644). It gave green solutions in ether and benzene and a brown solution in alcohol.

*$\alpha\alpha'\alpha''$ -Tetraphenyl- $\gamma\gamma'$ -dithiopyrylen (VIII).*— $\alpha\alpha'$ -Diphenyl- $\gamma$ -thiopyrone (XI) (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, 58, 1640) (0.5 g.) was treated with thionyl chloride for 10 hours as described previously. The orange-coloured oil left after distillation of the excess of thionyl chloride was dissolved in dry benzene (30 c.c.) and refluxed with copper bronze (6 g.) for 7 hours. The deep red benzene solution was filtered hot and concentrated; on addition of light petroleum (b. p. 70—80°) dark green crystals separated, m. p. about 300° (decomp.) (Arndt, Nachtwey, and Pusch, *Ber.*, 1925, 58, 1640) (Found: C, 82.0; H, 4.1; S, 12.3.  $C_{34}H_{24}S_2$  requires C, 82.2; H, 4.9; S, 12.9%).

The substance (VIII) was recovered unchanged after 6 hours' refluxing in absolute alcohol with *N*-sodium hydroxide.

*$\beta\beta'$ -Dichloro- $\alpha\alpha'\alpha''$ -tetraphenyl- $\gamma\gamma'$ -dithiopyrylen (IX).*—This was prepared from  $\beta$ -chlorodiphenyl- $\gamma$ -thiopyrone (Arndt, Nachtwey, and Pusch *Ber.*, 1925, 58, 1640) by the method used for the preparation of (VIII). It separated from the concentrated benzene solution, on addition of light petroleum (b. p. 60—70°), in reddish-brown crystals, m. p. 282—284°, soluble in hot benzene and difficultly soluble in alcohol. With concentrated sulphuric acid, it gave a reddish-brown solution (Found: Cl, 13.1; S, 11.8. Calc. for  $C_{34}H_{22}Cl_2S_2$ : Cl, 12.6; S, 11.3%).

*Dixanthylen (I).*—Xanthone (15 g.) was dissolved in thionyl chloride at room temperature and refluxed for 8 hours. The oil obtained after distillation of thionyl chloride was dissolved in dry xylene (150 c.c.) and refluxed with copper bronze (8 g.) for 10 hours. The deep red xylene solution was filtered hot, concentrated, and cooled; dixanthylen separated in greenish-yellow needles (9.4 g.), m. p. 307°. A further 1 g. was extracted from the copper bronze with carbon disulphide.

*Action of Sulphur on Dixanthylen (I).*—Equal weights of dixanthylen and sulphur were ground together and heated in a wax-bath at 300° for 1 minute. After  $\frac{1}{2}$  minute a dark green liquid was formed. The product gave a bluish-green solution in carbon disulphide, in which mercuric chloride crystals acquired a superficial brownish-red colour after  $\frac{1}{2}$  hour [formation of the molecular compound of xanthione (IV) and mercuric chloride (Schönberg, *Ber.*, 1925, 58, 1793)].

*Dithioxanthylen (III).*—Thioxanthone (Davis and Smiles, *J.*, 1910, 97, 1296) (5 g.) was treated with thionyl chloride as described previously. The deep scarlet-red oil obtained after distillation of the excess of thionyl chloride was dissolved in dry boiling xylene, copper bronze (8 g.) added, 1 g. at a time at intervals of  $\frac{1}{2}$  hour, and boiling continued for 10 hours. The xylene solution was filtered hot and concentrated; on cooling, dithioxanthylen (III) separated in almost white needles (3 g.), m. p. above 350° (Schönberg, Schütz, and Nickel, *Ber.*, 1928, 61, 1384). A further 0.4 g. was obtained by extracting the copper bronze several times with boiling xylene (Found: S, 15.9. Calc. for  $C_{26}H_{16}S_2$ : S, 16.3%).

Dithioxanthylen was dissolved in benzene and treated with animal charcoal; colourless needles showing a blue fluorescence in the solid state and in cold benzene solution were obtained. They dissolved in boiling ethyl phthalate; the cold solution showed a blue fluorescence, which diminished rapidly on heating.

*Action of Sulphur on Dithioxanthylen (III).*—Dithioxanthylen (1 g.) was ground with sulphur (0.5 g.) and heated at 260—270° (bath temp.) for  $\frac{1}{2}$  hour. The green melt was allowed to cool, powdered, and extracted repeatedly with boiling benzene. The benzene solution was concentrated, cooled, filtered from sulphur, further concentrated, and cooled; brownish-green crystals were obtained, m. p. 168° after recrystallisation from light petroleum (b. p. 100—110°), not depressed by thioxanthione (Schönberg, Schütz, and Nickel, *Ber.*, 1928, 61, 1382).

*Action of Sulphur on Diflavylen (VI).*—Diflavylen (Schönberg and Nickel, *Ber.*, 1931, 64, 2325) (0.2 g.) was ground with sulphur (0.5 g.) and heated at 290° for 1 hour. A cold acetone extract of the product was evaporated, and the residual oil crystallised from ether-light petroleum (b. p. 30—50°). After recrystallation from light petroleum (b. p. 70—80°) it formed red needles, m. p. 86°, not depressed by authentic 4-thioflavone (XIII) (Schönberg and Nickel, *Ber.*, 1931, 64, 2325).