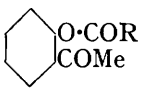
344. *Chromones of the Naphthalene Series. Part I. Transformation of* o-*Aroyloxyacetoarones into* o-*Hydroxydiaroylmethanes.*

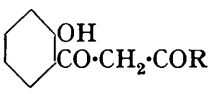
By V. V. Virkar and T. S. Wheeler.

Metallic sodium has been found to be an effective reagent for the transformation of *o*-aroyloxyacetoarones into the corresponding *o*-hydroxydiaroylmethanes, which can be readily cyclised to the corresponding chromones. The synthesis of a number of 2-naphthylbenzochromones, the naphthalene analogues of the flavones, is described.

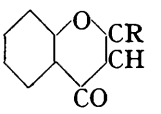
BAKER (J., 1933, 1381; 1934, 1953) showed that *o*-aroyloxyacetophenones (I) rearrange with anhydrous potassium carbonate in benzene or toluene into the corresponding *o*-hydroxydibenzoylmethanes (II), from which flavones (III; R = aryl) may readily be obtained by elimination of water. Mahal and Venkataraman (*Current Sci.*, 1933, **2**, 214; J., 1934, 1767) and Bhalla, Mahal, and Venkataraman (J., 1935, 868) used sodamide in dry ether. It has now been found that satisfactory results can be obtained with finely divided sodium in ether or toluene; the use of sodamide or sodium has the advantage that no water is liberated when the product, the metallic salt of (II), is formed; the presence of water lessens the yield, as it produces hydrolysis of (I). A variety of reagents are available for the cyclisation of (II) (cf. Baker, 1933, *loc. cit.*); hydrogen bromide in acetic acid is satisfactory.



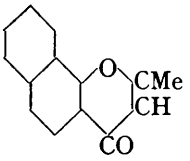
(I.)



(II.)



(III.)



(IV.)

The use of metallic sodium has provided a convenient synthesis of some 2-naphthylbenzochromones (naphthalene analogues of flavones) through the intermediate *o*-hydroxydinaphthoylmethanes. Sodium has also been applied to effect the transformation of *o*-benzoyloxyacetophenone into *o*-hydroxydibenzoylmethane, of dibenzoylresacetophenone into 2-hydroxy-4-benzoyloxydibenzoylmethane (Baker, 1933, *loc. cit.*), and of 1-benzoyloxy-2-acetonaphthone into benzoyl-1-hydroxy-2-naphthoylmethane (Mahal and Venkataraman, 1934, *loc. cit.*). 2 : 6-Dibenzoyloxyacetophenone with metallic sodium in toluene gives directly 5-hydroxy-3-benzoylflavone (cf. Baker, 1934, *loc. cit.*). Sodium also produces rearrangement of 1-acetoxy-2-acetonaphthone into 1-hydroxy-2-naphthoylacetone, which is readily cyclised into 2-methyl-7 : 8-benzochromone (IV). Baker (1933, *loc. cit.*) found that potassium carbonate cannot be employed for the rearrangement of *o*-acetoxyacetophenones.

Work in progress (Ullal and Wheeler, *Current Sci.*, 1938, **7**, 280) has shown that sodium ethoxide or hydroxide in alcoholic solution also produces rearrangement.

EXPERIMENTAL.

Preparation of o-Aroyloxyacetoarones.—*1-1′-Naphthoyloxy-2-acetonaphthone* (1), which separated when a mixture of 1-hydroxy-2-acetonaphthone (5 g.), α-naphthoyl chloride (5 g.), and pyridine (7 c.c.), which had been heated at 100° for 1 hour, was poured into dilute hydrochloric acid, had m. p. (alcohol) 135°, after it had been washed with dilute aqueous sodium hydroxide and with water (Found : C, 81·3; H, 4·7. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%).

1-2′-Naphthoyloxy-2-acetonaphthone (2), m. p. (alcohol) 113—114° (Found : C, 81·4; H, 4·8. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%), and *1-3′-methoxy-2′-naphthoyloxy-2-acetonaphthone* (3), m. p. (alcohol) 119° (Found : C, 78·0; H, 5·6. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%), were similarly prepared from the corresponding components.

Rearrangement of o-Aroyloxyacetoarones into o-Hydroxydiaroylmethanes and Cyclisation to Chromones.—*1-Hydroxy-2 : 1′-dinaphthoylmethane* (4) (2·3 g.), which separated as the sodium salt from a solution of (1) (5 g.) in dry toluene (35 c.c.) which had been heated under reflux with finely-divided sodium (0·4 g.) for 3 hours, was liberated by treatment with dilute acetic acid; it formed yellow needles and had m. p. (acetone) 142° (Found : C, 80·9; H, 4·9. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%).

2-1′-Naphthyl-7 : 8-benzochromone (0·5 g.), m. p. (alcohol) 205° (Found : C, 85·4; H, 4·5. $C_{23}H_{14}O_2$ requires C, 85·8; H, 4·3%), separated when a solution of (4) (1 g.) in acetic anhydride (5 c.c.) which had been carefully treated with hydriodic acid (*d* 1·7; 5 c.c.) and kept at room temperature for 2 hours was poured into sodium hydrogen sulphite solution.

The substance (2) on treatment with sodium in dry toluene as described above gave *1-hydroxy-di-2-naphthoylmethane*, m. p. (acetone) 164° (Found : C, 81·2; H, 4·9. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%), which formed a yellow powder and dissolved in warm acetic acid containing

hydrogen bromide to a solution from which 2-2′-*naphthyl*-7 : 8-*benzochromone*, m. p. (acetic acid) 190—191° (Found : C, 86·0; H, 4·8. $C_{23}H_{14}O_2$ requires C, 85·8; H, 4·3%), separated on dilution after ½ hour.

The compound (3) with sodium in dry toluene gave 1-*hydroxy*-3′-*methoxy*-2 : 2′-*dinaphthoylmethane*, m. p. (acetone) 163°, in orange needles (Found : C, 77·8; H, 5·1. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%), which with hydrogen bromide in acetic acid gave 2-(3′-*methoxy*-2′-*naphthyl*)-7 : 8-*benzochromone*, m. p. (acetic acid) 204—205° (Found : C, 81·5; H, 4·9. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·5%).

2-(3′-*Hydroxy*-2′-*naphthyl*)-7 : 8-*benzochromone* (0·4 g.), m. p. (acetic acid) above 300° (Found : C, 81·1; H, 4·7. $C_{23}H_{14}O_3$ requires C, 81·7; H, 4·1%), separated as a greenish-yellow powder when a solution of the foregoing methoxychromone (1 g.) in acetic anhydride (20 c.c.), which had been carefully treated with hydriodic acid (*d* 1·7; 20 c.c.) and heated under reflux for 24 hours, was poured into aqueous sodium hydrogen sulphite. The *acetyl* derivative, prepared by the acetic anhydride–pyridine method, formed yellow plates and had m. p. (alcohol) 180—181° (Found : C, 79·2; H, 4·2. $C_{25}H_{16}O_4$ requires C, 78·9; H, 4·2%).

Preparation of o-*Hydroxydibenzoylmethane*.—A suspension of *o*-benzoyloxyacetophenone (4 g.) and pulverised sodium (0·4 g.) in dry ether (20 c.c.), which had been kept overnight, was mechanically shaken for 5 hours; ether was evaporated (water-pump) and the residue was treated with alcohol to remove sodium and acidified with dilute acetic acid; the product (2 g.), m. p. (alcohol) 122° (lit. 121°), gave flavone on treatment at room temperature for 1 hour with hydrogen bromide in acetic acid.

Preparation of 1-*Hydroxy*-2-*naphthoylacetone*.—A solution of 1-acetoxy-2-acetonaphthone (2·3 g.) (Hantzsch and Blackler, *Ber.*, 1906, **39**, 3096) in toluene (25 c.c.) containing finely divided sodium (0·23 g.) in suspension was heated under reflux for 3 hours and the precipitated sodium salt was collected and treated with dilute acetic acid. The yellow product (1·2 g.) had m. p. (alcohol) 117—118° (cf. Wittig, Bangert, and Richter, *Annalen* 1926, **446**, 173) (Found : C, 73·8; H, 5·4. Calc. for $C_{14}H_{12}O_3$: C, 73·7; H, 5·3%).

2-Methyl-7 : 8-benzochromone, m. p. (alcohol) 178—179° (cf. Wittig *et al.*, *loc. cit.*) (Found : C, 80·2; H, 4·8. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·8%), separated when a solution of the foregoing diketone (0·5 g.) in acetic anhydride (5 c.c.), which had been carefully treated with hydriodic acid (*d* 1·7; 5 c.c.) and kept for 1 hour, was poured into sodium hydrogen sulphite solution.

The other transformations of known *o*-aroyloxyacetoarones mentioned in the introduction need no detailed description.

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