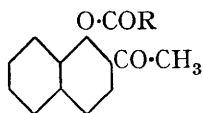


*Synthetical Experiments in the Chromone Group. Part XIV. 1767***387.** *Synthetical Experiments in the Chromone Group. Part XIV. The Action of Sodamide on 1-Acyloxy-2-acetonaphthones.*

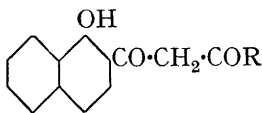
By HARBHAJAN S. MAHAL and KRISHNASAMI VENKATARAMAN.

CONTINUING the attempts made by Chadha and one of us (J., 1932, 1073) to effect dehydration of 1-acyloxy-2-acetonaphthones (I) to 1 : 4- α -naphthapyrones, we found that the action of sodamide on an ethereal solution of 2-acetyl-1-naphthyl benzoate (I; R = Ph)

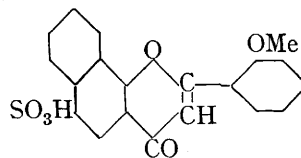
at room temperature, followed by decomposition of the precipitate with acid, gave the diketone (II; R = Ph) (compare Baker, J., 1933, 1381; Mahal and Venkataraman, *Current Science*, 1933, 2, 214). The last substance and its 3 : 4 : 5-trimethoxy-derivative



(I.)



(II.)



(III.)

were convertible into the corresponding α -naphthaflavones in the usual manner by means of sulphuric acid, which led, however, to a sulphonic acid, probably (III), in the case of the *o*-methoxy-analogue.

Treatment of the dibromide of the *O*-acetyl derivative of 2-*o*-methoxycinnamoyl-1-naphthol did not take either of the known courses leading to a flavone or a coumaranone.

EXPERIMENTAL.

2-*o*-Methoxycinnamoyl-1-naphthol.—Prepared by the addition of 50% caustic potash to a boiling alcoholic solution of 2-acetyl-1-naphthol and *o*-methoxybenzaldehyde, the *chalkone* separated as an orange oil which soon solidified. Repeated crystallisation from glacial acetic acid gave orange-yellow woolly needles, m. p. 155° (Found: C, 78.8; H, 5.4. $C_{20}H_{16}O_3$ requires C, 78.9; H, 5.3%). The *acetyl* derivative crystallised from alcohol in pale yellow plates, m. p. 93° (Found: C, 76.1; H, 5.4. $C_{22}H_{18}O_4$ requires C, 76.3; H, 5.2%). The *dibromide*, prepared in carbon disulphide solution, crystallised from alcohol-benzene in colourless prisms, m. p. 157° (Found: Br, 31.9. $C_{22}H_{16}O_4Br_2$ requires Br, 31.6%). The orange-red mixture produced by adding caustic potash (2.2 g. in 6 c.c. of water) to a suspension of the dibromide (6.4 g.) in alcohol (30 c.c.) deposited after some hours a yellow solid (2.2 g.), which was not a single substance. Many crystallisations from alcohol gave stout brownish-yellow needles (0.2 g.), m. p. 252° (decomp.) (Found: C, 79.4; H, 4.5. $C_{20}H_{14}O_3$ requires C, 79.5; H, 4.6%). The substance was not identical with 2'-methoxynaphthaflavone (see later).

ω -1-Hydroxy-2-naphthoylacetophenone (II; R = Ph).—A mixture of 2-acetyl-1-naphthyl benzoate (5 g.), powdered sodamide (5 g.), and dry ether (66 c.c.) was shaken mechanically for 5 hours and left over-night at room temperature (maximum temperature 22°). The yellowish-green precipitate, which darkened rapidly in air, was collected, washed with ether, and stirred immediately into dilute acetic acid; crystallisation of the product from acetone gave bright orange-yellow needles (1.5 g.), m. p. 147° (Found: C, 78.6; H, 5.0. $C_{19}H_{14}O_3$ requires C, 78.6; H, 4.8%). The yellow solution in sulphuric acid exhibits a bright green fluorescence, and an alcoholic solution gives a dark olive-green colour with ferric chloride.

α -Naphthaflavone.—A solution of the above diketone (0.5 g.) in concentrated sulphuric acid (10 c.c.) was left for 10 minutes and then poured on ice. The precipitate crystallised from alcohol in long, pale cream-coloured needles (0.4 g.), m. p. 157°, not depressed by admixture with the substance, pale yellow plates, m. p. 155°, prepared by the Robinson reaction (Bhullar and Venkataraman, J., 1931, 1165).

2-Acetyl-1-naphthyl *o*-Methoxybenzoate.—*o*-Methoxybenzoic acid is obtained in 80% yield by methylating salicylic acid under the conditions described for 2 : 4-dimethoxybenzoic acid (Robinson and Venkataraman, J., 1929, 62). The chloride (5 g.), obtained by means of thionyl chloride, was heated with 2-acetyl-1-naphthol (5 g.) and pyridine (10 c.c.) for 20 minutes on the water-bath, and the product shaken vigorously with dilute hydrochloric acid. The semi-solid mass was crystallised from alcohol, giving stout colourless needles, m. p. 115° (Found: C, 75.1; H, 5.0. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%).

ω -1-Hydroxy-2-naphthoyl-*o*-methoxyacetophenone (II; R = *o*-C₆H₄·OMe).—Contact of the ester (6 g.) with sodamide (12 g.) and ether (50 c.c.) during 12 hours (maximum temperature 23°), followed by 6 hours' mechanical shaking, resulted in a dark green gel, which was collected, washed with ether, and decomposed with ice and acetic acid. The product crystallised from acetone in golden-yellow needles (1.5 g.), m. p. 113° (Found: C, 75.0; H, 4.9. $C_{20}H_{16}O_4$ requires C, 75.0; H, 5.0%). The colour reactions were similar to those of the previous diketone.

2'-Methoxy- α -naphthaflavone.—When the diketone (0.9 g.) was boiled with absolute alcohol (100 c.c.) and sulphuric acid (*d* 1.84; 10 c.c.) for 90 minutes, the colour changed from deep

brown to pale yellow. Dilution with water gave a colourless precipitate, which crystallised from alcohol in long silky needles (0.7 g.), m. p. 164° (Found : C, 79.4; H, 4.8. $C_{20}H_{14}O_3$ requires C, 79.5; H, 4.6%). Demethylation with hydriodic acid and acetic anhydride or phenol did not lead to a homogeneous alkali-soluble substance (compare Robinson and Venkataraman, *loc. cit.*).

Dissolution of the diketone in concentrated sulphuric acid and addition to ice gave a yellow substance, which was insoluble in the common organic solvents. A clear solution was obtained when the substance was suspended in boiling glacial acetic acid and treated with an equal volume of water. On cooling, bright yellow needles separated, m. p. 326° (decomp.) (Found : S, 8.1; SO_3H , by titration with standard caustic soda solution, 21.0. $C_{20}H_{14}O_6S$ requires S, 8.2; SO_3H , 21.2%).

2-Acetyl-1-naphthyl 2 : 4-Dimethoxybenzoate.—Prepared, as in the case of the *o*-methoxybenzoate, from 2-acetyl-1-naphthol (2.5 g.), 2 : 4-dimethoxybenzoyl chloride (2.7 g.), and pyridine (6 g.), and twice crystallised from alcohol, the substance formed colourless rectangular plates (2.0 g.), m. p. 126° (Found : C, 72.2; H, 4.8. $C_{21}H_{18}O_5$ requires C, 72.0; H, 5.1%).

ω -1'-Hydroxy-2'-naphthoyl-2 : 4-dimethoxyacetophenone [II; R = $C_6H_3(OMe)_2$].—A mixture of the above ester (1.4 g.), sodamide (2.8 g.), and ether (15 c.c.), kept at room temperature (maximum 39°), became yellow in 20 minutes and greenish-yellow after 8 days. The diketone separated from alcohol in long orange-yellow needles (0.4 g.), m. p. 133° (Found : C, 72.2; H, 4.7. $C_{21}H_{18}O_5$ requires C, 72.0; H, 5.1%). The substance fluoresced (brilliant green) in sulphuric acid.

2' : 4'-Dimethoxy- α -naphthaflavone.—The diketone (0.19 g.) was boiled with alcohol (12 c.c.) and concentrated sulphuric acid (1.5 c.c.) for 1 hour, and the solution poured into water. The product crystallised from alcohol in long, colourless, silky needles (0.13 g.), m. p. 214° (Found : C, 76.2; H, 4.5. $C_{21}H_{16}O_4$ requires C, 75.9; H, 4.8%). The colourless solution in sulphuric acid exhibited a bright green fluorescence.

2-Acetyl-1-naphthyl O-Trimethylgallate [I; R = $C_6H_2(OMe)_3$].—The product obtained by heating 2-acetyl-1-naphthol (5 g.), trimethylgalloyl chloride (6.5 g.), and pyridine (13 g.) on the water-bath for $\frac{1}{2}$ hour and pouring the mixture into water was washed with dilute hydrochloric acid, ice-cold aqueous caustic soda, and water, and crystallised from alcohol until it gave no ferric chloride coloration; the colourless needles (8 g.) melted at 143° (Found : C, 69.3; H, 5.4. $C_{22}H_{20}O_6$ requires C, 69.4; H, 5.2%).

ω -1'-Hydroxy-2'-naphthoyl-3 : 4 : 5-trimethoxyacetophenone [II; R = $C_6H_2(OMe)_3$].—A clear solution of the ester (3 g.) in toluene (50 c.c.) was mechanically shaken with sodamide (7 g.) for 30 hours and kept at room temperature (maximum 19°) for a week. The viscous yellow gel was collected, washed with toluene, and triturated with ice-cold aqueous acetic acid. The product crystallised from alcohol in deep yellow needles (1.2 g.), m. p. 142° (Found : C, 69.2; H, 5.3. $C_{22}H_{20}O_6$ requires C, 69.4; H, 5.2%). The crystals were coloured orange by sulphuric acid; unlike the previous diketones, the solution exhibited only a faint green fluorescence. The coloration with ferric chloride was dark green as in the other cases.

3' : 4' : 5'-Trimethoxy- α -naphthaflavone.—Dissolved in sulphuric acid (10 c.c.) and, after 90 minutes, added to ice, the diketone (0.7 g.) gave the *naphthaflavone* (0.6 g.), which crystallised from alcohol-acetic acid in pale yellow needles, m. p. 224° (Found : C, 72.8; H, 4.9. $C_{22}H_{18}O_5$ requires C, 72.9; H, 5.0%).

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