238. *Synthetical Experiments in the Chromone Group. Part XII. Synthesis of 7-Hydroxy*iso*flavone and of α- and β-Naphtha*iso*flavone.*

By Harbhajan S. Mahal, Harcharan S. Rai, and Krishnasami Venkataraman.

In the absence of a solvent and under suitable conditions the reaction between ethyl formate, sodium, and an *o*-hydroxyphenyl benzyl ketone (Joshi and Venkataraman, this vol., p. 513) is a general one, giving an *iso*flavone * in excellent yield as the only product.

The action of benzyl chloride on 2 : 4-dihydroxyphenyl benzyl ketone led exclusively to the 4-*benzyl* ether, from which 7-*benzyloxy*iso*flavone* was prepared. Debenzylation of

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* The m. p.'s of *iso*flavone itself recorded in Part XI (*loc. cit.*) should be 132° and 138° instead of 142° and 148° respectively.

this gave 7-*hydroxy*iso*flavone*, which was methylated by methyl iodide and potassium carbonate, yielding 7-methoxy*iso*flavone. The reverse process was carried out, 7-methoxy*iso*flavone being prepared from 2-hydroxy-4-methoxyphenyl benzyl ketone and demethylated to give 7-hydroxy*iso*flavone.

3-*Phenyl*-1 : 4-α-*naphthapyrone* and 2-phenyl-1 : 4-β-naphthapyrone (Badhwar and Venkataraman, J., 1932, 2420) also have been prepared by the general method.

EXPERIMENTAL.

2-*Hydroxy*-4-*benzyloxyphenyl Benzyl Ketone*.—A mixture of 2 : 4-dihydroxyphenyl benzyl ketone (20 g.), anhydrous potassium carbonate (36 g.), benzyl chloride (66 g.), and acetone (200 c.c.) was boiled for 8 hours; the solvent was then recovered, and the residue diluted and distilled with steam to remove the excess of benzyl chloride. The 4-*benzyl* ether crystallised from alcohol in colourless plates (17 g.), m. p. 111° (Found : C, 79·0; H, 5·5. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·6%), which gave a blood-red colour with alcoholic ferric chloride.

7-*Benzyloxy*iso*flavone*.—A clear solution of the preceding ether (10 g.) in dry redistilled ethyl formate (150 c.c.), cooled in ice, was added during 1 hour to sodium dust (6 g.), the mixture being kept in ice–salt. After 12 hours, the orange-brown semi-solid mass was treated with ice, and the yellow precipitate was washed and crystallised successively from alcohol, glacial acetic acid, alcohol–acetic acid, and alcohol. The colourless rhombohedral plates (7 g.) obtained, m. p. 171° (Found : C, 80·6; H, 5·0. $C_{22}H_{16}O_3$ requires C, 80·5; H, 4·9%), gave no coloration with alcoholic ferric chloride and were insoluble in aqueous alkali. They were coloured yellow by sulphuric acid, and the colourless solution exhibited a sky-blue fluorescence.

7-*Hydroxy*iso*flavone*.—7-Benzyloxy*iso*flavone (6 g.) was dissolved in glacial acetic acid (170 c.c.) on the water-bath, concentrated hydrochloric acid (80 c.c.) added in two lots during 1 hour, and the mixture boiled for a few minutes. Dilution with water precipitated a crystalline substance which, recrystallised twice from alcohol, formed thick opaque leaflets (3·4 g.), m. p. 215° (Found : C, 75·5; H, 4·2. $C_{15}H_{10}O_3$ requires C, 75·6; H, 4·2%). The colourless solution of 7-*hydroxy*iso*flavone* in sulphuric acid exhibited a sky-blue fluorescence. The colourless alcoholic solution gave no colour with ferric chloride or sodium amalgam and a pale yellow colour with magnesium and hydrochloric acid. The *acetyl* derivative crystallised from alcohol in fine lustrous needles, m. p. 139° (Found : C, 73·0; H, 4·2. $C_{17}H_{12}O_4$ requires C, 72·8; H, 4·2%).

7-Benzyloxy*iso*flavone was also debenzylated when its solution in sulphuric acid was kept for 3 hours and poured into water.

7-*Methoxy*iso*flavone*.—(1) To a boiling solution of 7-hydroxy*iso*flavone (0·1 g.) in acetone (3 c.c.) and methyl iodide (1 c.c.), anhydrous potassium carbonate (0·5 g.) was added in small portions. After being heated for 5 hours, the mixture was poured into water; the precipitate obtained crystallised from dilute alcohol in colourless plates (0·06 g.), m. p. 156°. (2) A vigorous reaction ensued when a solution of 2-hydroxy-4-methoxyphenyl benzyl ketone (Baker and Robinson, J., 1929, 160) (2 g.) in ethyl formate (50 c.c.) was added to sodium dust (1 g.) cooled in ice–salt. After 12 hours, ice and ether were added, the mixture was shaken, and the ether–ester layer separated, washed, and distilled. The pale brown, oily residue solidified in contact with alcohol and then crystallised from alcohol in colourless, six-sided, irregular plates (1·2 g.), m. p. 156° alone or mixed with the above specimen (Found : C, 76·0; H, 4·7. Calc. for $C_{16}H_{12}O_3$: C, 76·1; H, 4·8%). The colourless solution in sulphuric acid exhibited a bright blue fluorescence. When the substance (0·1 g.) was heated with hydriodic acid (*d* 1·7; 2 c.c.) and acetic anhydride (2 c.c.) for 2 hours and poured into sodium bisulphite solution, the product obtained crystallised in leaflets and plates, m. p. (and mixed m. p. with 7-hydroxy*iso*flavone prepared from the benzyl ether) 215°.

3-*Phenyl*-1 : 4-α-*naphthapyrone*.—The interaction of 2-phenylacetyl-1-naphthol (Cheema and Venkataraman, J., 1932, 920) (10 g.), ethyl formate (120 g.), and sodium (5 g.) produced in 15 minutes a deep orange-yellow solid. Ice was added after 12 hours and the pale yellow solid was separated and crystallised from alcohol, forming a felted mass of colourless needles (3·5 g.), m. p. 187° (Found : C, 83·6; H, 4·3. $C_{19}H_{12}O_2$ requires C, 83·8; H, 4·4%). The substance was coloured yellow by sulphuric acid and the very pale yellow solution had an intense bluish-green fluorescence; when it was poured into water, the *naphthapyrone* was recovered unchanged. The substance was also unaffected by boiling acetic anhydride and gave no colour with alcoholic ferric chloride.

*2-Phenyl-*1 : 4-β-*naphthapyrone.*—The reaction between 1-phenylacetyl-2-naphthol (Chadha, Mahal, and Venkataraman, J., 1933, 1462) (1·6 g.), ethyl formate (50 c.c.), and sodium (1 g.) was somewhat violent and strong cooling in ice-salt and very gradual addition of the ethyl formate solution were essential. The addition of ice after 12 hours gave a sticky solid which, after two crystallisations from warm dilute acetic acid and one from aqueous alcohol, formed very pale cream-coloured clusters of curved needles (0·5 g.), m. p. 129—130°, not depressed by admixture with the naphthapyrone prepared by Badhwar and Venkataraman (*loc. cit.*). The present specimen, however, did not contain difficultly removable water of crystallisation (Found in material dried at 110—115° : C, 83·6; H, 4·7. Calc. for $C_{19}H_{12}O_2$: C, 83·8; H, 4·5%). A final crystallisation from alcohol gave long, colourless, prismatic needles, m. p. 133°. The colourless solution in sulphuric acid exhibited a bright, pure blue fluorescence.

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FORMAN CHRISTIAN COLLEGE, LAHORE.

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