9. *Reactions of* o-*Hydroxybenzylidenediacetophenones. Part VII. Flavylium Salts from Dihydrochalkones.*

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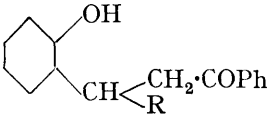
The mechanism of the disproportionation which takes place as a result of the action of acids upon salicylidenediacetophenones with the formation of phenacylideneflavenes is still obscure. None of the changes introduced into the structure (I; R = CH_2·COPh) have inhibited the dehydrogenation effect and it was intended to extend the investigation to compounds in which the group R had been varied. Circumstances prevent this plan being carried out and it is not proposed to continue the work. The results so far obtained are, however, of interest from other points of view and some compounds are here described in which the phenacyl group has been replaced by hydrogen.



(I.)

Of the many methods introduced for the preparation of flavylium salts, oxidation reactions have received least attention. A number of such reactions have recently been described (see Hill, *Chem. Rev.*, 1936, **19**, 37, for summary) and it seemed worth recording that the ω-salicylacetophenones investigated were converted readily into flavylium chlorides (isolated as ferrichlorides) by the action of hydrogen chloride in acetic acid without the aid of an oxidising agent. In their oxidation to flavylium salts, therefore, the salicylacetophenones behave in a manner analogous to the diacetophenones, the group R, whether H or CH_2·COPh, being removed to permit the formation of the salt. This behaviour does not extend to salicylacetone, since we were unable thus to change it, and Miller and Robinson (J., 1934, 1535) found it necessary to introduce an oxidising agent (chloranil) to effect the conversion of β-(2-hydroxy-1-naphthyl)ethyl methyl ketone into a naphthapyrylium salt.

The difference between salicylacetone and ω-salicylacetophenones is further emphasised by their respective behaviours towards attempts at cyclisation. Baker and Walker (J., 1935, 646) described the very ready cyclisation of salicylacetone to a carbinol which lost water easily to form a chromene. If the salicylacetophenones described here are to exhibit

similar changes to the salicylidenediacetophenones, they must do so with the formation of a dimer through the intermediate carbinols and chromenes resembling the product of Baker and Walker. No evidence has been found for any of these compounds.

ω-Salicylacetophenone, 4-*methoxy*-ω-*salicylacetophenone*, and 3′ : 4-*dimethoxy*-ω-*salicylacetophenone*, unlike salicylacetone, could not be cyclised by any of the methods adopted by Baker and Walker. They were unaffected by acids, and the action of acetic anhydride led only to the formation of *acetyl* derivatives, as with hydroxychalkones themselves (Zwayer and Kostanecki, *Ber.*, 1908, **41**, 1337).

Experimental.

4-Methoxy-ω-salicylacetophenone.—A solution of 4-methoxysalicylideneacetophenone (5 g.) in warm methyl alcohol (300 c.c.) was reduced by shaking with hydrogen in the presence of Adams's platinum oxide catalyst (0·1 g.). The required volume of hydrogen was rapidly absorbed and the previously yellow solution became colourless. It was filtered from the catalyst and evaporated to 50 c.c., and sufficient water added to produce a turbidity. On standing, colourless hard rhombs separated, which were recrystallised from alcohol and water; m. p. 64—65° (Found : C, 75·0; H, 6·3. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·3%). The *phenylhydrazone* formed almost colourless needles from aqueous alcohol, m. p. 140—141° (Found : N, 7·5. $C_{22}H_{22}O_2N_2$ requires N, 8·0%).

3′ : 4-Dimethoxy-ω-salicylacetophenone.—A solution of 3′ : 4-dimethoxysalicylideneacetophenone (5 g.) in warm methyl alcohol (300 c.c.) was treated as described above. The colourless solution was evaporated to low bulk and allowed to crystallise. The *product*, recrystallised twice from alcohol, formed colourless needles, m. p. 89—90° (Found : C, 71·1; H, 6·35. $C_{17}H_{18}O_4$ requires C, 71·3; H, 6·3%). The *phenylhydrazone* crystallised in very pale yellow needles from alcohol, m. p. 145—146° (Found : N, 7·55. $C_{23}H_{24}O_3N_2$ requires N, 7·45%).

Flavylium Ferrichloride from ω-Salicylacetophenone.—Hydrogen chloride was passed through a suspension of salicylacetophenone (1 g.) in glacial acetic acid (10 c.c.) for 5 minutes. All the solid had then dissolved and the solution assumed a deep red colour. Ferric chloride in glacial acetic acid (0·5 g. in 7 c.c.) was added to the mixture, which soon began to deposit yellow plates. These, when crystallised from glacial acetic acid, had m. p. 138—140° (flavylium ferrichloride has m. p. 138—140°).

4′-Methoxyflavylium Ferrichloride from 4-Methoxy-ω-salicylacetophenone.—By the same treatment 4-methoxysalicylacetophenone (1 g.), suspended in glacial acetic acid (10 c.c.), was converted into 4′-methoxyflavylium ferrichloride, obtained as orange-coloured blades from glacial acetic acid, m. p. 155—156° (Perkin, Robinson, and Turner, J., 1908, **93**, 1112, give m. p. 156°).

8 : 4′-Dimethoxyflavylium Ferrichloride from 3′ : 4-Dimethoxy-ω-salicylacetophenone.—3′ : 4-Dimethoxysalicylacetophenone (1 g.), suspended in glacial acetic acid (10 c.c.), was treated as above. The deep red solution on treatment with ferric chloride (0·5 g. in 6 c.c. of glacial acetic acid) yielded a solid, which separated from glacial acetic acid in fine red needles, m. p. 178° (Robinson and Williams, J., 1924, **125**, 209, give m. p. 180°).

O-Acetyl-ω-salicylacetophenone.—Salicylacetophenone (3 g.) was refluxed for 2 hours with acetic anhydride (20 c.c.), and the solution then poured into water. The thick oil remaining after the acetic anhydride had been decomposed was extracted with ether, and the extract washed with sodium carbonate solution, dried over anhydrous sodium sulphate, and evaporated. The residue crystallised from alcohol in colourless needles, m. p. 65° (Found : C, 76·1; H, 6·1. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%).

O-Acetyl-4-methoxy-ω-salicylacetophenone.—By the same procedure, 4-methoxy-ω-salicylacetophenone (1·5 g.) was converted into its *acetyl* derivative, which separated from alcohol in colourless plates, m. p. 84—85° (Found : C, 72·5; H, 6·4. $C_{18}H_{18}O_4$ requires C, 72·5; H, 6·1%).

O-Acetyl-3′ : 4-dimethoxy-ω-salicylacetophenone.—3′ : 4-Dimethoxy-ω-salicylacetophenone (2 g.) was refluxed with acetic anhydride (15 c.c.) for 1 hour, and the mixture treated as above. The *acetyl* derivative separated from alcohol, after long standing, in colourless needles, m. p. 55—56° (Found : C, 69·4; H, 6·3. $C_{19}H_{20}O_5$ requires C, 69·5; H, 6·1%).

Refluxing with glacial acetic acid had no effect on any of the salicylacetophenones described above, nor had hydrogen chloride in alcohol.

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