DIPYRYLENES, DICHROMYLENES, DIXANTHYLENES, AND THEIR SULFUR ANALOGUES

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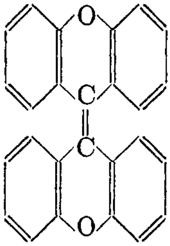
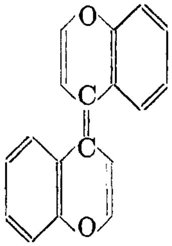
I. INTRODUCTION

Whereas dixanthylene (I) (14) and dithioxanthylene (IV) (19) were synthesized many years ago, dichromylenes (II) (32) and dipyrylenes (III) (2) have only recently been discovered. The same is true for dithiochromylenes (V) (33) and dithiopyrylenes (VI) (3).



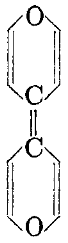
I

Dixanthylene



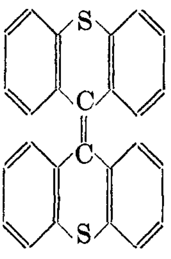
II

Dichromylene



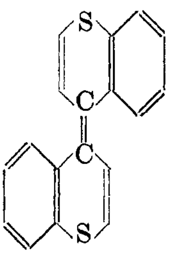
III

Dipyrylene



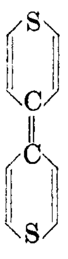
IV

Dithioxanthylene



V

Dithiochromylene



VI

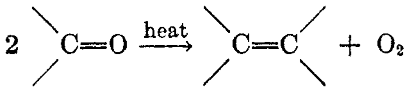
Dithiopyrylene

Cis–trans isomers of dichromylenes and dipyrylenes (and their sulfur analogues) have not yet been found with certainty. According to Taylor (38) 2,2′-diphenyldichromylene (diflavylene) (XXVII) (page 5) has the *trans*-form. Formulas II and V represent the *trans*-forms of dichromylene and dithiochromylene. The present review summarizes the methods of preparation and chemical properties of these compounds. A discussion of the theories concerning their color is also given.

II. METHODS OF PREPARATION

A. By the thermal decomposition of thioketones

Although it has not been observed that ketones change at ordinary temperature or at temperatures below 200°C. according to the following scheme:



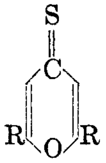
$$2\ \rangle C{=}O \xrightarrow{\text{heat}} \rangle C{=}C\langle\ + O_2$$

the analogous process has been observed in the case of thioketones. Thiobenzophenone is transformed to tetraphenylethylene when heated at 160–170°C., according to the following scheme (37):

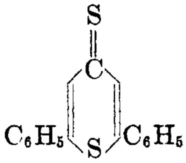
$$2(C_6H_5)_2C{=}S \xrightarrow{\text{heat}} (C_6H_5)_2C{=}C(C_6H_5)_2 + 2S \qquad (A)$$

Many derivatives of thiobenzophenone are stable towards heat; for example, xanthione (XX) (page 4) is not changed when heated to 220°C. for 4 hr. (4); also in the 4-thiochrome series (see compound XXIVa) reactions analogous to that in equation A have not yet been observed. But Arndt (2) found that diethyl 4-thiochelidonate (IX) is transformed into ethyl 4,4′-dipyrylenetetracarboxylate (XII) at high temperatures. The reaction takes place very slowly at room temperature and is accelerated by the influence of light.

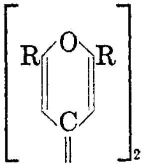
It has also been found that 2,6-diphenyl-4-thiopyrone (X) reacts similarly to compound IX, giving 2,2′,6,6′-tetraphenyl-4,4′-dipyrylene (XIII) (4). 2,6-Dimethyl-4-thiopyrone (VIII) and 4-thiopyrone (VII) do not react according to equation A (4), but 2,6-diphenyl-1,4-dithiopyrone (XI) when heated at 145°C. gives tetraphenyldithiopyrylene (XIV) (3).



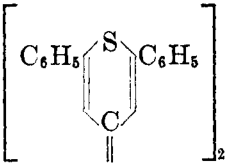
VII, R = H
VIII, R = CH_3
IX, R = $COOC_2H_5$
X, R = C_6H_5



XI

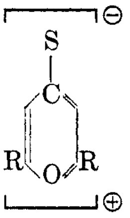


XII, R = $COOC_2H_5$
XIII, R = C_6H_5

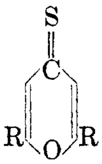


XIV

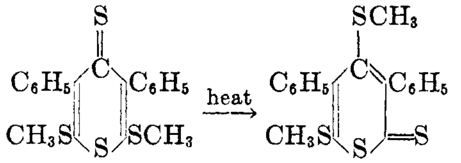
Arndt (4) investigated the relation between the constitution of the thiopyrones and their stability towards heat and concluded that 4-thiopyrones change into dipyrylenes, provided they carry an acidifying substituent such as —$COOC_2H_5$ or —C_6H_5 in the α-position, and that such a change is easier when the group is more acidic. This is probably due to the basic properties of the pyrone oxygen ring, which can be weakened or neutralized by the introduction of acidic groups in the 2- and 6-positions. The compound tends to acquire more or less the constitution shown in formula B and to behave therefore as a real thioketone which undergoes the "dipyrylene reaction." The thermostable 2,6-dimethyl-4-thiopyrone (XIII) has more the character of a betain (formula A).



A



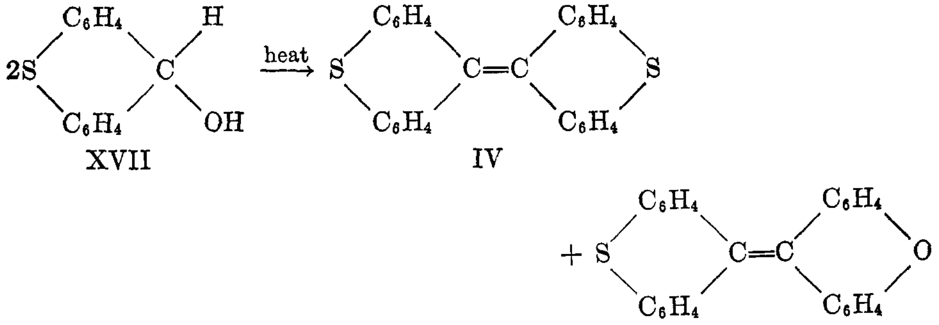
B



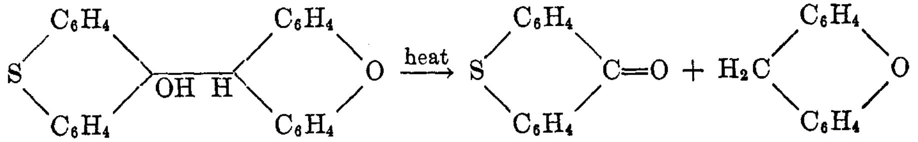
XV XVI

When the thioketone (XV) was heated, no loss of sulfur was observed, but an isomeric change took place. The constitution of the new compound is believed to be as shown in formula XVI (27).

Dithioxanthylene (IV) has been obtained by the action of heat on thioxanthohydrol (XVII) (30). An attempt was made to obtain substance XVIII by the elimination of water from XIX by heat, but a mixture of thioxanthone and xanthene was formed instead (31).



XVII IV XVIII



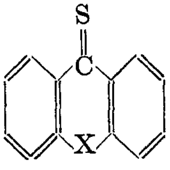
XIX

B. By the action of copper on aromatic thioketones

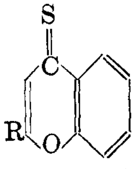
Thiobenzophenone and some of its derivatives are transformed by the action of heavy metals (for example, copper) to the corresponding ethylene derivatives. According to Gattermann (11, 12), who first carried out the reaction, a mixture of certain thioketones and copper powder (obtained by the reduction of pure copper oxide with hydrogen) when heated at 200–220°C. for 15–30 min. in a stream of carbon dioxide yields the corresponding ethylene derivatives and cupric sulfide.

$$2Ar_2C{=}S \xrightarrow{Cu} Ar_2C{=}CAr_2 + 2CuS \text{ (Ar = aromatic group)}$$

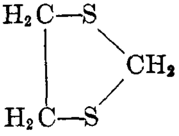
Schönberg (36) and coworkers modified the process and obtained a purer product by refluxing the thioketone with copper bronze in toluene or xylene solution. The different behavior of the thioketones towards copper bronze is as follows: thiobenzophenone reacts readily, *p,p'*-dimethoxythiobenzophenone, xanthione (XX), and thioxanthione (XXI) less readily, whereas *N*-phenylthioacridone (XXII) and Michler's thioketone are very resistant.



XX, X = O
XXI, X = S
XXII, X = NC_6H_5
XXIII, X = NCH_3



XXIV, R = C_6H_5
XXIVa, R = H

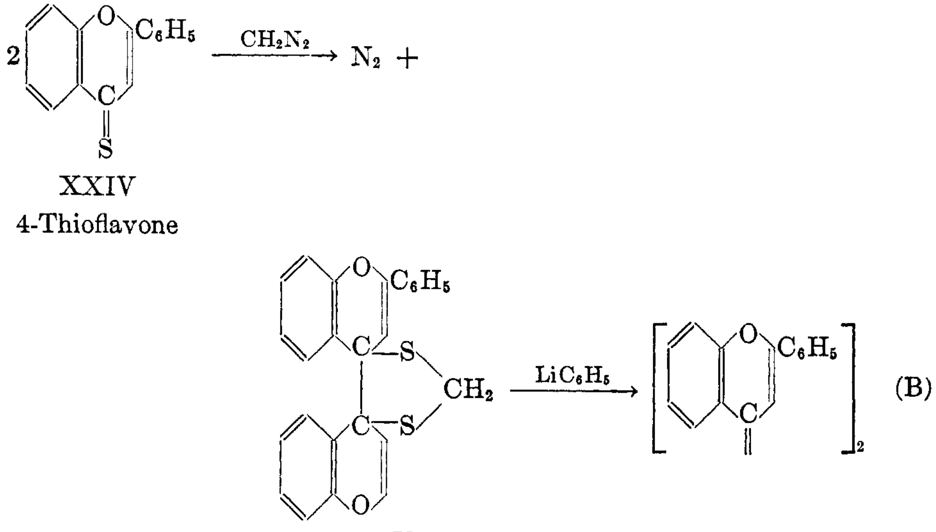


XXV

Diflavylene (2,2′-diphenyldichromylene) (XXVII) can also be obtained from 4-thioflavone (XXIV), but the yield is not good (29).

C. By the action of diazomethane on thioketones, followed by the action of lithium phenyl

Derivatives of trimethylene 1,3-disulfide (XXV)—for example, compound XXVI—are obtained by the action of diazomethane on thioketones. Scheme B represents the action of diazomethane on 4-thioflavone (XXIV), according to Schönberg (32).



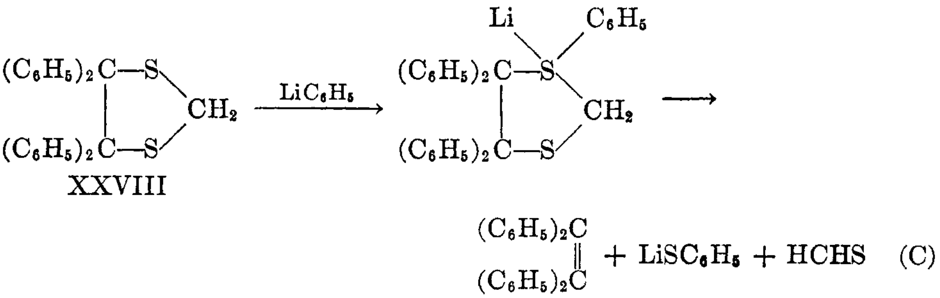
XXIV

4-Thioflavone

XXVI

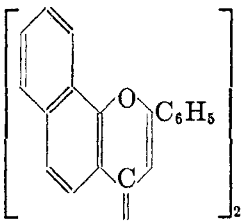
XXVII

Such products are of special interest, for they are decomposed by lithium phenyl into the corresponding ethylene derivatives with the formation of lithium thiophenolate (C_6H_5SLi) and thioformaldehyde. The action of lithium phenyl on XXVI, leading to the formation of diflavylene (XXVII), is similar to the action of lithium phenyl on 4,4′,5,5′-tetraphenyltrimethylene 1,3-disulfide (XXVIII), which leads to the formation of tetraphenylethylene according to scheme C (29):



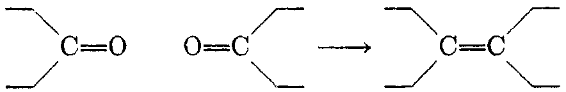
XXVIII

By this method not only dichromylenes (32) have been prepared, but also dixanthylene (I), dithioxanthylene (IV), and the naphthalene product (XXIX) (29):

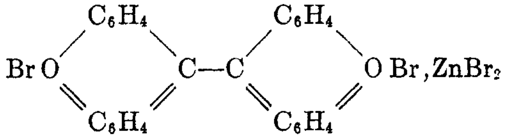


XXIX

D. By the reduction of ketones

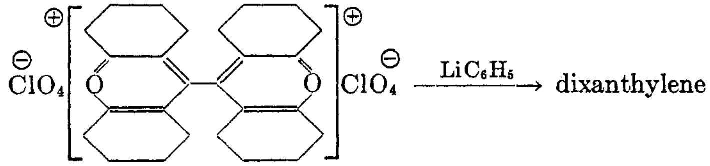


Xanthone and some of its derivatives when boiled with acetic acid and zinc dust in the presence of some drops of hydrochloric acid are converted into dixanthylene (I) or the corresponding dixanthylene derivatives (14). By the reduction of xanthone with zinc and hydrobromic acid, dixanthonium bromide zinc bromide is obtained (39).

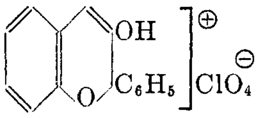


The reduction of thioxanthone with zinc and hydrochloric acid gives dithioxanthylene (IV) (19). Baeyer and Piccard (5, 6) reduced 2,6-dimethylpyrone with zinc dust and hydrochloric acid, but did not isolate the corresponding tetramethyldipyrylene.

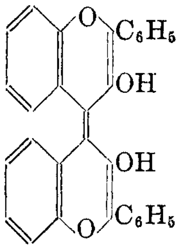
The reduction of xanthone with a mixture of zinc wool and sodium perchlorate in acetic acid and acetic anhydride yields red crystals of 9,9-dihydroxybixanthyl perchlorate, which reacts with lithium phenyl or with phenylmagnesium bromide giving dixanthylene (33):



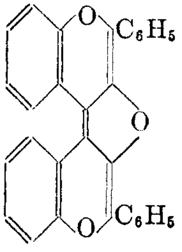
Dilthey (9) heated 3-hydroxyflavenium perchlorate (XXX) with sodium acetate in ethyl alcohol; the intermediate compound 3,3-dihydroxy-4,4-diflavylene (XXXI) was obtained and converted into 4,4-diflavylene 3,3-oxide (XXXII) by the action of hot acetic acid, but not by sulfuric acid. The mother liquor of XXXII contained (4,4-diflavylene 3,3-oxide)-4,4-glycol (XXXIII).



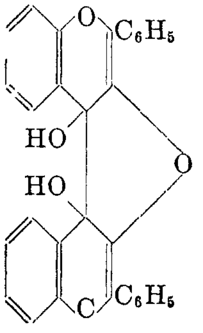
XXX



XXXI



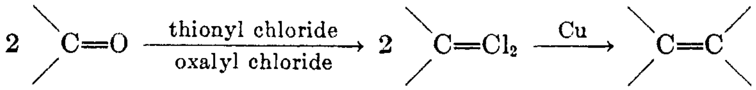
XXXII



XXXIII

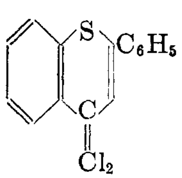
E. By the action of copper bronze on keto chlorides

Schönberg and coworkers (25, 33) treated the ketones (for example, 1-thioflavone in the case of dithioflavylene (XXXVII)) with thionyl chloride or oxalyl chloride in the absence of moisture; the keto chlorides were obtained in good yield, and these in turn when refluxed with copper bronze in benzene solution gave the corresponding ethylene derivatives according to the following scheme:

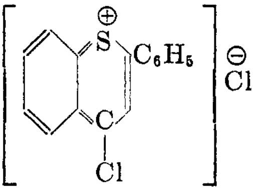


$$2\ {>}C{=}O \xrightarrow[\text{oxalyl chloride}]{\text{thionyl chloride}} 2\ {>}C{=}Cl_2 \xrightarrow{Cu} {>}C{=}C{<}$$

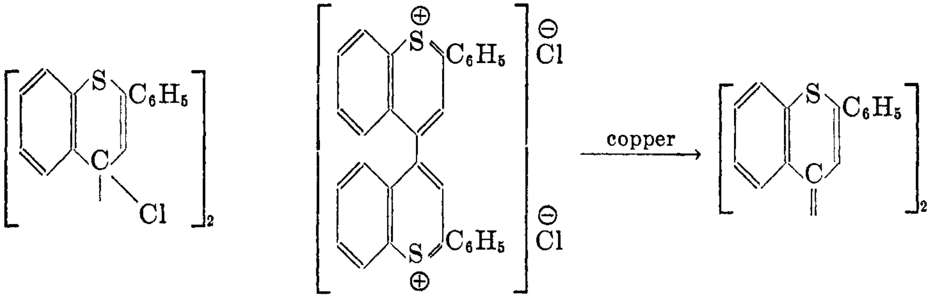
It must be pointed (25) out that it may be more correct to represent the products obtained by the action of thionyl chloride on chromones, pyrones, and xanthones as salts. For example, the product obtained by the action of thionyl chloride on 1-thioflavone can be represented by formula XXXV instead of XXXIV. A compound (XXXVIa or b) was obtained by the action of copper bronze on XXXIV or XXXV, which must be regarded



XXXIV



XXXV

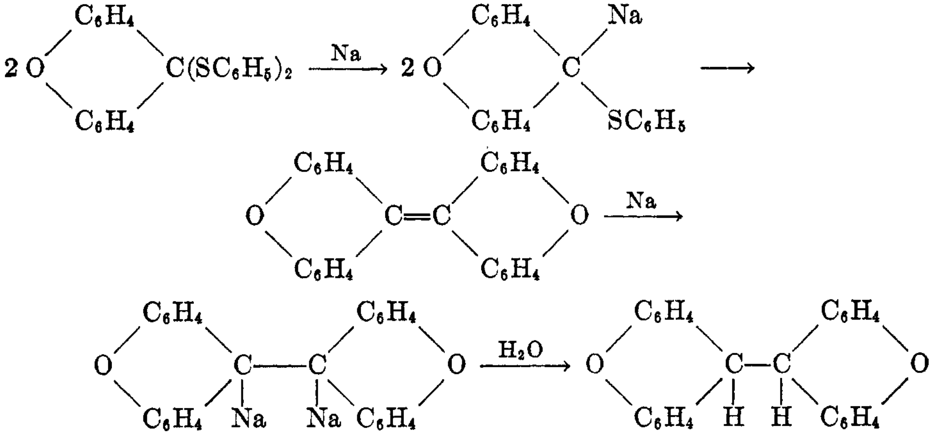


XXXVIa XXXVIb XXXVII

as an intermediate product in the preparation of dithioflavylene (XXXVII), since it yields dithioflavylene on further treatment with copper bronze.

F. By the action of sodium on xanthone diphenyl mercaptole

Schönberg (34) obtained dixanthylene, together with dixanthyl, by the action of sodium on xanthone diphenyl mercaptole. The reaction proceeds according to the following scheme:



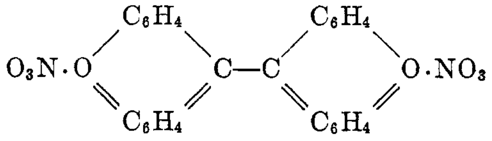
XXXVIII

A similar reaction is brought about by the action of sodium on benzophenone diphenyl mercaptole.

III. CHEMICAL PROPERTIES

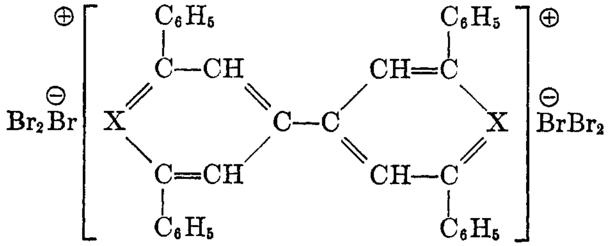
A. Action with oxidizing and reducing agents

It was found by Arndt (1) that dithioxanthylene (IV) is oxidized by hydrogen peroxide in acetic acid to dithioxanthylene disulfone. Dithioflavylene (XXXVII) and dithioxanthylene (IV) were not changed when air was passed through their solutions in thiophene-free benzene for 10 hr. at room temperature, but dixanthylene (I) was broken down at 300°C. into xanthone by the action of air in the presence of selenium (27). Dixanthylene (I) was converted by Werner (39) into dixanthonium nitrate (XXXIX), by suspending it in benzene and saturating the suspension with nitrous fumes at 60–70°C. The nitrate is a brown crystalline substance with bluish lustre, and is converted by hydrobromic acid into the corresponding bromide.



XXXIX

Dixanthonium nitrate

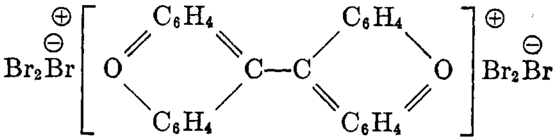


XL, X = O or S

Very little is known about the behavior of the substances mentioned in the title of this paper towards reducing agents.

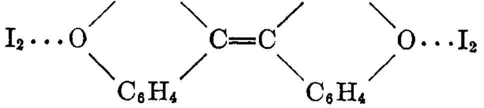
B. Action with halogens and with phosphorus pentachloride

When a solution of tetraphenyldipyrylene (XIII) or of its sulfur analogue (XIV) in chloroform is mixed wth a solution of bromine in the same solvent, XL is formed (1, 4). Dixanthylene hexabromide (XLI) is formed by mixing the solution of dixanthylene in carbon disulfide with a solution of bromine in the same solvent (4, 15). It regenerates dixanthylene (I) when treated with an aqueous solution of sulfurous acid (15). Dixanthylene tetraiodide (XLII) is



XLI

Dixanthylene hexabromide



XLII

Dixanthylene tetraiodide

obtained when a solution of dixanthylene in carbon disulfide is mixed with a solution of iodine in the same solvent. The iodine is removed by the action of an alcoholic solution of sodium thiosulfate. When the solution of bromine in carbon tetrachloride is mixed with a solution of dithioxanthylene (IV) in *o*-dichlorobenzene, dithioxanthonium perbromide ($C_{26}H_{16}S_2Br_6$) is formed and dithioxanthylene is regenerated on treatment with zinc dust and acetic acid. Dithioxanthylene disulfone does not react with bromine solution or vapor even when heated (1).

Magidson and Damaskina (18) heated dixanthylene with phosphorus pentachloride and obtained 9,9-dichloroxanthene.

C. Action with acids

The substances mentioned in the title of this paper seem in general to be very stable towards acids as far as the ring system characteristic for them is concerned. Ethyl 4,4′-dipyrylenetetracarboxylate (XII) dissolves in cold concentrated sulfuric acid and on the addition of water, a great part of the ester is recovered unchanged (2). Tetraphenyldipyrylene (XIII) is stable towards aqueous acids (4); dithioflavylene (XXXVII) is stable towards an aqueous solution of hydrochloric acid (27); dixanthylene (I) and dithioxanthylene (IV) are stable towards acids, since they are prepared in a strong acid medium (14, 19).

D. Action with alkalies

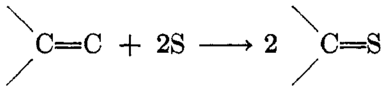
The stability of the ring system of the substances in question is illustrated by the following facts: Ethyl 4,4′-dipyrylenetetracarboxylate (XII) when boiled with an alcoholic solution of sodium hydroxide gives the sodium salt, but no break in the molecule takes place (2). Tetraphenyldipyrylene (XIII) is completely stable towards aqueous alkalies (4); tetraphenyldithiopyrylene (XIV) is also stable towards an alcoholic solution of sodium hydroxide (25).

E. Action with sodium and potassium

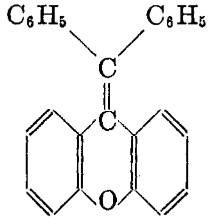
By the action of sodium on dixanthylene (I) the sodium salt (XXXVIII) is obtained, which gives 9,9′-dixanthyl-9,9′-dicarboxylic acid by the action of carbon dioxide followed by that of acids (22). Conant and Garvey (7) obtained the potassium salt by the action of a sodium–potassium alloy on dixanthylene.

F. Action with sulfur

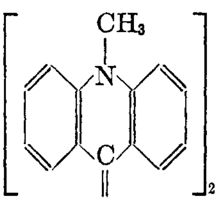
It has been shown by Schönberg (23) that the ethylene linkage in dixanthylene (I) is split by the action of elementary sulfur with the formation of xanthione (XX). This reaction takes place very quickly at 280°C., 2 min. being sufficient (25). This was the first example of the splitting of a double bond by sulfur; later (25) it was shown that diflavylene (XXVII), dithioflavylene (XXXVII), dithioxanthylene (IV), and *o*,*o*′-oxido-tetraphenylethylene (XLIII) (28) are also broken down readily by sulfur to the corresponding thioketones at 280°C., according to the scheme:



Tetraphenyldithiopyrylene (XIV) does not undergo this reaction (25). This is explained by the fact that 1,4-dithio-2,6-diphenylpyrone (XI), which should be the product of this reaction, loses sulfur easily at 145°C. with the formation of XIV (3).

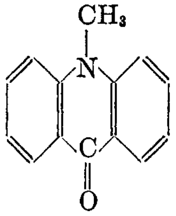


XLIII



XLIV

N,*N*-Dimethyldiacridene



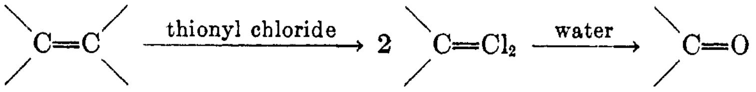
XLV

N-Methylacridone

A similar reaction (13) has been carried out with *N*,*N′*-dimethyldiacridene (XLIV), which is an analogue of dixanthylene (I).

G. Action with thionyl chloride

The central ethylene linkage in diflavylene (XXVII), dithioflavylene (XXXVII), dixanthylene (I), dithioxanthylene (IV) (26), and *o*,*o′*-oxido-tetraphenylethylene (XLIII) (28) can easily be split, by refluxing these substances with thionyl chloride, to the corresponding keto chlorides according to the scheme:

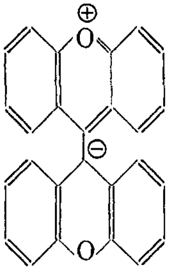


If, for example, dixanthylene is boiled with thionyl chloride, it gives an oil which on treatment with water at 30°C. yields xanthone in practically quantitative yield; when aniline is used instead of water, xanthone anil is obtained (26). *o*,*o′*-Oxido-tetraphenylethylene (XLIII) gives a mixture of xanthone and benzophenone (28). *N*,*N′*-Dimethyldiacridene (XLIV) gives *N*-methylacridone (XLV). Tetraphenylethylene when treated with thionyl chloride and water, as described in the case of dixanthylene, was practically unchanged (26).

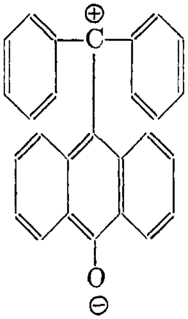
IV. THE COLOR OF DIPYRYLENES, DICHROMYLENES, AND DIXANTHYLENES

All dipyrylenes, dichromylenes, and their sulfur analogues are brilliantly colored substances. Dithioxanthylene (IV) is almost colorless and its melt is colorless (1). Dixanthylene (I) in the crystalline state is colorless at the temperature of liquid air; it is slightly colored at room temperature and gives a very bright blue melt; its solutions in indifferent solvents are bright blue green (23, 24).

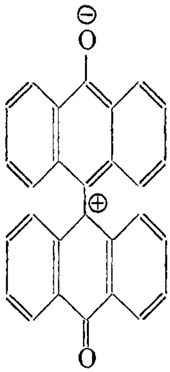
To explain this phenomenon, it is suggested that dixanthylene is a true ethylene in the crystalline state, especially at low temperatures, as indicated by formula I, but that in the melt and in solution the molecules acquire the structure of betains (XLVI).



XLVI



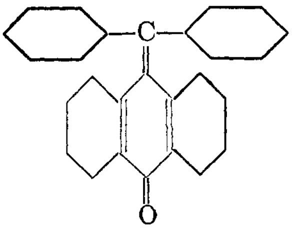
XLVII



XLVIII

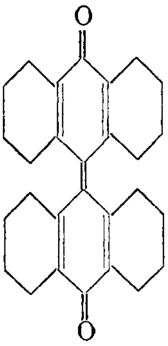
It is perhaps more correct to state that the molecule of dixanthylene is to be regarded as a resonance hybrid with contribution *inter alia* from the true ethylene structure and the betain structure, and that there is a large contribution from the betain structure when the substance is in the melted state or in solution, and a small contribution under these conditions from the true ethylene form. The reverse is the case with regard to the molecules of the crystallized dixanthylene (28).

Similar changes of color with temperature (thermochromism) have been observed *inter alia* with diphenylmethyleneanthraquinone (XLIX) (21) and dianthraquinone (L) (20) and may be explained similarly (compare the betain formulas XLVII and XLVIII).



XLIX

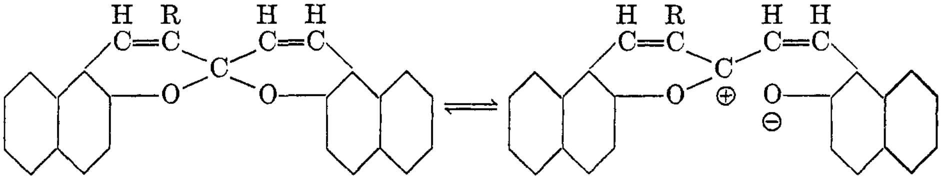
Diphenylmethyleneanthraquinone



L

Dianthraquinone

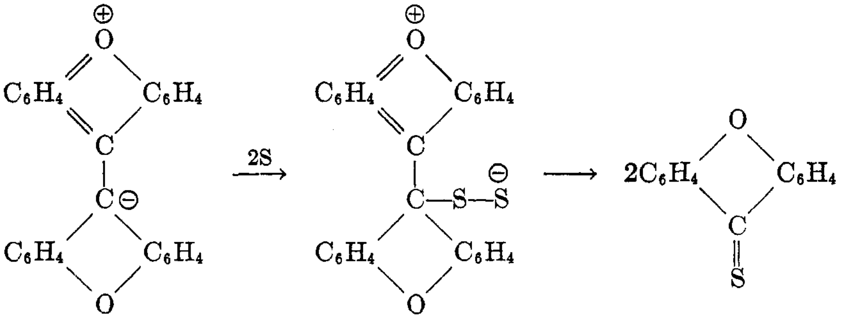
The color changes of the ethylenes (I, XLIX, and L) may be compared (28) with the color changes of certain spiro compounds (8, 10, 16). This phenomenon has also been explained by the formation of betains, as illustrated below:



$R = —CH_2C_6H_5$

The above spiro compound forms colorless crystals which become blue on melting. Its solution in hot xylene is deep blue; on cooling it becomes paler and finally colorless (17).

It is possible that the action of sulfur and the action of thionyl chloride on dixanthylene (compare pages 10 and 11) may be explained by the above ethylene-betain theory. That is to say that the action of sulfur on dixanthylene is not the action of sulfur on a true ethylenic compound but proceeds as shown below (25):



The yellow crystals of diflavylene (XXVII) change from yellow to dark red when subjected to pressure (about 100 kg. per 0.01 $cm.^2$) (25) (piezochromism). A similar change of color has been reported in the case of dianthraquinone (L), the yellow crystals becoming bluish green (20).

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