18. *Reactions of* o-*Hydroxybenzylidenediacetophenones. Part II. Conversion into Pyrylium and Benzopyrylium Salts.*

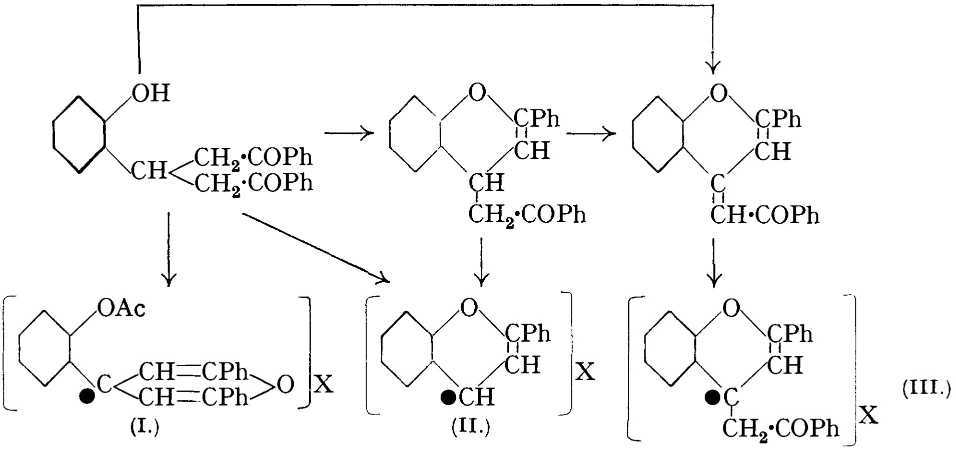
By Douglas W. Hill.

Dilthey and his collaborators have shown that benzylidenediacetophenones are converted into triphenylpyrylium salts by the action of ferric chloride in acetic anhydride (*J. pr. Chem.*, 1916, **94**, 53; 1917, **95**, 107; *Ber.*, 1917, **50**, 1008; 1919, **52**, 1195; 1920, **53**, 252). It is at once apparent that such a reaction applied to the *o*-hydroxy-derivatives might lead either, by ring closure of the enolic form of the ketonic side chains, to 2 : 6-diphenyl-4-(*o*-hydroxyphenyl)pyrylium salts of type (I) or, by ring closure on the phenolic hydroxyl, to 4-phenacylflavylium salts of type (III). A representative of the latter class of compound was described by Irvine and Robinson (J., 1927, 2086), who prepared 6-methoxy-4-phenacylflavylium ferrichloride by the action of hydrogen chloride on 6-methoxy-4-phenacylideneflavene, followed by the addition of ferric chloride. Dilthey and Floret (*Annalen*, 1924, **440**, 89) obtained salts of type (I)—with an *o*-hydroxyl group in the 4-phenyl nucleus—by demethylation of the salts formed from *o*-methoxybenzylidenediacetophenone.

The preparation of triphenylpyrylium salts as described by Dilthey has been confirmed by experiments on benzylidenediacetophenone, *o*-methoxy-, *p*-methoxy-, and 2 : 4-dimethoxy-benzylidenediacetophenones, all of which yielded the corresponding triphenylpyrylium salts when treated in acetic anhydride with a solution of ferric chloride in 20% hydrochloric acid. On passing to the *o*-hydroxy-derivatives, however, the results were different. The previous reactions had always been vigorous, but when carried out in the same way with *o*-hydroxybenzylidenediacetophenones, only simple flavylium salts of type (II) could be isolated : the phenacyl group in position 4 had been eliminated. Triphenylpyrylium salts of type (I) in which both salt formation and acetylation of the hydroxy-group had occurred were obtained by maintaining the temperature during the reaction at about 25°.

The 4-phenacylflavylium salts which might reasonably have been expected in the first case from the above reaction were readily prepared by the method of Irvine and Robinson (*loc. cit.*) starting from the 4-phenacylideneflavenes. The same salts might also be expected to be formed by this method from the parent *o*-hydroxybenzylidenediacetophenones or from the 4-phenacylflavenes intermediate between the diacetophenones and the phenacylideneflavenes (see Part I, J., 1934, 1255). Contrary to expectation, in both cases the products were, not 4-phenacylflavylium salts, but simple flavylium salts unsubstituted in position 4. The indications previously obtained of the ease with which the phenacyl-group is removed from these compounds are emphasised by these results and it appears that the formation of flavylium salts from them is dependent on the elimination of the 4-substituent, except in the case of 4-phenacylideneflavenes where unsaturation, to which the salt-forming groups can add, occurs at the 4-position. Dilthey has shown that, in the benzopyrylium salts he has examined, salt formation occurs on the 2-carbon atom (*J. pr. Chem.*, 1933, **138**, 42). The results now obtained indicate that in other cases the 4-carbon may be the heteropolar atom.

The reaction scheme given in Part I can now be extended as shown below, in which Dilthey's " carbenium " formula has been adopted for the salts.



(I.) (II.) (III.)

Experimental.

Flavylium Ferrichloride.—(a) Through a suspension of *o*-hydroxybenzylidenediacetophenone (5 g.) in glacial acetic acid (30 c.c.), dry hydrogen chloride was rapidly passed for 5 minutes, with cooling. Ferric chloride (2·5 g., anhydrous) in acetic acid (15 c.c.), added to the deep red solution, at once produced a brown crystalline ferrichloride. Collected after an hour and recrystallised from glacial acetic acid, this formed golden-yellow plates, m. p. 140° (flavylium ferrichloride prepared from chalkone melts at 140°) (Found : C, 44·45; H, 2·9; Fe, 13·5; Cl, 34·9. Calc. for $C_{15}H_{11}OCl_4Fe$: C, 44·4; H, 2·7; Fe, 13·5; Cl, 35·05%).

(b) A similar procedure with 4-phenacylflavene (2 g.) in glacial acetic acid (10 c.c.) gave an orange-yellow ferrichloride, which crystallised from glacial acetic acid in golden-yellow plates, m. p. 138°.

(c) A suspension of *o*-hydroxybenzylidenediacetophenone (1 g.) in acetic anhydride (10 c.c.) was treated, with stirring but without cooling, with ferric chloride (1 g.) in 20% hydrochloric acid (5 c.c.); a vigorous reaction occurred. The precipitate was collected after 12 hours; it crystallised from glacial acetic acid in golden-yellow blades, m. p. 138° (Found : C, 44·7; H, 2·8; Fe, 13·5%).

Flavylium Perchlorate.—Dry hydrogen chloride was passed through a suspension of *o*-hydroxybenzylidenediacetophenone (2 g.) in a mixture of dry ether (25 c.c.) and 20% perchloric acid (10 c.c.) for 4 hours; after 12 hours, the deep red solution was treated with dry ether. The precipitated perchlorate crystallised from glacial acetic acid in golden-yellow plates, m. p. 184° alone or mixed with an authentic specimen (Löwenbein, *Ber.*, 1924, **57**, 1526, describes yellow plates with a metallic sheen, m. p. 186—187°).

6-*Methoxyflavylium Ferrichloride.*—(a) 2-Hydroxy-5-methoxybenzylidenediacetophenone (2 g.) was suspended in glacial acetic acid and treated as described in (a) above. The ferrichloride separated from glacial acetic acid as brown platelets with a greenish-golden sheen, m. p. 205° (Irvine and Robinson describe the salt as brown platelets with green nuance, m. p. 203°).

(b) The same procedure with 6-methoxy-4-phenacylflavene (1·5 g.) led to a solid ferrichloride, which separated from glacial acetic acid as brown platelets with a green sheen, m. p. 204—205°.

7-*Methoxyflavylium Ferrichloride.*—(a) 2-Hydroxy-4-methoxybenzylidenediacetophenone (1 g.), suspended in dry ether (50 c.c.), was treated with a rapid stream of dry hydrogen chloride. The yellow flocculent precipitate was collected after 12 hours, washed with dry ether, and dissolved in warm concentrated hydrochloric acid. An excess of ferric chloride dissolved in concentrated hydrochloric acid was added and the precipitated oil was allowed to solidify and then crystallised twice from glacial acetic acid, forming brown needles, m. p. 147° (Found : C, 44·3; H, 3·1; Fe, 12·3; Cl, 32·0. Calc. for $C_{16}H_{13}O_2Cl_4Fe$: C, 44·1; H, 3·0; Fe, 12·9; Cl, 32·6%).

(b) A suspension of 2-hydroxy-4-methoxybenzylidenediacetophenone (3 g.) in acetic anhydride (20 c.c.) was treated, with stirring but without cooling, with ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.). The solid that separated slowly on cooling crystallised from acetone, on addition of ether, as brown needles, m. p. and mixed m. p. 147°.

7-Methoxyflavylium perchlorate, prepared, in the manner previously described for flavylium perchlorate, from the diketone (1 g.) in dry ether (50 c.c.) and 20% perchloric acid (10 c.c.), crystallised from glacial acetic acid in bright yellow needles, m. p. and mixed m. p. 222°.

4-*Phenacylflavylium Ferrichloride.*—A rapid stream of dry hydrogen chloride was passed through 4-phenacylideneflavene (2 g.) in glacial acetic acid (10 c.c.) for 10 minutes. The deep red solution was then treated with ferric chloride (1 g. in 10 c.c. of glacial acetic acid). The oily precipitate formed solidified when scratched; it was washed with ether and crystallised from glacial acetic acid, separating as orange-coloured needles, m. p. 156—157° (Found : C, 52·45; H, 3·2; Fe, 10·7; Cl, 27·2. $C_{23}H_{17}O_2Cl_4Fe$ requires C, 52·3; H, 3·25; Fe, 10·7; Cl, 27·15%).

6-Methoxy-4-phenacylflavylium ferrichloride, prepared as described by Irvine and Robinson (*loc. cit.*), crystallised from glacial acetic acid in red-brown needles, m. p. 173—174° (decomp.) (Irvine and Robinson give m. p. 170° with blackening).

7-*Methoxy*-4-*phenacylflavylium Ferrichloride.*—The usual procedure (suspension of 7-methoxy-4-phenacylideneflavene, 2 g., in cold glacial acetic acid, 20 c.c.; rapid stream of dry hydrogen chloride for 3 minutes; ferric chloride, 1 g., in 10 c.c. of glacial acetic acid) gave a precipitate which, recrystallised from glacial acetic acid, formed fine, matted, yellow needles, m. p. 168° (Found : C, 51·95; H, 3·5; Fe, 10·4; Cl, 25·6. $C_{24}H_{19}O_3Cl_4Fe$ requires C, 52·1; H, 3·4; Fe, 10·1; Cl, 26·3%).

2 : 6-*Diphenyl*-4-(2′ : 4′-*dimethoxyphenyl*)*pyrylium Ferrichloride.*—A solution of 2 : 4-dimethoxybenzylidenediacetophenone (3 g.) in acetic anhydride (20 c.c.) was stirred and treated, without cooling, with a solution of anhydrous ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.), added drop by drop; a vigorous reaction occurred. The red oil obtained solidified on cooling; collected after 12 hours, the solid crystallised from cold acetone, on addition of ether, in red needles, m. p. 190—191° (Found : C, 53·1; H, 4·0; Fe, 9·5; Cl, 24·1. $C_{25}H_{21}O_3Cl_4Fe$ requires C, 52·9; H, 3·7; Fe, 9·9; Cl, 25·0%).

2 : 6-*Diphenyl*-4-(o-*acetoxyphenyl*)*pyrylium Ferrichloride*.—To a stirred and well-cooled suspension of *o*-hydroxybenzylidenediacetophenone (5 g.) in acetic anhydride (40 c.c.), a solution of ferric chloride (5 g.) in 20% hydrochloric acid (20 c.c.) was added very slowly, rise of temperature being prevented. Stirring was continued for an hour and the precipitate was collected and crystallised several times from glacial acetic acid, forming greenish-brown plates, m. p. 181° (Found : C, 53·1; H, 3·4; Fe, 9·8; Cl, 24·8. $C_{25}H_{19}O_3Cl_4Fe$ requires C, 53·1; H, 3·4; Fe, 9·9; Cl, 25·1%).

2 : 6-*Diphenyl*-4-(2'-*acetoxy*-4'-*methoxyphenyl*)*pyrylium Ferrichloride*.—2-Hydroxy-4-methoxybenzylidenediacetophenone (2 g.) was suspended in acetic anhydride (35 c.c.) and treated below 25° with ferric chloride (1·5 g.) in 20% hydrochloric acid (7 c.c.). A small amount of solid separated, and more on addition of dry ether. It crystallised from glacial acetic acid in purple-brown needles, m. p. 162° (Found : C, 52·35; H, 3·5; Fe, 9·2; Cl, 24·0. $C_{26}H_{21}O_4Cl_4Fe$ requires C, 52·4; H, 3·5; Fe, 9·4; Cl, 23·9%).

2 : 6-*Diphenyl*-4-(2'-*acetoxy*-5'-*methoxyphenyl*)*pyrylium Ferrichloride*.—The reaction described above was carried out with 2-hydroxy-5-methoxybenzylidenediacetophenone (3 g.) in acetic anhydride (20 c.c.). The solid obtained, crystallised from cold acetone by the addition of ether, formed long, slender, golden-yellow needles with a greenish lustre, m. p. 225—226° (Found : C, 52·4; H, 3·6; Fe, 9·3; Cl, 23·85. $C_{26}H_{21}O_4Cl_4Fe$ requires C, 52·4; H, 3·5; Fe, 9·4; Cl, 23·9%).

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THE UNIVERSITY, BRISTOL

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