54. *Reactions of* o-*Hydroxybenzylidenediacetophenones. Part VI. Diacetophenones derived from 3-Methoxysalicylaldehyde.*

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THE investigation of the reactions of *o*-hydroxybenzylidenediacetophenones derived from salicylaldehyde and its 4- and 5-methoxy-derivatives (J., 1934, 1255; 1935, 85) has been extended to derivatives of 3-methoxysalicylaldehyde. Acetophenone, *p*-methoxyacetophenone, and *p*-methylacetophenone were each condensed with 3-methoxysalicylaldehyde in alcoholic solution under the influence of concentrated sodium hydroxide solution to give 3-*methoxysalicylidene-diacetophenone*, -*di*-(p-*methoxyacetophenone*), and -*di*-(p-*methylacetophenone*) respectively. In each case the corresponding 3-*methoxychalkone* also was isolated. The separation of the diketone from the sodium salt of the chalkone was a tedious operation, owing to the sparing solubility of the latter in water.

The diketones were converted by boiling glacial acetic acid into the corresponding substituted 4-*phenacylideneflavenes*, which, contrary to previous experience, crystallised from the cold reaction mixtures. So readily were the latter compounds formed that the 4-*phenacylflavenes* were obtained only with great difficulty and in small yields. In an attempt to effect ring closure without conversion into 4-phenacylidene derivatives, recourse was had to non-acidic reagents: anhydrous sodium sulphate (compare Baker and Walker, J., 1935, 646) was without effect, and treatment of 3-methoxysalicylidenedi-(*p*-methylacetophenone) with acetic anhydride in place of acetic acid led to 2-*acetoxy*-3-*methoxybenzylidenedi*-(p-*methylacetophenone*). Simple flavylium salts were obtained from the diketones on treatment in cold glacial acetic acid with dry hydrogen chloride in the manner previously described and substituted 4-*phenacylflavylium* salts were similarly prepared without difficulty from the 4-phenacylideneflavenes.

The diketones of salicylaldehyde and its 4- and 5-methoxy-derivatives resemble one another closely in behaviour, but differ considerably from the derivatives of 3-methoxysalicylaldehyde, most markedly in ease of formation and purification and in the difficulty of obtaining the 4-phenacyl derivatives. The divergence in behaviour of derivatives of 3- and of 4-methoxysalicylaldehyde has been commented upon by Robinson (J., 1924, **125**, 207).

EXPERIMENTAL.

3-*Methoxysalicylidenediacetophenone*.—A solution of 3-methoxysalicyladehyde (15 g.) and acetophenone (25 g.) in alcohol (120 c.c.) was treated with a hot solution of sodium hydroxide (30 g. in 30 c.c. of water). The resulting deep red solution was heated on the water-bath for

1 hour, kept over-night, poured into water (5 l.), and heated to dissolve as much as possible of the sparingly soluble sodium salt of the chalkone formed as a by-product. The insoluble portion was filtered off and fractionally crystallised from alcohol, the *diketone* being obtained as colourless sandy crystals (10 g.), m. p. 145—146° (Found: C, 76·5; H, 5·9. $C_{24}H_{22}O_4$ requires C, 77·0; H, 5·9%). The aqueous mother-liquor on acidification yielded 3-methoxychalkone, which separated from alcohol in yellow prisms, m. p. 112° (Robinson, J., 1924, **125**, 207, gives m. p. 112°).

3-*Methoxysalicylidenedi*-(p-*methoxyacetophenone*).—In the same manner this diketone was prepared from the aldehyde (10 g.) and *p*-methoxyacetophenone (20 g.). After the reaction mixture had been poured into water, the solution was heated on the steam-bath with acetic acid, and the resulting mixture of chalkone and diketone fractionally crystallised from alcohol. The *diketone* separated in colourless plates (4·0 g.), m. p. 163—164° (Found: C, 71·8; H, 6·1. $C_{26}H_{26}O_6$ requires C, 71·9; H, 6·0%). 3 : 4′-*Dimethoxychalkone* was obtained from the alcohol in bright yellow plates, m. p. 142° (Found: C, 71·6; H, 5·7. $C_{17}H_{16}O_4$ requires C, 71·8; H, 5·6%).

3-*Methoxysalicylidenedi*-(p-*methylacetophenone*).—This compound was prepared from the aldehyde (10 g.) and *p*-methylacetophenone (18 g.) in the above-described manner. The product was extracted with benzene after the pouring into water, and the benzene-soluble portion crystallised from alcohol, giving soft colourless needles (4·0 g.), m. p. 112° (Found: C, 77·7; H, 6·5. $C_{26}H_{26}O_4$ requires C, 77·6; H, 6·5%). The aqueous mother-liquor yielded on acidification 3-*methoxy*-4′-*methylchalkone*, which separated from alcohol in hard yellow needles, m. p. 131° (Found: C, 76·0; H, 6·0. $C_{17}H_{16}O_3$ requires C, 76·1; H, 6·0%).

8-*Methoxy*-4-*phenacylideneflavene*.—3-Methoxysalicylidenediacetophenone (4 g.) was refluxed in glacial acetic acid (25 c.c.) for 1 hour. On cooling, the sparingly soluble *product* crystallised; recrystallised from alcohol, it formed bright yellow needles (1·5 g.), m. p. 192° (Found: C, 81·1; H, 5·3. $C_{24}H_{18}O_3$ requires C, 81·4; H, 5·1%).

8-*Methoxy*-4-*phenacylflavene*.—The same diketone (2 g.) was refluxed for 10 minutes with glacial acetic acid (30 c.c.), the solution poured into water (500 c.c.), and the yellow precipitate collected and crystallised alternately from light petroleum (b. p. 60—80°) and alcohol, yielding finally almost colourless, fine needles (0·2 g.), m. p. 136—137° (Found: C, 80·7; H, 5·7. $C_{24}H_{20}O_3$ requires C, 80·9; H, 5·6%).

8-*Methoxyflavylium Ferrichloride*.—Dry hydrogen chloride was passed for 5 minutes through a suspension of 3-methoxysalicylidenediacetophenone (1 g.) in acetic acid (10 c.c.), and the resulting clear reddish-brown solution treated with ferric chloride (0·5 g. in 7 c.c. of acetic acid). The rosettes of reddish-brown needles that separated were crystallised from glacial acetic acid; m. p. 162° (yield, 0·5 g.) (Found: Fe, 12·7. Calc. for $C_{16}H_{13}O_2Cl_4Fe$: Fe, 12·9%). Robinson (J., 1924, **125**, 209) gives m. p. 157°.

8-*Methoxy*-4-*phenacylflavylium Ferrichloride*.—In a similar way, from a cooled suspension of 8-methoxy-4-phenacylideneflavene (0·75 g.) in glacial acetic acid (8 c.c.) (dry hydrogen chloride passed for 5 minutes; then ferric chloride, 0·4 g., in acetic acid, 4 c.c., added), a precipitate was obtained, which was washed with ether and recrystallised from acetic acid, forming bronze-coloured needles (0·7 g.), m. p. 197—198° (Found: C, 52·1; H, 3·5; Fe, 10·0; Cl, 27·1. $C_{24}H_{19}O_3Cl_4Fe$ requires C, 52·1; H, 3·4; Fe, 10·1; Cl, 25·7%).

8 : 4′-*Dimethoxy*-4-(p-*methoxyphenacylidene*)*flavene*.—3-Methoxysalicylidenedi-(*p*-methoxyacetophenone) (2 g.) was refluxed with glacial acetic acid (15 c.c.) for 1 hour. On cooling, the *product* separated in yellow needles; after twice crystallising from alcohol, it had m. p. 195° (yield, 0·7 g.) (Found: C, 75·0; H, 5·3. $C_{26}H_{22}O_5$ requires C, 75·3; H, 5·3%).

8 : 4′-*Dimethoxyflavylium Ferrichloride*.—The same diketone (0·75 g.) was suspended in glacial acetic acid (7·5 c.c.) and treated in the usual way with hydrogen chloride and ferric chloride. The product crystallised from glacial acetic acid in dark red needles (0·5 g.), m. p. 179° (Robinson, *loc. cit.*, gives m. p. 180°).

8 : 4′-*Dimethoxy*-4-(p-*methoxyphenacyl*)*flavylium Ferrichloride*.—8 : 4′-Dimethoxy-4-(*p*-methoxyphenacylidene)flavene (0·5 g.), suspended in glacial acetic acid (5 c.c.), was treated in the normal manner with hydrogen chloride and the sparingly soluble chloride which separated was filtered off rapidly, washed with dry ether, and transferred to hot glacial acetic acid. Ferric chloride (0·3 g.), dissolved in glacial acetic acid (3 c.c.), was added. The *ferrichloride* crystallised on cooling and was recrystallised from hot acetic acid, forming dark red plates with an intense purple glance (0·3 g.), m. p. 193° (Found: C, 50·8; H, 3·7; Fe, 9·1; Cl, 24·8. $C_{26}H_{23}O_5Cl_4Fe$ requires C, 50·9; H, 3·7; Fe, 9·1; Cl, 23·2%).

8-*Methoxy*-4-(p-*methylphenacylidene*)-4′-*methylflavene*.—3-Methoxysalicylidenedi-(*p*-methylacetophenone) (1 g.) was refluxed in the usual way with acetic acid (20 c.c.). The *product* crystallised from alcohol in deep yellow needles (0·3 g.), m. p. 200° (Found: C, 81·4; H, 5·7. $C_{26}H_{22}O_3$ requires C, 81·7; H, 5·8%).

2-*Acetoxy*-3-*methoxybenzylidenedi*-(p-*methylacetophenone*).—The same diketone (0·5 g.) was refluxed with acetic anhydride (15 c.c.) for 30 minutes. After cooling, the pale yellow solution was poured into water (500 c.c.), and the precipitated solid removed after 12 hours. It separated from light petroleum (b. p. 60—80°) in hard colourless crystals (0·4 g.), m. p. 120° (Found: C, 75·6; H, 6·4. $C_{28}H_{28}O_5$ requires C, 75·7; H, 6·3%).

8-*Methoxy*-4′-*methylflavylium Ferrichloride*.—The above diketone (0·7 g.) in glacial acetic acid (7 c.c.) was treated in the usual manner with hydrogen chloride and ferric chloride. The resulting *ferrichloride* separated from glacial acetic acid in brown crystals (0·5 g.), m. p. 179° (decomp.) (Found: C, 45·6; H, 3·4; Fe, 12·3; Cl, 32·0. $C_{17}H_{15}O_2Cl_4Fe$ requires C, 45·4; H, 3·3; Fe, 12·5; Cl, 31·6%).

8-*Methoxy*-4-(p-*methylphenacyl*)-4′-*methylflavylium Ferrichloride*.—The corresponding phenacylideneflavene above (0·5 g.) was suspended in glacial acetic acid (5 c.c.) and converted into the *ferrichloride* in the usual manner. The latter crystallised from acetic acid in rosettes of orange-brown needles (0·3 g.), m. p. 192° (decomp.) (Found: C, 53·5; H, 4·0; Fe, 9·5; Cl, 24·6. $C_{26}H_{23}O_3Cl_4Fe$ requires C, 53·7; H, 4·0; Fe, 9·6; Cl, 24·4%).

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