

83. Reactions of Thermochromic Ethylenes.

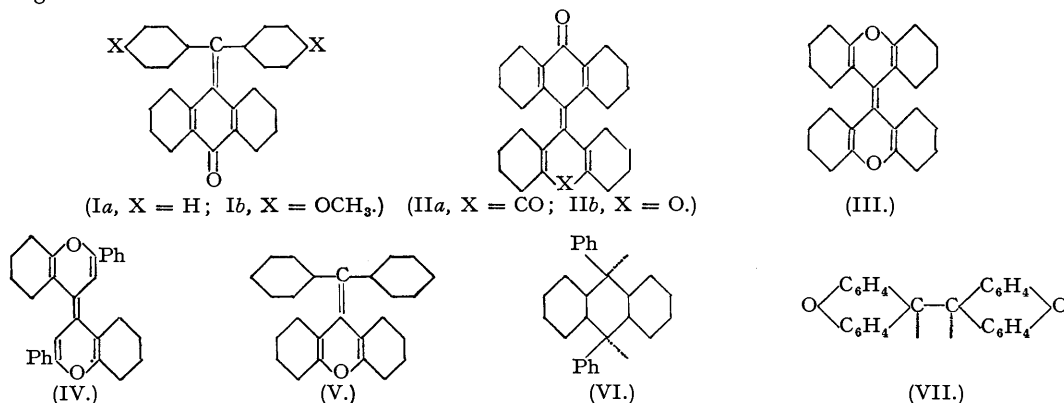
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A number of ethylenes are described which show physical and chemical properties in accordance with the classical formulæ [(Ia)—(V)]. The unexpected properties discussed are thermochromism, cleavage with sulphur (see scheme A) or thionyl chloride, and photochemical reactions partly in sunlight. These photoreactions lead to the formation of highly condensed ring systems by the loss of hydrogen atoms from aromatic nuclei [*e.g.*, formation of (XI) from (IIb)]. A theory is advanced to explain the strange behaviour of these ethylenes: it is based on the assumption that they are true ethylenes in the classical sense at low temperature, but in the melt and in hot solutions they have the structure of betaines [see, *e.g.*, (III) and (VIII) in the case of dixanthylene]; the theory of resonance is applied.

A similar explanation is advanced for the observation that some of the above-mentioned ethylenes, *viz.*, (Ib), (IIa), and (IIb), change their colour when subjected to pressure (piezochromism).

THE substances (Ia)—(V) show remarkable physical and chemical properties; in the crystalline state their colour is different from that of the melts and the solutions. Dixanthylene (III) is colourless at the temperature of liquid air and almost colourless at room temperature; the crystals turn bluish-green on heating, and both the melt and the hot solution are bluish-green (Schönberg and Schütz, *Ber.*, 1928, 61, 478).

Diphenylmethylenanthrone (Ia) (Padova, *Compt. rend.*, 1906, 143, 122), *di-p-anisylmethylenanthrone* (Ib), and diflavylene (IV) * form light yellow crystals at the temperature of liquid air, at room temperature they are yellow, the melts are ruby-red, and the colour of the hot solutions varies from orange-red to deep red depending on the concentrations.



The crystals of diphenylmethylenexanthen (V) are colourless at room temperature but orange-red when molten, and the hot solutions are orange (Schönberg and Nickel, *Ber.*, 1931, 64, 2323).

Dianthraquinone (IIa) is light yellow at the temperature of liquid air, citron-yellow at room temperature, green when molten, and bluish-green in hot solutions (Meyer, *Monatsh.*, 1909, 30, 174), and 10-(9'-xanthylene)-anthrone (IIb) is light yellow, yellowish-green, deep green, and deep bluish-green, respectively, under these four conditions.

Some of the above ethylenes form solutions the colour of which changes strongly with temperature; *e.g.*,

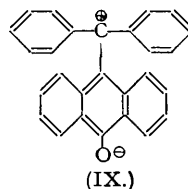
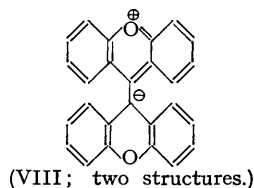
* Reactions denoted by an asterisk were carried out by Miss Asker.

solutions of (IIa) and (IIb) in benzonitrile, anisole, or xylene change from yellow or yellowish-green to bluish-green on heating. These colour changes are reversible.

Under a pressure of *ca.* 100 kg./mm.², some of the above ethylenes also undergo a remarkable change of colour. This phenomenon was first observed by Meyer (*loc. cit.*), who found that the yellow crystals of (IIa) become bluish-green on pressing. Similarly, (IV) changes from yellow to dark red (Schönberg and Asker, J., 1942, 272), (Ib) from yellow to deep red, and (IIb) from yellowish-green to deep green. For this phenomenon the name "piezochromism" is proposed. Very little is known about it, but Löwenbein observed (*Ber.*, 1927, 60, 1855) that some solid ethanes seem to dissociate into free radicals when subjected to high pressures, for the solid assumes the colour of the radical. This would indicate that one molecule of the ethane occupies more space than two single radicals.

Theories of Thermochromism and Piezochromism.—It is well known that certain crystals (colourless or coloured), *e.g.*, nitrosobenzene, give melts or solutions of markedly different colour, the change being ascribed to depolymerisation; and Padova (*loc. cit.*), who found that (Ia) (yellow) gives deep red solutions in neutral solvents, believed that the reversible colour change was due to polymerisation and depolymerisation, but this was disproved by Bergmann and Corte (*Ber.*, 1933, 66, 39).

Ingold and Marshall (J., 1926, 3080), finding that the nearly colourless 9 : 10-diphenylanthracene gave yellow solutions, the colour of which became deeper on heating but faded again on cooling, explained the change by the formation of a biradical (VI). A similar explanation has been advanced for the reversible colour change of dixanthhylen (compare VII) and other ethylenes exhibiting thermochromism (Schönberg and Schütz, *loc. cit.*; Schönberg, Kaltschmidt, and Schulten, *Ber.*, 1933, 66, 247; Bergmann and Corte, *loc. cit.*).



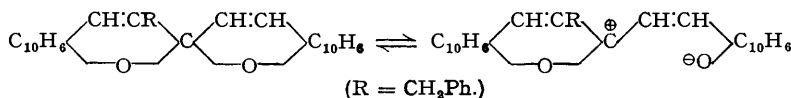
Ethylene-Betaine Theory.—The following hypothesis is now advanced, which explains not only the above-mentioned colour changes by the action of heat and pressure, but also the remarkable chemical properties of these substances and connects these phenomena with facts known in other fields of chemistry.

It is suggested that these substances are true ethylenes in the crystalline state, especially at low temperatures, as indicated by the formulæ (Ia)—(V), but in the melt and in hot solutions the molecules acquire the structure of betaines, those of (III) and (Ia) being written as (VIII) and (IX), respectively.

It is more correct to state that the molecules of dixanthhylen (III) and of related substances are to be regarded as resonance hybrids with contributions *inter alia* from the true ethylene structure and the betaine structure, and that when the substances are molten or in hot solution there is a large contribution to the mesomeric state from the latter structures and a relatively small contribution from the true ethylene form. The reverse is the case with the molecules of the *crystallised* dixanthhylen and of the other thermochromic ethylenes, especially at low temperatures.

A similar explanation is proposed to explain the above phenomenon of piezochromism. It should be noted that the colour obtained by pressure is of the same shade as that of the melt or of hot solutions.

The colour changes of the above ethylenes may be compared with those of certain *spiro*-compounds (Löwenbein and Katz, *Ber.*, 1926, 59, 1377; Dickinson and Heilbron, J., 1927, 14; Dilthey and Wübken, *Ber.*, 1928, 61, 963), which have also been explained by the formation of betaines as illustrated below :

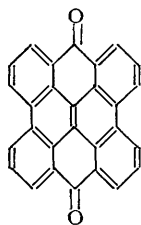


The above *spiro*-compound forms colourless crystals which become blue on melting; the solution in hot xylene is deep blue, and on cooling it becomes paler and finally colourless (Löwenbein and Katz, *ibid.*, p. 1382).

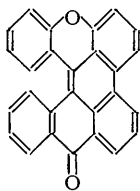
The betaine structures of the ethylenes (Ia)—(V) may be divided into two groups of which (VIII) and (IX) are representative and show the principal difference. In (VIII) the atom of the highest electron density is a carbon atom, whereas in (IX) it is a hetero-atom. To the former group belong (III), (IV), and (V) and the sulphur analogues of (III) and (IV), and to the latter group belong (Ia), (Ib), (IIa), and (IIb). Each of the two groups shows remarkable chemical properties.

Photochemical Reactions.—Three of the substances belonging to the latter group, *viz.*, (Ia), (IIa), and (IIb), are easily dehydrogenated under the influence of light, and a new condensed ring system is formed. This remarkable reaction occurs only with these compounds, and takes place in the case of (IIa) (Meyer and co-workers, *Monatsh.*, 1912, 33, 1465) and (IIb) by the action of sunlight filtered through glass, but in the case of (Ia) by the action of ultra-violet light (Clar, *Ber.*, 1930, 63, 869). The reaction products obtained are

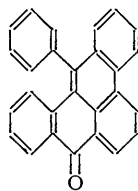
respectively (X), (XI) (the name "oxapenenon" is given to this substance), and (XII); (XI) forms red crystals, in contrast to helianthron (XIII) which is blue and (IIa) which is yellow.



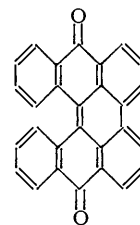
(X.)



(XI.)

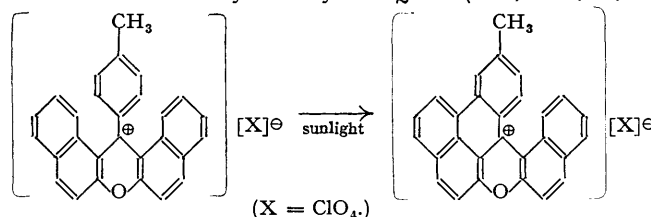


(XII.)



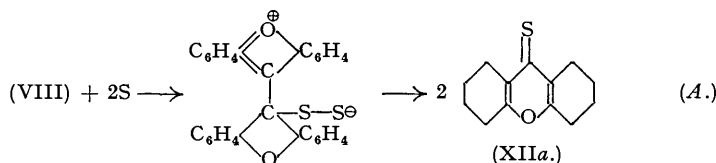
(XIII.)

There is no process strictly analogous to this photo-dehydrogenation, in which hydrogen atoms directly attached to an aromatic nucleus play a rôle, except among betaines or salts; for salts (which are closely related to betaines) similar reactions are described by Dilthey and Quint (*Ber.*, 1936, **69**, 1584):



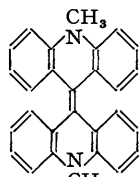
We suggest that, in these reactions of diphenylmethylenedianthracene (Ia) and related substances, the light should be considered as acting, not on the ethylenes, but on the betaines, and this makes the similarity between the cases of (Ia), (IIa), and (IIb) and those described by Dilthey more striking.

Sulphur and Thionyl Chloride Cleavage.—Substances (III), (IV), their sulphur analogues, and (V) * show very remarkable behaviour with sulphur (Schönberg, *Ber.*, 1925, **58**, 1796; Schönberg and Asker, *loc. cit.*), as well as with thionyl chloride (Schönberg and Asker, *J.*, 1942, 725). When heated with elementary sulphur they rapidly react to form thioketones; e.g., the reaction with dioxanthylene takes place in a few minutes at 290°. As this reaction does not occur with the ethylenes (C₆H₄R)₂C:C(C₆H₄R)₂, where R = H, *p*-OMe, *p*-NMe₂, or *p*-C₆H₅, or with C₆H₄>C:C<C₆H₄ or C₆H₄>C:C<Ph* (*idem, ibid.*, p. 272), it is believed that the cleavage should be described as the action of sulphur on a betaine, as formulated in (A).

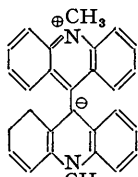


When the ethylenes are treated with thionyl chloride (*idem, ibid.*, p. 725), the ethylene bond is broken and the corresponding keto-chloride is formed; e.g., (VIII) gave 9:9-dichloroxanthene.

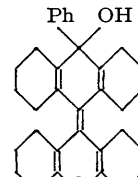
This reaction has been carried out with dioxanthylene (III), diflavylene (IV), and their sulphur analogues (Schönberg and Asker, *loc. cit.*), also with (V)*, but no case of cleavage has been found with substances not closely related to these. It is believed, for the reason explained above (compare scheme A), that the thionyl chloride reacts with the betaine form.



(XIV.)



(XV.)

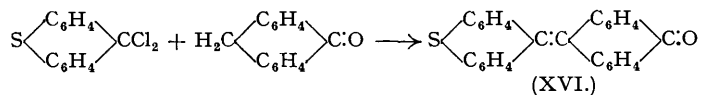


(XVII.)

Constitution of NN'-Dimethyldiacridine.—The substances (Ia)—(V) may be contrasted with tetraphenylethylene, which does not show the phenomenon of thermochromism or piezochromism or undergo photo-dehydrogenation or react with elementary sulphur or thionyl chloride in the manner described above. On the other hand, dioxanthylene and diflavylene may be compared with NN'-dimethyldiacridine (XIV) which shows cleavage with sulphur (Gleu and Schaarschmidt, *Ber.*, 1939, **72**, 1246) and with thionyl chloride (Schönberg and Asker, *loc. cit.*, p. 725). The deep colour of the substance at room temperature makes it probable that it should be described as a betaine (XV), which should be compared with (VIII).

These phenomena require investigation by modern physical methods, but a review of the organic chemistry is given by Schlenk ("Ausführliches Lehrbuch der organischen Chemie," 1939, II, 626).

Special Part.—When the keto-chlorides of 4:4'-dimethoxybenzophenone, xanthone, and thioxanthone are allowed to react with anthrone in dry xylene, dianisylmethylenanthrone (Ib), 10-(9'-xanthylen)anthrone (IIb), and 10-(9'-thioxanthylen)anthrone (XVI), respectively, are obtained, *e.g.*,



These reactions are similar to the formation of diphenylmethylenanthrone (Ia) by interaction between benzophenone keto-chloride and anthrone (Padova, *loc. cit.*). The presence of one carbonyl group in (IIb) was ascertained by its reaction with phenylmagnesium bromide, followed by hydrolysis in the usual manner, whereby 9-phenyl-10-(9'-xanthylen)-9:10-dihydroanthranol (XVII) was formed; it is a light yellow substance which gives strong halochromy with concentrated sulphuric acid.

When the light yellowish-green compound (XVI) in benzene solution is illuminated with direct sunlight, it forms a deep red solution showing an intense green fluorescence.

EXPERIMENTAL.

Dianisylmethylenanthrone (Ib).—4:4'-Dimethoxybenzophenone (11 g.) and oxalyl chloride (10 g.) were mixed and heated under reflux for 3 hours; the excess of oxalyl chloride was driven off under vacuum. The residue (4:4'-dimethoxydiphenyldichloromethane; Straus and Dützmann, *J. pr. Chem.*, 1921, **103**, 46) was dissolved in dry xylene (30 c.c.; sulphur-free), and the mixture dropped slowly into a solution of anthrone (8.8 g.) dissolved in dry xylene (35 c.c.); an immediate evolution of hydrogen chloride occurred and the solution became darker and finally reddish-brown. After the addition was complete, the mixture was refluxed for two hours, then cooled; the brown precipitate formed was filtered off and treated with boiling acetone (100 c.c.); the acetone solution was filtered while hot and the filtrate treated with acidulated water, whereupon a brown crystalline precipitate separated (12 g.). *Dianisylmethylenanthrone (Ib)*, crystallised from acetone (animal charcoal) and repeatedly from glacial acetic acid, formed shining canary-yellow crystals, m. p. 190° (ruby-red melt). It gave an intense violet coloration with concentrated sulphuric acid. It is soluble in cold anisole with an orange-red colour (Found: C, 82.9; H, 5.4. $\text{C}_{29}\text{H}_{22}\text{O}_3$ requires C, 83.2; H, 5.3%). When pressed strongly with a glass pestle, the crystals attained a permanent orange-red colour, which changed back to yellow when they were subjected to ether vapour.

10-(9'-Xanthylen)anthrone (IIb).—Xanthone (10 g.) was dissolved in thionyl chloride at room temperature and heated under reflux for 10 hours. The thionyl chloride was then distilled off under vacuum, and the residue treated with dry xylene (70 c.c.). The mixture was dropped slowly into a boiling solution of anthrone (10 g.) in dry xylene (35 c.c.); an immediate evolution of hydrogen chloride occurred and the solution gradually became deep green. After the addition was complete, the mixture was heated under reflux for 12 hours, evolution of hydrogen chloride then being complete. The product was cooled in ice, the deep green crystalline precipitate filtered off (10 g.), boiled for about 15 minutes with glacial acetic acid (200 c.c.), and filtered off while hot. The insoluble part was crystallised once from acetylene tetrachloride and then repeatedly from benzene-ligroin (b. p. 45–75°), forming yellowish-green crystals, m. p. 301–302°, giving a deep green melt with slight sublimation (Found: C, 86.6; H, 4.4. $\text{C}_{22}\text{H}_{16}\text{O}_2$ requires C, 87.0; H, 4.3%). *10-(9'-Xanthylen)anthrone* gave a yellowish-green coloration with concentrated sulphuric acid. The crystals became deep green on pressing, the colour being restored by ether vapour. They show reversible and pronounced thermochromic effects in very dilute solutions, *e.g.*, in benzonitrile, anisole, or xylene.

10-(9'-Thioxanthylen)anthrone (XVI).—Thioxanthone (8 g.) (Gomberg and Britton, *J. Amer. Chem. Soc.*, 1921, **43**, 1946) was dissolved in thionyl chloride at room temperature and heated under reflux for ten hours. The thionyl chloride was then distilled off under vacuum, and the residue treated with dry xylene (100 c.c.) and then with anthrone (7.8 g.), evolution of hydrogen chloride occurring; after 15 minutes at room temperature, the mixture was heated under reflux for 12 hours, the evolution then being complete. The mixture was allowed to cool to room temperature, left for ½ hour, and filtered from the dark resin. The dark brown filtrate was concentrated under reduced pressure to about 50 c.c., cooled, and the very dark precipitate filtered off; a further quantity was obtained from the mother-liquor by slow concentration to about 20 c.c. The combined crops were triturated with ether (50 c.c.) and separated (yield about 6 g.). Repeated crystallisation from benzene afforded *10-(9'-thioxanthylen)anthrone (XVI)* as greenish-yellow crystals, m. p. 308°. It showed no thermochromic effects in benzonitrile, anisole, or xylene and gave a deep reddish-violet coloration with concentrated sulphuric acid (Found: C, 83.0; H, 4.2; S, 8.1. $\text{C}_{27}\text{H}_{16}\text{OS}$ requires C, 83.5; H, 4.1; S, 8.2%).

Action of Phenylmagnesium Bromide on 10-(9'-Xanthylen)anthrone (IIb).—To an ethereal solution of phenylmagnesium bromide, prepared from magnesium (0.73 g.), bromobenzene (4.7 g.), and dry ether (20 c.c.), dry benzene (100 c.c.) was added, and the hot solution treated gradually with powdered (IIb) (3.7 g.). The ether was evaporated slowly and refluxing continued with stirring for 3 hours. The product was cooled, then decomposed with ammonium chloride and ice, and the benzene layer separated, washed with water, and dried over anhydrous sodium sulphate. The benzene solution was evaporated to dryness and the deep green oily residue solidified after two days. *9-Phenyl-10-(9'-xanthylen)-9:10-dihydroanthranol (XVII)* crystallised from acetone (1.1 g.) then from acetone-alcohol as light yellow crystals, m. p. 255° giving a dark melt. It gave a deep bluish-green coloration with concentrated sulphuric acid (Found: C, 87.4; H, 5.0; active H, 0.24. $\text{C}_{33}\text{H}_{22}\text{O}_2$ requires C, 87.9; H, 5.0; active H, 0.22%).

Photochemical Experiments.—The experiments were carried out in Monax glass tubes, the air being displaced by dry carbon dioxide and the tube sealed by fusion. The benzene used was thiophen-free (Kahlbaum) and dried over sodium.

(A) *10-(9'-Xanthylen)anthrone (IIb)* (1 g.) was dissolved in benzene (25 c.c.) and left in direct sunlight for one week (June); the solution became red with an intense green fluorescence, and on concentration to 5 c.c. under reduced pressure and cooling, it afforded crystals of *oxapenenon (XI)* (0.5 g.); this crystallised from benzene as red crystals, m. p. 245–246° (Found: C, 87.0; H, 3.8. $\text{C}_{27}\text{H}_{14}\text{O}_2$ requires C, 87.5; H, 3.8%). It gave a malachite-green coloration with concentrated sulphuric acid. It is sparingly soluble in cold and hot alcohol with an orange-red colour and a yellow fluorescence, the fluorescence being more intense in the cold. It dissolves in cold benzene with a yellowish-green fluorescence. When a drop of the benzene solution was put on a glazed white porcelain plate, it looked bright yellow without any red coloration, but it dried to orange red crystals.

(B) *Action of sunlight on 10-(9'-thioxanthyl)anthrone (XVI)*. The compound (1 g.) was dissolved in benzene (25 c.c.) and left in direct sunlight for two weeks (July); the colour of the solution became red with green fluorescence, but the compound was only obtained as a red oil which gave an intense green coloration with concentrated sulphuric acid.

*Action of Sulphur on Diphenylmethylenexanthen (V) **.—The substance (Schönberg and Mustafa, J., 1944, 67) (1 g.) was ground with sulphur (1 g.) and heated gradually in a paraffin-bath. At 140° the mixture melted and became orange-coloured; this colour remained up to 270°, and then changed immediately to green. After 10 minutes, the melt was allowed to cool, powdered, and extracted with benzene. The extract was concentrated, cooled, filtered from sulphur, concentrated again, and cooled; green crystals were obtained, m. p. 156°, not depressed by admixture with authentic xanthone (XIIa) (Schönberg and co-workers, *Ber.*, 1928, **61**, 1382).

*Action of Thionyl Chloride on (V) **.—The substance (0.5 g.) was dissolved in thionyl chloride (yellow solution) and heated under reflux on a water-bath for 3 hours. The excess of thionyl chloride was distilled off under reduced pressure, and the residual orange oil was dissolved in benzene (20 c.c.) and shaken with water (10 c.c.). The benzene layer was isolated and evaporated; the yellow substance obtained was extracted with ligroin (b. p. 30—50°). After evaporation, colourless crystals were obtained, m. p. 49°, not depressed by admixture with authentic benzophenone. The residue was then extracted with ligroin (b. p. 100—110°) from which xanthone was obtained, m. p. 174°, not depressed by admixture with an authentic specimen.

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