19. *Reactions of* o-*Hydroxybenzylidenediacetophenones. Part III. Formation of a 4-Phenacylideneflavene during the Preparation of 4'-Methoxyflavylium Chloride.*

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Since benzylidenediacetophenones without an *o*-hydroxyl group are readily prepared by the agency of hydrogen chloride (Blumstein and Kostanecki, *Ber.*, 1900, **33**, 1481; Rupe and Veit, *Chem. Zentr.*, 1906, I, 1417), it is apparent that the condensation of *o*-hydroxybenzaldehydes and acetophenones to give flavylium salts may result in the formation of appreciable amounts of the corresponding *o*-hydroxybenzylidenediacetophenones. Besides diminishing the yield of the desired product, these compounds are capable of forming 4-phenacylflavylium salts which may contaminate the final material. In glacial acetic acid, these *o*-hydroxybenzylidenediacetophenones are converted smoothly and rapidly into the simple flavylium salts (preceding paper) and the question of contamination appears therefore to be eliminated. The condensation of aldehyde and acetophenone is, however, often carried out in ether and we have repeatedly found that attempts to prepare flavylium ferrichloride by treatment of *o*-hydroxybenzylidenediacetophenone with hydrogen chloride in ethereal solution resulted in a well-defined crystalline salt, giving analyses in which the values for carbon and hydrogen were high and for iron and chlorine low. Repeated crystallisations of the salt from glacial acetic acid failed to improve these values and we were forced to conclude that the salt was contaminated by the presence of 4-phenacylflavylium ferrichloride.

We have demonstrated the production of a 4-phenacylflavylium salt in at least one such case. When salicylaldehyde and *p*-methoxyacetophenone are condensed by means of hydrogen chloride in dry ether and the resulting flavylium chloride is taken up in 0·5% hydrochloric acid, a part of the product is decomposed with the formation of *4'-methoxy*-4-(p-*methoxyphenacylidene*)*flavene*. The same compound is obtained in the usual manner from o-*hydroxybenzylidenedi*-(p-*methoxyacetophenone*), which behaves normally with acids and can be converted also into *4'-methoxy*-4-(p-*methoxyphenacyl*)*flavene*. The phenacylidene derivative yields 4′-methoxy-4-(*p*-methoxyphenacyl)flavylium salts, of which the *chloride* is immediately hydrolysed in 0·5% hydrochloric acid to 4′-methoxy-4-(*p*-methoxyphenacylidene)flavene. There can therefore be no doubt that this salt is formed together with the simple flavylium chloride during the condensation referred to above, and the possibility of the formation of such salts as by-products of the preparation of flavylium salts in ether by this procedure cannot be overlooked.

EXPERIMENTAL.

Action of Hydrogen Chloride on o-*Hydroxybenzylidenediacetophenone in Ether.*—The diacetophenone (3 g.) was suspended in dry ether, and dry hydrogen chloride rapidly passed through it for 2 hours. After 12 hours, the chloride separated as thick red needles. The salt was unstable and the reaction mixture was therefore extracted with concentrated hydrochloric acid, the solution freed from ether on the water-bath, and an excess of solid ferric chloride added. There was an immediate oily precipitate, which solidified on cooling and was crystallised from glacial acetic acid many times. It separated as greenish-yellow blades, m. p. 159—161° (Found : C, 46·4; H, 3·2; Fe, 12·6; Cl, 33·2. $C_{15}H_{11}OCl_4Fe$ requires C, 44·4; H, 2·7; Fe, 13·5; Cl, 35·05. $C_{23}H_{17}O_2Cl_4Fe$ requires C, 52·3; H, 3·25; Fe, 10·7; Cl, 27·15%).

Condensation of p-*Methoxyacetophenone and Salicylaldehyde by Hydrogen Chloride in Ether.*—Dry hydrogen chloride was passed for 2 hours into a solution of *p*-methoxyacetophenone (7·5 g.) and salicylaldehyde (6·1 g.) in dry ether (50 c.c.). After 48 hours the small orange needles were collected, washed with dry ether, dried, and extracted with 0·5% hydrochloric acid at about 40°. The flavylium chloride was partly dissolved; the greenish-yellow residue of 4′-*methoxy*-4-(p-*methoxyphenacylidene*)*flavene*, crystallised from alcohol, formed deep yellow needles (1·06 g.), m. p. 167—168° (Found : C, 78·3; H, 5·3; OMe, 16·25. $C_{25}H_{20}O_4$ requires C, 78·1; H, 5·2; OMe, 16·15%).

o-*Hydroxybenzylidenedi*-(p-*methoxyacetophenone*).—A solution of *p*-methoxyacetophenone (7 g.) and salicylaldehyde (3 g.) in alcohol (30 c.c.) was treated with a hot solution of sodium hydroxide (8 g. in 8 c.c. of water). The mixture was kept over-night and then poured into water (1500 c.c.). The precipitate solidified after 2 days and was then washed with water and crystallised from alcohol, forming colourless needles (6 g.), m. p. 167° (Found : C, 74·2; H, 6·0. $C_{25}H_{24}O_5$ requires C, 74·2; H, 5·9%).

4′-*Methoxy*-4-(p-*methoxyphenacyl*)*flavene.*—The above diacetophenone (1·5 g.) was dissolved in glacial acetic acid (30 c.c.) with slight warming on the water-bath, and the solution left at room temperature for 24 hours. It was then poured into water and the yellow solid precipitated was filtered, dried, and extracted with petroleum (b. p. 60—80°). A considerable quantity of unchanged material and phenacylideneflavene remained undissolved. The pale yellow solution deposited faintly yellow needles, which were recrystallised several times from the same solvent and obtained as colourless fine needles, m. p. 122° (Found : C, 77·5; H, 5·75. $C_{25}H_{22}O_4$ requires C, 77·7; H, 5·7%).

4′-*Methoxy*-4-(p-*methoxyphenacylidene*)*flavene.*—The diacetophenone (4 g.), dissolved in glacial acetic acid (30 c.c.), was gently boiled for ¾ hour. The solution was cooled, poured into water, and steam-distilled, the residue basified with 10% caustic potash solution, and the solid product filtered off and crystallised from alcohol; it formed deep yellow needles, m. p. 167—168° and mixed m. p. with phenacylideneflavene above, 167—168°.

4′-*Methoxy*-4-(p-*methoxyphenacyl*)*flavylium Chloride.*—Through the above phenacylideneflavene (1 g.), suspended in glacial acetic acid (10 c.c.), hydrogen chloride was passed for 3 minutes, with cooling. The red crystalline solid obtained was washed with ether and recrystallised from glacial acetic acid, forming red needles which decomposed on exposure to air and could not be analysed. M. p. 120° (decomp.). The compound was immediately decomposed in 0·5% hydrochloric acid, more slowly in 7%, reverting to the yellow phenacylideneflavene, m. p. 167°.

4′-*Methoxy*-4-(p-*methoxyphenacyl*)*flavylium Ferrichloride.*—This compound was obtained from the chloride prepared as above by the addition of ferric chloride (0·5 g.) in glacial acetic acid (10 c.c.) to the reaction mixture. A cloudy precipitate appeared which solidified, when scratched, after some hours. It crystallised from acetone, on addition of ether, in rosettes of fine red needles. The m. p. was indefinite, since the compound slowly decomposed on heating (Found : C, 50·8; H, 4·1; Fe, 9·2. $C_{25}H_{21}O_4Cl_4Fe$ requires C, 51·0; H, 3·6; Fe, 9·6%).

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