CCLI.—*Styrylbenzopyrylium Salts. Part VII. The Conversion of 7-Methoxy-2 : 3-dimethylchromone into Styrylpyrylium Salts.*

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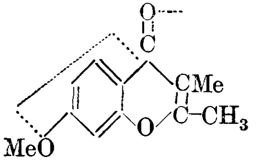
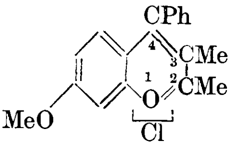
It has been shown by one of us (J., 1923, **123**, 2559) that the reactivity of the 2-methyl group in 2 : 3-dimethylchromone is completely inhibited by suitable substitution in the benzene ring. For example, 7-methoxy-2 : 3-dimethylchromone fails to condense with aromatic aldehydes to form styryl derivatives, and this failure has been attributed to a complete neutralisation of the partial valency forces (I). In this compound, the carbonyl group may be regarded as the essential primary centre of activity and consequently its removal should enable the characteristic reactivity of the 2-methyl group to be re-established. In order to test this point, 7-methoxy-2 : 3-dimethylchromone has been converted into 7-*methoxy*-4-*phenyl*-2 : 3-*dimethylbenzopyrylium chloride* (II) as detailed in the experimental part. This salt possesses extraordinary activity, condensing rapidly with aromatic aldehydes in alcoholic solution, without the presence of any catalyst, to yield 2-styrylbenzopyrylium salts. In this respect, it is analogous to 1-ethyl-2-methylene-1 : 2-dihydroquinoline in its condensation with *p*-dimethylaminobenzaldehyde (Mills and Raper, J., 1925, **127**, 2466) and is more active than the similarly constituted 7-hydroxy-2-phenyl-4-methylbenzopyrylium chloride, which requires the presence of dry hydrogen chloride to bring about condensation (Buck and Heilbron, J., 1923, **123**, 2521).

(I.)





(II.)

Owing to the ease with which the Grignard reagent reacts with the chromone, the opportunity has been taken of studying the effect of introducing auxochromic groups into the substituting phenyl group in position 4. This has been found to produce a decided influence on the colour of the salts; *e.g.* the unsubstituted salt (II) is yellow and dissolves in alcohol to an intensely yellow solution, the 4-*anisyl* derivative is orange and gives red to brown solutions, whilst 7-*methoxy*-4-p-*dimethylaminophenyl*-2 : 3-*dimethylbenzopyrylium chloride*, containing the more powerful auxochromic dimethylamino-group, separates in microscopic reddish-purple needles which dissolve in alcohol with an intense purple colour. The styrylbenzopyrylium salts are, in general, similar in their properties to the γ-styryl derivatives (Buck and Heilbron, J., 1923, **123**, 2521). They differ from these, however, in their more ready solubility and in the ease with which they yield the carbinol bases. All the styrylbenzopyrylium chlorides of this series crystallise from solvents with indefinite addenda, and for analysis the *ferrichlorides* or *perchlorates* were invariably employed.

EXPERIMENTAL.

7-Methoxy-4-phenyl-2 : 3-dimethylbenzopyrylium Chloride (II).—7-Methoxy-2 : 3-dimethylchromone (10 g.) was dissolved in carefully dried benzene (100 c.c.) and treated in the heat with a concentrated solution of magnesium phenyl bromide (2 mols.). The yellow solution was heated under reflux for 1½ hours and, after cooling, decomposed with concentrated hydrochloric acid (50 c.c.), added in small portions at a time; the pyrylium chloride was thus precipitated in quantitative yield. It separated from dilute hydrochloric acid in long, yellow needles which contained indefinite addenda together with a small quantity of some magnesium complex. The chloride was therefore dissolved in aqueous alcohol and treated with dilute ammonium hydroxide solution. The colourless carbinol base was extracted with ether, and the chloride reprecipitated by saturating the dried ethereal solution with dry hydrogen chloride. The *ferrichloride*, prepared by heating together ferric chloride and the pure chloride in glacial acetic acid, separated from acetone–light petroleum in large, greenish-yellow needles, m. p. 114°, freely soluble in alcohol and acetone, but insoluble in ether and benzene (Found: C, 46·7; H, 3·7; Cl, 30·7; Fe, 12·1. $C_{18}H_{17}O_2Cl_4Fe$ requires C, 46·7; H, 3·6; Cl, 30·8; Fe, 12·1%). The *perchlorate*, prepared by the addition of 20% perchloric acid to a solution of the chloride in alcohol, crystallised from alcohol containing perchloric acid in orange-yellow needles, m. p. 206°, readily soluble in hot water, alcohol, and glacial acetic acid (Found : C, 59·2; H, 4·7. $C_{18}H_{17}O_6Cl$ requires C, 58·9; H, 4·9%).

*7-Methoxy-4-phenyl-2-*p*-hydroxystyryl-3-methylbenzopyrylium chloride* was prepared by gently boiling a solution of the crude parent chloride (6 g.) and *p*-hydroxybenzaldehyde (2·4 g.) in methyl alcohol (18 c.c.). The solution rapidly became deep red and on cooling in the ice-chest the whole set to a crystalline mass. The salt was purified by regeneration from the colour base and separated from methyl alcohol containing a few drops of concentrated hydrochloric acid in glistening, brick-red crystals, m. p. 275° (decomp.). On treating an aqueous-alcoholic solution with dilute aqueous sodium hydroxide, a blue solution is formed from which the colour base is rapidly precipitated, but this, on being shaken with more alkali, passes into the carbinol base. The *perchlorate* separates from either glacial acetic acid or dilute alcohol containing perchloric acid in red needles (Found : C, 64·0; H, 4·6. $C_{25}H_{21}O_7Cl$ requires C, 64·0; H, 4·5%).

*7-Methoxy-4-phenyl-2-*p*-methoxystyryl-3-methylbenzopyrylium chloride* was obtained, after two recrystallisations from alcoholic hydrochloric acid, in red needles, soluble in cold water to a red solution which on treatment with alkali immediately yields the carbinol base. The *ferrichloride* forms brick-red needles (Found: C, 53·7; H, 4·1; Fe, 9·8. $C_{26}H_{23}O_3Cl_4Fe$ requires C, 53·7; H, 4·0; Fe, 9·7%).

7-*Methoxy*-4-*phenyl*-2-p-*hydroxy*-m-*methoxystyryl*-3-*methylbenzopyrylium chloride*, prepared from the crude parent chloride and purified through the colour base, separates from dilute alcohol containing hydrochloric acid in glistening, dark green crystals, soluble in dilute hydrochloric acid, alcohol and glacial acetic acid to deep-red solutions. The alcoholic solution changes to deep blue on addition of aqueous sodium hydroxide. The *ferrichloride* forms dark green needles readily soluble in water, alcohol, or acetone (Found: C, 51·9; H, 4·1; Fe, 9·5. $C_{26}H_{23}O_4Cl_4Fe$ requires C, 52·3; H, 3·9; Fe, 9·4%).

7-*Methoxy*-4-*phenyl*-2-p-*dimethylaminostyryl*-3-*methylbenzopyrylium Chloride.*—7-Methoxy-4-phenyl-2:3-dimethylbenzopyrylium chloride (5 g.) was dissolved in boiling alcohol (20 c.c.), and *p*-dimethylaminobenzaldehyde (2·5 g.) added to the hot solution, the colour instantly changing to olive-green. The mixture was heated for 10 minutes on a water-bath and, on cooling, solidified to a bright green, crystalline mass. The salt separates from alcohol in green crystals easily soluble in acidified water to a green solution which on high dilution changes to blue. It is readily soluble in alcohol, acetone, or chloroform, giving deep blue solutions. When an alcoholic solution of the chloride is treated with a few drops of aqueous potassium hydroxide, a colourless solution is formed from which, on addition of water, the colourless carbinol base is precipitated. Sodium acetate precipitates the anhydro colour base as a violet precipitate. The *ferrichloride* crystallises from acetone in green crystals (Found: C, 54·4; H, 4·4; Fe, 9·4. $C_{27}H_{26}O_2NCl_4Fe$ requires C, 54·5; H, 4·4; Fe, 9·4%). The *diperchlorate*, obtained in yellow crystals by treating the chloride with boiling perchloric acid, passes on treatment with solvents into the *monoperchlorate*, which forms dark bluish-green crystals (Found: C, 65·2; H, 5·5. $C_{27}H_{26}O_6NCl$ requires C, 65·4; H, 5·2%).

7-*Methoxy*-4-p-*anisyl*-2:3-*dimethylbenzopyrylium chloride* was prepared by treating 7-methoxy-2:3-dimethylchromone with magnesium *p*-anisyl bromide. It crystallises from alcohol in orange-yellow needles, m. p. 160°, readily soluble in dilute hydrochloric acid, alcohol, or glacial acetic acid. The *ferrichloride* separates from absolute alcohol in orange-yellow crystals (Found: C, 46·1; H, 4·1; Fe, 11·3; Cl, 29·1. $C_{19}H_{19}O_3Cl_4Fe$ requires C, 46·2; H, 3·9; Fe, 11·3; Cl, 28·8%).

7-*Methoxy*-4-p-*anisyl*-2-p-*hydroxystyryl*-3-*methylbenzopyrylium chloride* crystallises from alcohol in red needles which behave in an exactly similar manner to the 4-phenyl analogue. The *ferrichloride* forms red needles (Found: C, 51·9; H, 4·0; Fe, 9·4. $C_{26}H_{23}O_4Cl_4Fe$ requires C, 52·2; H, 3·9; Fe, 9·4%).

The corresponding p-*methoxy-chloride* forms long, red needles soluble in alcohol to a red solution from which the carbinol base is precipitated on addition of dilute aqueous sodium hydroxide. The *ferrichloride* forms brownish-red needles (Found: C, 52·7; H, 4·3; Fe, 9·1. $C_{27}H_{25}O_4Cl_4Fe$ requires C, 53·0; H, 4·1; Fe, 9·2%).

7-*Methoxy*-4-p-*anisyl*-2-p-*dimethylaminostyryl*-3-*methylbenzopyrylium chloride* separates from absolute alcohol in olive-green crystals with an intense bronze sheen. Its behaviour with alkali and sodium acetate is exactly analogous to that of the 4-phenyl analogue. The *ferrichloride* crystallises from acetone in green needles, m. p. 125° (Found: C, 53·6; H, 4·8; Fe, 9·1. $C_{28}H_{29}O_3NCl_4Fe$ requires C, 53·8; H, 4·6; Fe, 9·0%).

7-*Methoxy*-4-p-*dimethylaminophenyl*-2 : 3-*dimethylbenzopyrylium chloride* was prepared by the interaction of 7-methoxy-2 : 3-dimethylchromone with magnesium *p*-dimethylaminophenyl iodide. A deep brown colour at once developed and the reaction was completed by boiling the mixture for an hour on the water-bath. When cold, the liquid portion was decanted and decomposed with concentrated hydrochloric acid. The pyrylium chloride, which separated as a deep purple oil, was taken up in a very small quantity of boiling absolute alcohol and, after vigorous scratching, crystallised in dark olive-green crystals giving a purple streak on paper. It is sparingly soluble in water, readily so in alcohol, to purple-red solutions. With dilute hydrochloric acid, a yellow solution is formed which, on large dilution with water, changes to purple-red. The *perchlorate*, obtained through the colourless carbinol base, crystallises from glacial acetic acid in dark purple needles readily soluble in alcohol or glacial acetic acid (Found: C, 58·6; H, 5·5. $C_{20}H_{22}O_6NCl$ requires C, 58·9; H, 5·4%). Condensations of this pyrylium salt were carried out and although styryl derivatives were undoubtedly formed, these separated as oils which could not be induced to crystallise.

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