196. *Synthetical Experiments in the Chromone Group. Part XVII. Further Observations on the Action of Sodamide on* o-*Acyloxyacetophenones.*

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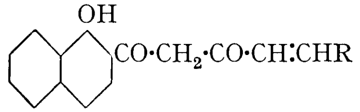
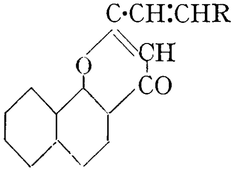
Further examples are now recorded of the production of dibenzoylmethanes from *o*-benzoyloxyacetophenones in presence of sodamide (Mahal and Venkataraman, J., 1934, 1767; *Current Sci.*, 1933, **2**, 214; compare Baker, J., 1933, 1381).

Two substances, both convertible into flavone, were obtained from *o*-benzoyloxyacetophenone and sodamide; one was *o*-hydroxydibenzoylmethane, identical with the product of the hydrolytic fission of flavone (Müller, J., 1915, **107**, 872). The interaction of sodamide with the o-*methoxy*- and the 2 : 4-*dimethoxy-benzoyl* derivative of *o*-hydroxyacetophenone gave complex mixtures, from which homogeneous material was not isolable. 2-*Benzoyloxy*-5-*benzyloxyacetophenone* behaved normally and led through the diketone to 6-benzyloxy- and 6-hydroxy-flavone. 1-*Acetyl*-2-*naphthyl benzoate* yielded an oil, which consisted mainly of the diketone and gave β-naphthaflavone on treatment with sulphuric acid; fractionation of the oil, however, gave a small amount of a substance of undetermined structure. 1-*Acetyl*-2-*naphthyl* o-*methoxybenzoate* provided an example of partial direct conversion into the pyrone.

2-*Acetyl*-1-*naphthyl cinnamate* and p-*methoxycinnamate* gave the respective diketones (I, R = Ph or *p*-C_6H_4·OMe), transformable in the usual way into the 2-styrylnaphthapyrones (II) identical with the substances prepared by the Heilbron method. The production of (I) is noteworthy, since the unsaturated diketone cannot be prepared by a Claisen condensation between 2-acetyl-1-naphthol and ethyl cinnamate (Cheema, Gulati, and Venkataraman, J., 1932, 926). In the case of the *p*-methoxycinnamate the diketone was accompanied by the styrylpyrone.

(I.)





(II.)

In line with the observation that an ω-substituent in an *o*-hydroxyaryl methyl ketone is an aid to chromone formation (Chadha, Mahal, and Venkataraman, J., 1933, 1460), 2-phenylacetyl-1-naphthyl acetate led directly to 3-phenyl-2-methyl-1:4-α-naphthapyrone. The *cinnamate* behaved similarly and gave the analogous 2-styryl compound.

EXPERIMENTAL.

The acid chlorides were prepared by means of thionyl chloride and crystallised from light petroleum. The *O*-acyl derivatives of the ketones were prepared in pyridine solution. When the product was difficult to crystallise or gave a coloration with ferric chloride, it was taken up in ether and washed with weak caustic soda solution; the material recovered from the ethereal layer was crystallised from alcohol. The sodamide reaction was carried out by mechanically shaking a mixture of the *O*-acyl derivative with twice its weight of sodamide and a convenient volume of ether in a glass-stoppered bottle for 1—10 days. The bulky precipitate was washed with ether and decomposed with ice and acetic acid.

o-*Hydroxydibenzoylmethane*.—Crystallisation of the brown semi-solid mass from a large volume of light petroleum (b. p. 50—60°) gave a mixture of large orange prisms (A) and tiny yellow plates (B), which were mechanically separated and recrystallised. The former, m. p. 110—111° (Found * : C, 77·2; H, 4·7. $C_{15}H_{12}O_3$ requires C, 75·0; H, 5·0%), gave a bright red colour with alcoholic ferric chloride. (B), m. p. 121—122°, was identified as *o*-hydroxydibenzoylmethane (Müller, *loc. cit.*) (Found * : C, 75·2; H, 5·2. Calc. for $C_{15}H_{12}O_3$: C, 75·0; H, 5·0%). A mixture of (A) and (B) melted at 95—100°. Treatment of (A) or (B) with sulphuric acid gave long colourless needles (from light petroleum) of flavone, m. p. 99° (Found * : C, 81·3; H, 4·7. Calc. for $C_{15}H_{10}O_2$: C, 81·1; H, 4·5%).

o-*Acetylphenyl* o-*methoxybenzoate* had m. p. 81° (Found : C, 71·1; H, 5·0. $C_{16}H_{14}O_4$ requires C, 71·1; H, 5·2%), and o-*acetylphenyl* 2 : 4-*dimethoxybenzoate* formed colourless plates, m. p. 77° (Found : C, 68·0; H, 5·3. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·3%).

2-*Hydroxy*-5-*benzyloxyacetophenone*.—Benzylation as in the case of resacetophenone (Gulati, Seth, and Venkataraman, J., 1934, 1766) and successive crystallisations from alcohol and light petroleum gave pale yellow plates, m. p. 70° (Found : C, 74·6; H, 5·4. $C_{15}H_{14}O_3$ requires C, 74·4; H, 5·8%). The alcoholic solution gave a deep greenish-brown colour with ferric chloride.

2-*Benzoyloxy*-5-*benzyloxyacetophenone* formed stout, pale yellow needles from ligroin, m. p. 68° (Found : C, 76·2; H, 5·3. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%), and 2-*hydroxy*-5-*benzyloxydibenzoylmethane* long, deep yellow needles, m. p. 103—104° (Found : C, 76·1; H, 4·9. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%), giving a dark brown ferric chloride coloration.

6-*Benzyloxyflavone* formed stout cream-coloured needles, m. p. 144—145° (Found : C, 80·4; H, 4·6. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%). Debenzylation gave colourless woolly needles of 6-hydroxyflavone, m. p. and mixed m. p. with the substance prepared by the Robinson method (Chadha and Venkataraman, J., 1933, 1075), 234°.

1-*Acetyl*-2-*naphthyl benzoate* formed colourless rectangular plates, m. p. 85—86° (Found : C, 78·8; H, 4·5. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8%).

β-*Naphthaflavone*.—The dark brown oily product at the end of the sodamide reaction was taken up in ether, washed with 5% sodium carbonate solution, then with water, and dried, and the ether removed. Crystallisation of the semi-solid residue from chloroform–ligroin gave a minute amount of colourless plates, m. p. 171° (Found* : C, 74·0; H, 4·3. $C_{19}H_{14}O_3$ requires C, 78·6; H, 4·8%). The colourless solution in sulphuric acid exhibited a deep green fluorescence and the alcoholic solution gave no colour with ferric chloride. The sticky residue obtained by evaporation of the chloroform–ligroin mother-liquor was treated with sulphuric acid and led to β-naphthaflavone, m. p. 163°, identical with the substance previously described (Menon and Venkataraman, J., 1931, 2594) (Found* : C, 83·7; H, 4·5. Calc. for $C_{19}H_{12}O_2$: C, 83·8; H, 4·4%).

1-*Acetyl*-2-*naphthyl* o-*methoxybenzoate* formed thick colourless plates, m. p. 102—103° (Found : C, 75·2; H, 4·8. $C_{20}H_{16}O_4$ requires C, 75·0; H, 5·0%).

2′-*Methoxy*-β-*naphthaflavone*.—The dark-brown semi-solid product of the sodamide reaction gave on repeated crystallisation from acetone or on treatment with sulphuric acid and crystallisation from alcohol cream-coloured cubes of the *methoxynaphthaflavone*, m.p. 188—189° (Found* : C, 79·5; H, 4·7. $C_{20}H_{14}O_3$ requires C, 79·5; H, 4·6%).

2-*Acetyl*-1-*naphthyl cinnamate* formed colourless shining needles, m. p. 111° (Found : C, 79·8; H, 4·8. $C_{21}H_{16}O_3$ requires C, 79·8; H, 5·1%).

ω-*Cinnamoyl*-2-*acetyl*-1-*naphthol* (I, R = Ph) crystallised from alcohol–acetic acid in long, bright orange needles, m. p. 158° (Found : C, 79·7; H, 4·8. $C_{21}H_{16}O_3$ requires C, 79·8; H, 5·1%), giving a deep brown colour with alcoholic ferric chloride.

2-*Styryl*-1 : 4-α-*naphthapyrone* (II, R = Ph) formed golden-yellow prisms from aqueous alcohol, m. p. 177° (Found : C, 84·3; H, 4·6. $C_{21}H_{14}O_2$ requires C, 84·5; H, 4·7%).

2-*Acetyl*-1-*naphthyl* p-*methoxycinnamate* formed long, colourless, flat needles from alcohol, m. p. 137—138° (Found : C, 76·4; H, 5·1. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%).

ω-p-*Methoxycinnamoyl*-2-*acetyl*-1-*naphthol* (I, R = p-C_6H_4·OMe) formed brownish-yellow needles from glacial acetic acid, m. p. 176—177° (Found* : C, 76·3; H, 5·3. $C_{22}H_{18}O_4$ requires C, 76·3; H, 5·2%). Addition of water to the mother-liquor and crystallisation of the precipitate from aqueous acetic acid gave long, lustrous, yellow needles of the 2-*p*-methoxystyrylpyrone, m. p. 207° (see below).

2-p-*Methoxystyryl*-1 : 4-α-*naphthapyrone* (II, R = p-C_6H_4·OMe).—Ring closure of the diketone was best effected by boiling alcoholic sulphuric acid. The long golden-yellow needles melted at 207° (Cheema, Gulati, and Venkataraman, J., 1932, 931) (Found* : C, 80·3; H, 4·9. Calc. for $C_{22}H_{16}O_3$: C, 80·5; H, 4·9%).

3-*Phenyl*-2-*methyl*-1 : 4-α-*naphthapyrone*.—The product (A) of the sodamide reaction was filtered off and washed with ether. Removal of ether from the filtrate and two crystallisations from aqueous alcohol gave the pyrone, m. p. 203—204° (Cheema and Venkataraman, J., 1932, 922). Treatment of (A) with acetic acid and crystallisation of the semi-solid orange mass gave more of the pyrone.

2-*Phenylacetyl*-1-*naphthyl cinnamate* formed yellow triangular plates, m. p. 146—147° (Found : C, 82·6; H, 4·9. $C_{27}H_{20}O_3$ requires C, 82·6; H, 5·1%).

2-*Styryl*-3-*phenyl*-1 : 4-α-*naphthapyrone*.—Worked up in the usual way after the sodamide reaction, the semi-solid orange product crystallised from alcohol–acetic acid in long, pale cream-coloured needles, m. p. 262—263° (Cheema, Gulati, and Venkataraman, J., 1932, 929).

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* Microanalyses by Dr. Friedrich Fischer, Frankfurt-am-Main.