

### 156. *Cleavage of the Ethylene Linkage by the Action of Thionyl Chloride.*

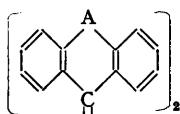
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Dixanthylene (I), dithioxanthylene (II), *NN'*-dimethyldiacridine (III), diflavylene (IV), and dithioflavylene (V) are cleaved by the action of thionyl chloride, followed by that of water, to the corresponding ketones; e.g., xanthone (VIII) is formed from dixanthylene (I), and flavone (XI) from diflavylene (IV).

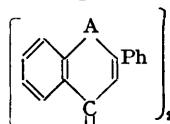
SCHÖNBERG (*Ber.*, 1925, 58, 7096) showed that dixanthylene (I), when treated with sulphur, yielded xanthione (VI), which was the first example of the cleavage of the ethylene linkage by sulphur with the formation of a thioketone. Recently (this vol., p. 272) the authors have shown that a similar reaction takes place with dithioxanthylene (II), diflavylene (IV), and dithioflavylene (V).

We have now found that the ethylene linkage in (I), (II), (III), (IV), and (V) can also be easily split by refluxing these substances with thionyl chloride for one hour; e.g., dixanthylene (I) gives an oil which on short treatment with water at 30° yields xanthone in practically quantitative yield. If aniline is used instead of water, xanthoneanil is obtained. *NN'*-Dimethyldiacridine (III), which reacts with sulphur with formation of *N*-methylthioacridone (VII) (Gleu and Schaarschmidt, *Ber.*, 1939, 72, 1246), gives *N*-methylacridone (X) when treated with thionyl chloride and then with water.

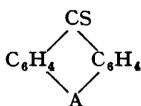
Tetraphenylethylene, when treated with thionyl chloride and water, is practically unchanged.



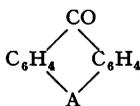
(I, A = O; II, A = S; III, A = NMe.)



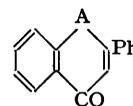
(IV, A = O; V, A = S.)



(VI, A = O; VII, A = NMe.)



(VIII, A = O; IX, A = S; X, A = NMe.)



(XI, A = O; XII, A = S.)

#### EXPERIMENTAL.

*Xanthone (VIII) from Dixanthylene (I).*—Dixanthylene (0.5 g.) was refluxed with thionyl chloride (25 c.c.) for 1 hour, the excess of thionyl chloride distilled off completely (pump), and the residual orange oil dissolved in benzene and shaken with water at 30° for 10 mins. The benzene layer was evaporated, and the residual yellowish-white xanthone crystallised from alcohol; the mother-liquor also contained pure xanthone. The yield was practically quantitative.

*Xanthoneanil from Dixanthylene.*—Dixanthylene (1 g.) was refluxed with thionyl chloride (50 c.c.) for 1 hour, the excess of thionyl chloride distilled off, and the residual oil dissolved in dry benzene (30 c.c.) and refluxed with aniline (2 g.) for 1 hour. The mixture was evaporated to dryness, and dilute hydrochloric acid added to the residue. Xanthoneanil was extracted with ether and crystallised from light petroleum; it did not depress the m. p. of an authentic specimen (Schönberg and Schütz, *Annalen*, 1927, 454, 51).

*Thioxanthone (IX) from Dithioxanthylene (II).*—The reaction was carried out as described in the case of dixanthylene, and the thioxanthone obtained crystallised from benzene. It did not depress the m. p. of an authentic specimen (Gomberg and Britton, *J. Amer. Chem. Soc.*, 1921, 43, 1946).

*Flavone (XI) from Diflavylene (IV).*—Diflavylene (Schönberg, *Ber.*, 1931, 64, 2326) was treated with thionyl chloride and water as described above. Flavone thus obtained was crystallised from light petroleum. It gave no depression of m. p. with an authentic specimen (Löwenbein, *Ber.*, 1924, 57, 1516).

*N-Methylacridone (X) from NN'-Dimethyldiacridine (III).*—The diacridine (Decker and Petsch, *J. pr. Chem.*, 1935, 143, 227) (0.5 g.) was treated with thionyl chloride for 12 hours, the excess of thionyl chloride distilled off, and the yellow solid treated with water as described above. The product was crystallised from alcohol; it did not depress the m. p. of *N*-methylacridone (Decker and Petsch, *loc. cit.*, p. 222).

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