279. *Chromones of the Naphthalene Series. Part III. Rapid Quantitative Transformation at Room Temperature of* o-*Aroyloxyacetoarones into* o-*Hydroxydiaroylmethanes.*

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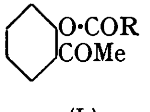
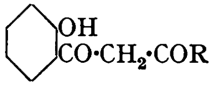
Sodium ethoxide in alcoholic solution has been found to be an effective reagent for the rapid quantitative transformation at room temperature of *o*-aroyloxyacetoarones into the corresponding *o*-hydroxydiaroylmethanes, which can be readily cyclised at room temperature to the corresponding chromones. The synthesis of a number of naphthalene analogues of flavones is described.

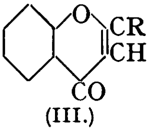
Anhydrous potassium carbonate in boiling benzene or toluene (Baker, J., 1933, 1381; 1934, 1953), sodamide in dry ether (Mahal and Venkataraman, *Current Sci.*, 1933, **2**, 214; J., 1934, 1767; Bhalla, Mahal, and Venkataraman, J., 1935, 868), and finely divided sodium in ether or boiling toluene (Virkar and Wheeler, J., 1939, 1679) have been used to effect in moderate yield the slow transformation of *o*-aroyloxyacetoarones (I) into the corresponding *o*-hydroxydiaroylmethanes (II); the latter readily give 2-substituted chromones (III) on cyclisation with, for example, hydrogen bromide in acetic acid.



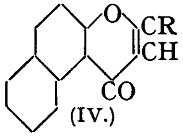
(I.)



(II.)



(III.)



(IV.)

It has now been found that the above transformation takes place rapidly, almost in quantitative yield, at room temperature in presence of sodium ethoxide in alcoholic solution. The method has been applied to the synthesis of some 2-naphthyl-5 : 6-benzochromones (IV; R = naphthyl), of 2-*pentadecyl*-5 : 6-*benzochromone* (IV; R = $C_{15}H_{31}$), and of 7-methoxy-2-styrylchromone, so that it is not necessary that R in (I) should be aryl.

The unambiguous synthesis described below of 2-(3′-*methoxy*-2′-*naphthyl*)-5 : 6-*benzochromone* (V) from 2-*hydroxy*-3′-*methoxy*-1 : 2′-*dinaphthoylmethane* obtained by rearrangement of 2-(3′-*methoxy*-2′-*naphthoyloxy*)-1-*acetonaphthone* confirms the suggestion of Virkar and Wheeler (*loc. cit.*, p. 1682) that the cyclisation of 2 : 3′-dimethoxy-1 : 2′-dinaphthoylmethane yielded 2-(2′-methoxy-1′-naphthyl)-6 : 7-benzochromone and not the alternative product (V).

The fact that the transformation of (I) into (II) and the cyclisation of (II) into (III) are rapidly and quantitatively effected at room temperature is of phytochemical interest in view of the production of flavones in plants. Virkar (private communication) has found that sodium hydroxide in alcoholic solution also converts (I) into (II).

Experimental.

Preparation of o-*Acyloxyacetoarones.*—2-p-*Anisoyloxy*-1-*acetonaphthone*, which separated when a mixture of 2-hydroxy-1-acetonaphthone (18·6 g.), anisoyl chloride (17 g.), and pyridine

(20 g.), which had been heated at 100° for 1 hour, was poured into dilute hydrochloric acid, had m. p. (alcohol) 122° after it had been washed with dilute aqueous sodium hydroxide and with water (Found : C, 75·2; H, 5·0. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

2-(1'-*Naphthoyloxy*)-1-*acetonaphthone*, m. p. (alcohol) 113° (Found : C, 81·6; H, 4·9. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%), 2-(2'-*naphthoyloxy*)-1-*acetonaphthone*, m. p. (alcohol) 103° (Found : C, 81·7; H, 4·8. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%), 2-(3'-*methoxy*-2'-*naphthoyloxy*)-1-*acetonaphthone*, m. p. (alcohol) 116° (Found : C, 78·0; H, 4·8. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%), 2-(1'-*methoxy*-2'-*naphthoyloxy*)-1-*acetonaphthone*, m. p. (aqueous alcohol) 122° (Found : C, 78·5; H, 5·0. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%), 2-*palmityloxy*-1-*acetonaphthone*, m. p. (alcohol) 40° (Found : C, 78·7; H, 9·8. $C_{28}H_{40}O_3$ requires C, 79·2; H, 9·4%), and 2-*cinnamoyloxy*-4-*methoxyacetophenone*, m. p. (alcohol) 99° (Found : C, 72·8; H, 6·2. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%), were similarly prepared from the corresponding components.

Rearrangement of o-*Acyloxyacetoarones into* o-*Hydroxydiaroylmethanes.*—*Benzoyl*-2-*hydroxy*-1-*naphthoylmethane* (0·85 g.), m. p. (alcohol) 137° (Found : C, 78·7; H, 4·8. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8%), separated from an alcoholic solution of 2-benzoyloxy-1-acetonaphthone (1 g.) containing sodium ethoxide (0·1 g. of sodium) which had been kept at room temperature for 15 minutes and then acidified with dilute acetic acid. Bhalla *et al.* (J., 1935, 870), who employed sodamide in dry ether to effect the transformation, did not obtain a solid product.

p-*Anisoyl*-2-*hydroxy*-1-*naphthoylmethane*, m. p. (alcohol) 102° (Found : C, 75·0; H, 4·9. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%), 2-*hydroxy*-*di*-1-*naphthoylmethane*, m. p. (acetone) 163° (Found : C, 81·2; H, 4·8. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%), 2-*hydroxy*-1 : 2'-*dinaphthoylmethane*, m. p. (acetone) 136° (Found : C, 81·5; H, 4·7. $C_{23}H_{16}O_3$ requires C, 81·2; H, 4·7%), 2-*hydroxy*-3'-*methoxy*-1 : 2'-*dinaphthoylmethane*, m. p. (alcohol) 175° (Found : C, 77·7; H, 4·9. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%), 2-*hydroxy*-1'-*methoxy*-1 : 2'-*dinaphthoylmethane*, m. p. (acetone) 165° (Found : C, 77·6; H, 5·0. $C_{24}H_{18}O_4$ requires C, 77·8; H, 4·9%), 2-*hydroxy*-1-*naphthoylpalmitylmethane*, m. p. (alcohol) 112° (Found : C, 78·7; H, 9·5. $C_{28}H_{40}O_3$ requires C, 79·2; H, 9·4%), and 2-*hydroxy*-4-*methoxybenzoylcinnamoylmethane*, m. p. (acetic acid) 140° (Found : C, 72·6; H, 5·8. $C_{18}H_{16}O_4$ requires C, 73·0; H, 5·4%), were similarly prepared from the corresponding *o*-acyloxyacetoarones described in the preceding section. All these diketones are yellow.

Cyclisation of o-*Hydroxydiaroylmethanes.*—β-Naphthaflavone, m. p. 163° (lit., 163°), and 4'-methoxy-5 : 6-benzoflavone m. p. 165° (lit., 165°), separated in quantitative yield on addition of water to solutions of benzoyl-2-hydroxy-1-naphthoylmethane and *p*-anisoyl-2-hydroxy-1-naphthoylmethane, respectively, in glacial acetic acid containing hydrogen bromide, which had been kept at room temperature for one hour. 2-(1'-*Naphthyl*)-5 : 6-*benzochromone*, m. p. (alcohol) 159° (Found : C, 85·7; H, 4·4. $C_{23}H_{14}O_2$ requires C, 85·8; H, 4·3%), 2-(2'-*naphthyl*)-5 : 6-*benzochromone*, m. p. (acetic acid) 198° (Found : C, 85·5; H, 4·3. $C_{23}H_{14}O_2$ requires C, 85·8; H, 4·3%), 2-(3'-*methoxy*-2'-*naphthyl*)-5 : 6-*benzochromone*, m. p. (alcohol) 168° (Found : C, 81·8; H, 4·6. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·5%), 2-(1'-*methoxy*-2'-*naphthyl*)-5 : 6-*benzochromone*, m. p. (alcohol) 144° (Found : C, 81·6; H, 4·5. $C_{24}H_{16}O_3$ requires C, 81·8; H, 4·5%), 2-*pentadecyl*-5 : 6-*benzochromone*, m. p. (alcohol) 89° (Found : C, 82·7; H, 9·6. $C_{28}H_{38}O_2$ requires C, 82·6; H, 9·3%), and 7-methoxy-2-styrylchromone, m. p. 189° (Gulati *et al.*, J., 1934, 1766, give the same m. p.), were similarly prepared from the corresponding *o*-hydroxy-diketones described in the preceding section.

Demethylation of Methoxybenzochromones.—2-(3'-*Hydroxy*-2'-*naphthyl*)-5 : 6-*benzochromone*, m. p. (nitrobenzene) above 300° (Found : C, 81·0; H, 4·2. $C_{23}H_{14}O_3$ requires C, 81·6; H, 4·1%), separated from a solution of the corresponding methoxy-compound (2·5 g.) in acetic anhydride (50 c.c.), which had been slowly treated with hydriodic acid (*d* 1·7; 50 c.c.) heated under reflux for 24 hours, and poured into sodium hydrogen sulphite solution. The *acetate* (pyridine–acetic anhydride) had m. p. (alcohol) 153° (Found : C, 78·8; H, 4·2. $C_{25}H_{16}O_4$ requires C, 78·9; H, 4·2%). 2-(1'-*Hydroxy*-2'-*naphthyl*-5 : 6-*benzochromone*, m. p. (nitrobenzene) above 300° (Found : C, 81·2; H, 4·3. $C_{23}H_{14}O_3$ requires C, 81·6; H, 4·1%) [*acetate*, m. p. (acetone) 189° (Found : C, 79·4; H, 4·5. $C_{25}H_{16}O_4$ requires C, 78·9; H, 4·2%)], was similarly prepared.

These hydroxy-chromones are yellow.

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