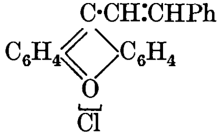
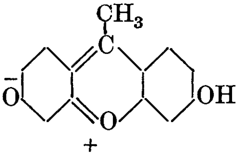
XCIV.—*Styrylpyrylium Salts. Part VI. Styryl Derivatives of 9-Methylxanthylium Chloride and 3 : 6-Dihydroxy-9-methylxanthylium Chloride.*

By Harold Atkinson and Isidor Morris Heilbron.

The only styrylxanthylium salt recorded in the literature is 9-styrylxanthylium chloride (I), which Ziegler and Ochs (*Ber.*, 1922, **55**, 2257) obtained by the action of β-bromostyrene and

(I.)

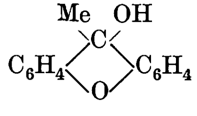




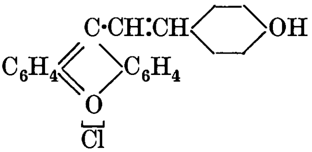
(II.)

magnesium upon xanthone. A more detailed study of styrylxanthylium salts has now been made in order to compare them with the members of the styrylbenzopyrylium series. As the method employed by Ziegler and Ochs could not readily be adopted for the preparation of salts containing substituents in either the styryl or the xanthylium residue, other methods of preparation had to be sought. The ease with which the anhydro-base, 6-hydroxy-9-methylfluorone (II), reacts with nitrous acid to form the *iso*nitroso-derivative (Kehrmann, *Annalen*, 1910, **372**, 287) rendered it probable that a methyl group in position 9 in a xanthylium nucleus would show the same reactivity as an α- or γ-methyl group does in the benzopyrylium series. In order to test this point, an attempt was made to prepare 9-methylxanthylium chloride which had previously been prepared by Decker (*Ber.*, 1905, **38**, 2493) in the form of its double ferrichloride salt by the action of magnesium methyl iodide upon xanthone. The free chloride can actually be isolated, but it is difficult to obtain in good yield. On the other hand, an ethereal solution of the easily accessible 9-methylxanthenol (III) may be utilised in place of the chloride itself. Thus, on saturation of the solution mixed with benzaldehyde with dry hydrogen chloride, 9-styrylxanthylium chloride, identical in all respects with the compound prepared by Ziegler and Ochs (*loc. cit.*), was readily obtained. Similar condensations have been effected with p-hydroxybenzaldehyde, p-methoxybenzaldehyde, piperonal, and vanillin, and in all cases excellent yields obtained.

(III.)



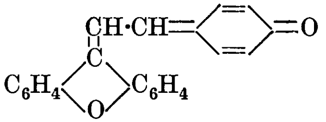
(IV.)

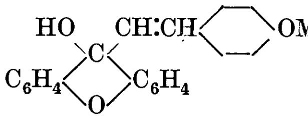


The styrylxanthylium salts containing substituents in the styryl residue are highly coloured, crystalline compounds, readily soluble in formic acid, giving deep red to purple solutions. In their reaction towards water and alkali, they behave similarly to the unsubstituted 2-styrylbenzopyryliums (Buck and Heilbron, J., 1922, **121**, 1198). Thus, when 4′-hydroxy-9-styrylxanthylium chloride (IV) was dissolved in dilute formic acid, a reddish-violet solution resulted which on dilution with a large excess of water slowly changed to blue. This colour effect we attribute, as in former cases, to formation of the quinonoid anhydro-base (V), for with 4′-methoxy-9-styrylxanthylium chloride, where such isomerisation is precluded, the solution rapidly becomes opalescent and decolorised, followed by deposition of the colourless carbinol base (VI).

3′ : 4′-Methylenedioxy-9-styrylxanthylium chloride, which dissolves in formic acid with a blue colour, reacts similarly. The same effect is noted on treatment of the formic acid solutions with dilute sodium hydroxide. On the other hand, with the 4′-hydroxy-derivatives the quinonoid anhydro-bases are first precipitated and then slowly isomerise to the colourless carbinol bases (compare Dilthey and Taucher, *Ber.*, 1920, **53**, 252). In all cases, the effect of heat on the colourless carbinol solutions produces a reversion in colour, a fact indicating that at higher temperatures the oxonium bases are more stable than the isomeric carbinol compounds. This phenomenon has also been observed by Bunzly and Decker (*Ber.*, 1904, **37**, 2931) in the case of 9-phenylxanthenol.

(V.)

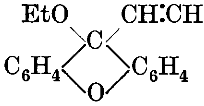


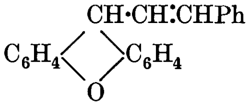


(VI.)

The behaviour of these styrylxanthylium chlorides towards alcohol is peculiar. Ziegler and Ochs (*loc. cit.*) noted that on trituration of 9-styrylxanthylium chloride with alcohol, 9-styrylxanthyl ethyl ether (VII) was formed, while, on the other hand, boiling with this solvent produced 9-styrylxanthen (VIII). A preliminary study of the styrylxanthylium chlorides containing substituents in the styryl residue has shown that when these are kept in contact with small quantities of alcohol, they are gradually converted into colourless substances, all of which crystallise from acetone in well-defined crystals with sharp melting point. The compounds thus prepared have been analysed, but in each case the carbon content is too high for formulation either as an ethyl ether, xanthen or allene derivative. The formation of the last type of compound from other styryl derivatives was noted by Meyer and Schuster (*Ber.*, 1922, **55**, 815), and Ziegler and Ochs, by boiling 9-styrylxanthenol with glacial acetic acid, obtained a compound the composition of which would agree with that of an allene derivative. A full investigation of these interesting compounds is at present being undertaken.

(VII.)



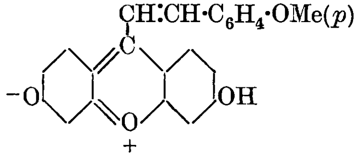


(VIII.)

Walker and Heilbron (J., 1925, **127**, 685) have shown that in the γ-styrylbenzopyryliums the presence of a free hydroxyl group in the meta-position to pyrylium oxygen inhibits the change to quinonoid anhydro-base on water dilution. In order to ascertain whether a similar effect holds in this series, styrylxanthylium salts prepared from 3 : 6-dihydroxy-9-methylxanthylium chloride have been examined. The latter compound, which has been described by Kehrmann (*loc. cit.*), can be isolated directly in good yield by continuously passing dry hydrogen chloride into a molten mixture of resacetophenone and resorcinol until the mass solidifies.

3 : 6-*Dihydroxy*-9-*styrylxanthylium Salts*.—The general method employed was to saturate with dry hydrogen chloride a suspension of 3 : 6-dihydroxy-9-methylxanthylium chloride in alcohol containing a slight excess of the required aldehyde. Condensation usually started in the cold and was completed by boiling under reflux; the suspended chloride then gradually disappeared and the condensation product separated either from the boiling solution or on cooling. These salts differ from those having the unsubstituted xanthylium nucleus in being soluble in alcohol without change, whilst the colour of the solutions both in this solvent and in formic acid is considerably lighter. A notable point is that whereas 3 : 6-dihydroxy-9-methylxanthylium chloride is characterised by its strong fluorescence in alkaline solution, substitution of the styryl radical for the methyl group caused the complete disappearance of this property. The colour changes observed on dilution with water or treatment with alkali differ essentially from those of the unsubstituted styrylxanthylium members. A neutral alcoholic solution of 3 : 4′ : 6-trihydroxy-9-styrylxanthylium chloride remains unaltered on dilution, and in presence of alkali the orange-red colour only changes to bright red, due doubtless to salt formation. 3 : 6-Dihydroxy-4′-methoxy-9-styrylxanthylium chloride reacts similarly, for neither on dilution nor in presence of alkali does isomerisation to the carbinol base occur. The non-formation of this can only be attributed to the presence of the hydroxyl groups, which stabilise the molecule, presumably by formation of the betaine (IX). The same phenomenon must consequently hold for the 4′-hydroxy-analogue, but apart from this no structural change from benzenoid to quinonoid can be assumed.

(IX.)



EXPERIMENTAL.

9-*Methylxanthylium chloride* was prepared by a modification of Decker's method (*loc. cit.*). Xanthen (30 g.) was dissolved in boiling benzene (250 c.c.), and the Grignard reagent (12 g. of magnesium and 66 g. of methyl iodide) gradually added. The solution immediately became orange and a yellow solid separated. This was rapidly reabsorbed, however, and later a colourless. crystalline compound separated from the greyish-green liquid. The whole was boiled under reflux for 1 hour, after which the ether and about half the benzene were removed. The solid was filtered off from the cold solution, washed with dry ether, and decomposed with cold water. The yellow solution so formed was repeatedly extracted with ether until the aqueous layer gave only a pale yellow colour on the addition of concentrated hydrochloric acid. After drying over sodium sulphate, this ethereal solution was employed directly for the preparation of the styryl salts. In order to obtain 9-methylxanthylium chloride, the solution was saturated with dry hydrogen chloride; the colour then changed from pale yellow to green and on standing in the ice-chest, dark red crystals separated. After recrystallisation from a mixture of anhydrous formic acid and ether containing hydrogen chloride, the salt was obtained in golden needles, m. p. 175°, and identified by means of the double ferrichloride, m. p. 204°, and mercurichloride (compare Decker, *loc. cit.*). The melting point of the ferrichloride is given in the literature as 240°, but this is possibly a typographical error.

9-*Styrylxanthylium Chlorides*.—The general method of preparation of these salts consisted in the addition of the aldehyde in slight excess to the dry ethereal solution of 9-methylxanthenol, the mixture being then saturated with dry hydrogen chloride, when condensation readily took place. The actual amount of xanthenol in solution was not ascertained, but the Grignard reaction, by means of which it was prepared, was assumed to have given a quantitative yield.

9-*Styrylxanthylium chloride* rapidly separated from the condensation mixture of 9-methylxanthenol and benzaldehyde either as golden, glistening plates or as red needles with a bright green sheen. The plates melted at 95°, the same melting point as that given by Ziegler and Ochs (*loc. cit.*), but the red needles melted over a range of temperature (66—92°) and probably contained some easily lost addenda. This salt was proved to be identical with that prepared by Ziegler and Ochs by means of the deep red double salt with zinc chloride (m. p. 188°) and its ethyl ether (m. p. 168—169°).

4′-*Hydroxy*-9-*styrylxanthylium chloride*. On passing dry hydrogen chloride into the well-dried ethereal solution of 9-methylxanthenol and excess of *p*-hydroxybenzaldehyde, the solution gradually passed through orange to dark red and a violet oil with bronze reflex separated. The mixture having been left in the ice-chest for several hours, the ether was poured off; the oil gradually solidified to a green, amorphous mass. This was taken up in a small amount of warm anhydrous formic acid previously saturated with hydrogen chloride, and dry ether was added to the cold filtered solution in small quantities at a time; the styryl salt then separated in long, bright-green, lustrous needles containing 1 mol. HCO_2H. These were immediately transferred to a large test-tube, which was then evacuated, whereby adherent hydrogen chloride was removed and the crystals were rendered stable. If this was not done, the compound tended to become resinous, a tendency exhibited by all members of this series. The salt was readily soluble in cold formic acid and in hot glacial acetic acid, giving dark violet solutions. It was sparingly soluble in cold chloroform to a blue solution which changed to reddish-brown on warming but reverted to blue on cooling. The same colour change on heating was shown by a solution in nitrobenzene. When a large volume of water was added to a very dilute formic acid solution (wine-red colour), no immediate change of colour occurred, but on standing (6 hours) the solution became pure blue. The addition of water to a more concentrated formic acid solution caused the immediate separation of a violet, amorphous precipitate, presumably the anhydro-base (V) (Found: C, 69·4; H, 4·5; Cl, 9·4. $C_{22}H_{17}O_4Cl,HCO_2H$ requires C, 69·4; H, 4·5; Cl, 9·3%). In contact with absolute alcohol, the salt was partly converted into a colourless, crystalline substance, but this change was not absolutely complete despite repeated trituration, even after 15 days. The substance crystallises from acetone in long, colourless needles, m. p. 228° (Found: C, 85·0; H, 5·8%).

4'-*Methoxy*-9-*styrylxanthylium chloride* separated from the condensation liquor in dark green crystals. Considerable difficulty was experienced in obtaining it in a stable crystalline state sufficiently pure for analysis, but this was ultimately accomplished by crystallisation from chloroform containing hydrogen chloride; it then separated in bright green needles, m. p. 98°, which were rendered stable by removal of all addenda in a vacuum. The salt dissolved readily in formic and glacial acetic acids, giving dark violet solutions. When a dilute solution in formic acid was treated with water, a strong opalescence immediately developed, the wine-red colour rapidly faded, and the colourless carbinol base was deposited. As with the 4'-hydroxystyryl salt, long trituration with alcohol gave a colourless compound, m. p. 194°, of undetermined constitution. The *ferrichloride*, prepared by the action of powdered hydrated ferric chloride on a solution of 4′-methoxy-9-styrylxanthylium chloride in formic acid, separated from glacial acetic acid in long, copper-coloured plates which softened and turned blue at 175° and decomposed with inflation at 212° (Found : C, 51·5; H, 3·2; Cl, 27·7; Fe, 10·5. $C_{22}H_{17}O_2Cl_4Fe$ requires C, 51·7; H, 3·3; Cl, 27·8; Fe, 10·9%).

4′-*Hydroxy*-3′-*methoxy*-9-*styrylxanthylium chloride* crystallised from formic acid in golden-brown needles which contained a molecule of formic acid (m. p. 135°). The salt was readily soluble in cold formic acid and in hot glacial acetic acid, giving royal-blue solutions. Neutralisation of a dilute formic acid solution with sodium carbonate precipitated the colour base, which was gradually converted into the colourless carbinol base (Found : C, 67·1; H, 4·6; Cl, 8·9. $C_{22}H_{17}O_3Cl,HCO_2H$ requires C, 67·2; H, 4·6; Cl, 8·7%).

3′ : 4′-*Methylenedioxy*-9-*styrylxanthylium chloride* could not be obtained pure, for although it separated from the condensation mixture in green crystals, attempts to recrystallise these from either formic acid or glacial acetic acid with or without the addition of hydrogen chloride resulted in the formation of a yellow oil, which gradually solidified to a colourless compound. Recourse was made, therefore, to analysis of the *zinc chloride* double salt, which was readily prepared by suspending the crude xanthylium chloride in cold formic acid and shaking vigorously with zinc chloride in hydrochloric acid. The salt separated from glacial acetic acid in glistening, green needles (Found : C, 49·6; H, 3·1; Cl, 20·3. $C_{22}H_{15}O_3Cl_3Zn,H_2O$ requires C, 51·2; H, 3·3; Cl, 20·6%).

3 : 6-*Dihydroxy*-9-*methylxanthylium Chloride*.—Dry hydrogen chloride was passed into a molten mixture of resacetophenone (10 g.) and resorcinol (7·2 g.) (oil-bath at 140—150°). The melt gradually turned red and, after several hours, became semi-solid. The stream of hydrogen chloride was continued until the mass became too viscous, the temperature being gradually raised to 170°. The solid mass was dissolved in boiling anhydrous formic acid (80 c.c.); the xanthylium chloride then separated in reddish-yellow needles with a characteristic blue metallic reflex. On several occasions, however, the salt was deposited as a chocolate powder, which was again recrystallised from formic acid containing hydrogen chloride. It is soluble in alcohol, acetone, or formic acid and insoluble in ether or benzene. It dissolves in sodium hydroxide solution to a reddish-brown solution which when dilute shows an intense green fluorescence. With sodium acetate it yields the base in the form of brick-red flocks.

3 : 4′ : 6-*Trihydroxy*-9-*styrylxanthylium Chloride*.—The parent

chloride (5 g.) was suspended in 70 c.c. of alcohol together with *p*-hydroxybenzaldehyde (2·6 g.), and dry hydrogen chloride was passed into the cold solution; the xanthylium chloride then gradually dissolved. After ½ hour the styrylxanthylium chloride (4·3 g.) separated from the deep red solution as a red, amorphous solid. On recrystallisation from anhydrous formic acid containing hydrogen chloride, it formed long needles which appeared red by transmitted and green by reflected light. On heating the chloride changed to red and melted with inflation at 273—274°. It is readily soluble in hot formic acid, sparingly soluble in alcohol or acetone to orange-red solutions, whilst in dilute sodium hydroxide it dissolves, giving a permanent bright claret-red solution (Found: C, 65·1; H, 4·2; Cl, 9·0. $C_{21}H_{15}O_4Cl,H_2O$ requires C, 65·5; H, 4·4; Cl, 9·2%).

3 : 6-*Dihydroxy-4'-methoxy-9-styrylxanthylium chloride* separated as a dark red, amorphous solid (70% yield) on passing hydrogen chloride into a boiling alcoholic suspension of equimolecular quantities of the parent chloride and anisaldehyde. It was purified by boiling with alcohol, which removed any uncondensed products, and was then crystallised from formic acid containing hydrogen chloride. It forms golden-coloured plates with a metallic sheen which on heating change to green and melt at 282° (decomp.). It is very sparingly soluble in boiling alcohol or acetone, but readily soluble in hot formic acid. It dissolves in warm dilute sodium carbonate to a bright red solution, from which the base separates on cooling (Found: C, 65·9; H, 4·6; Cl, 8·7. $C_{22}H_{17}O_4Cl,H_2O$ requires C, 66·2; H, 4·8; Cl, 8·9%).

3 : 4' : 6-*Trihydroxy-5'-methoxy-9-styrylxanthylium chloride* crystallises from formic acid in reddish-violet needles which appear green by reflected light (m. p. 244—245°). It is readily soluble in alcohol, acetone, or hot formic acid and dissolves in dilute sodium hydroxide solution with a deep reddish-violet colour. It is extremely hygroscopic and specimens were dried at 100° immediately prior to analysis (Found: C, 66·6; H, 4·4; Cl, 8·8. $C_{22}H_{17}O_5Cl$ requires C, 66·6; H, 4·3; Cl, 8·9%).

3 : 6-*Dihydroxy-4' : 5'-methylenedioxy-9-styrylxanthylium chloride* separates from formic acid containing hydrogen chloride in bronze-coloured needles which, on heating, turn green and decompose at 316°. It is very sparingly soluble in alcohol, but dissolves readily in boiling formic acid to a red solution (Found, in material heated at 80° for several hours: C, 66·8; H, 3·9; Cl, 9·3. $C_{22}H_{15}O_5Cl$ requires C, 66·9; H, 3·8; Cl, 9·0%).

3 : 6-*Dihydroxy-4'-dimethylamino-9-styrylxanthylium Chloride*.—A suspension of the parent chloride (5 g.) and *p*-dimethylamino-

benzaldehyde (3·2 g.) in 100 c.c. of alcohol was boiled for 10 minutes under reflux without addition of hydrogen chloride, the condensation product separating as a hard, green solid. On recrystallisation from a large volume of alcohol, it formed microscopic, green needles which on heating changed to red. It is sparingly soluble in alcohol or acetone, giving intense green solutions which change to claret-red on dilution with water. Addition of hydrochloric acid to the alcoholic solution produces a yellow solution of the xanthylium chloride hydrochloride. The salt dissolves in aqueous sodium hydroxide to a bright scarlet solution, which is not altered on further dilution (Found: C, 66·6; H, 5·2; Cl, 8·8. $C_{23}H_{20}O_3NCl,H_2O$ requires C, 67·1; H, 5·3; Cl, 8·6%).

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