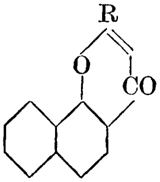
CLII.—*Synthetical Experiments in the Chromone Group. Part II.* 1 : 4-α-*Naphthapyrones.*

By Amar Singh Bhullar and Krishnasami Venkataraman.

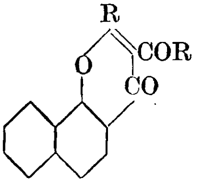
The Allan–Robinson condensation (J., 1924, **125**, 2192) of phenolic ketones with acid anhydrides to form chromones does not succeed with *o*-hydroxyacetophenone, but applies only to ketones derived from resorcinol, pyrogallol, and phloroglucinol. The Nencki method for the preparation of phenolic ketones (heating the phenol with an aliphatic acid and zinc chloride) does not apply to monohydric phenols; in the naphthalene series, however, 2-acetyl-1-naphthol can be prepared by this method. It seemed possible, therefore, that the acetylnaphthol might resemble resacetophenone in reactivity, and naphtha-γ-pyrones be produced by heating it with acid anhydrides. Such has been found to be the case, the reaction, in fact, proceeding more readily than with any of the ketones (resacetophenone, phloracetophenone, ω-methoxyphloracetophenone, and gallacetophenone) of the benzene series investigated by Robinson and Venkataraman and by Venkataraman (J., 1926, 2344; 1929, 61, 2219). One noteworthy feature of the condensation with the acetylnaphthol is the tendency to form the 3-acyl derivative. With phenyl ketones the only instance of acylation in the 3-position observed by Robinson and others in the course of their numerous syntheses of chromones was the formation of a substance, believed to be 7-hydroxy-3-benzoylflavone, when ω-methoxyresacetophenone was heated with benzoic anhydride and sodium benzoate (Allan and Robinson, J., 1924, **125**, 2192).

Hydrolysis of the product of the prolonged action of acetic anhydride and sodium acetate on 2-acetyl-1-naphthol gave a very good yield of a yellow crystalline substance which proved to be a mixture of 3-acetyl-2-methyl-1 : 4-α-naphthapyrone (II; R = Me) and 2-methyl-1 : 4-α-naphthapyrone (I; R = Me). Separation of the two was effected by repeated fractionation from dilute alcohol. The pyrone (I; R = Me) has been prepared by Wittig, Baugert, and Richter (*Annalen*, 1925, **446**, 155) by treatment of 2-acetyl-1-naphthyl acetate with sulphuric acid. They obtained only the 3-acyl derivative (II) by heating 2-acetyl-1-naphthol with acetic anhydride and sodium acetate.

(I.)



(II.)



According to the same authors the acyl group in 3-acylated chromones may be readily removed by boiling them for one hour with 2*N*-sodium hydroxide solution. This could not be accomplished with any of our 3-acylated naphthapyrones; either the substance was unaffected or, with increased concentration of alkali and time of heating, the pyrone ring was broken down.

When the reaction was carried out with benzoic and anisic anhydrides respectively, the corresponding naphthapyrones (I; R = Ph or C_6H_4·OMe) and their 3-acylated derivatives (II) were obtained. Naphthaflavone and 4′-methoxynaphthaflavone (I; R = Ph or C_6H_4·OMe) have previously been prepared by v. Kostanecki by suspending the dibromides of the acetyl derivatives of 1-hydroxy-2-naphthyl styryl ketone (*Ber.*, 1898, **31**, 705) and of 1-hydroxy-2-naphthyl *p*-methoxystyryl ketone (*Ber.*, 1899, **32**, 1034) respectively in alcohol and treating them with potassium hydroxide solution. Woker also has prepared naphthaflavone by heating 3-bromo-α-naphthaflavanone with alkali (*Ber.*, 1906, **39**, 1649). 3′-Hydroxynaphthaflavone has been made by v. Kostanecki (*Ber.*, 1899, **32**, 1035). The preparation of 3′ : 4′-*dihydroxynaphthaflavone* [I; R = $C_6H_3(OH)_2$] has been included in the present work, but in view of the tendency for 3-acylation the chalkone dibromide method of v. Kostanecki was employed: bromine was added to the acetate of 1-hydroxy-2-naphthyl 3 : 4-dimethoxystyryl ketone (Bigler and v. Kostanecki, *Ber.*, 1906, **39**, 4034), the *dibromide*,

$$OAc\cdot C_{10}H_6\cdot CO\cdot CHBr\cdot CHBr\cdot C_6H_3(OMe)_2,$$

treated with alcoholic potash, and the resulting *dimethoxynaphthaflavone* demethylated.

EXPERIMENTAL.

2-*Methyl*-1 : 4-α-*naphthapyrone* (I; R = Me) *and* 3-*Acetyl*-2-*methyl*-1 : 4-α-*naphthapyrone* (II; R = Me).—A mixture of 2-acetyl-1-naphthol (5 g.), acetic anhydride (25 g.), and fused sodium acetate (10 g.) was heated, with protection from moisture, at 160—170° for 8 hours and the product was hydrolysed with 10% sodium carbonate solution. The precipitate obtained on cooling was crystallised from alcohol, yielding a substance (A) (0·8 g.), m. p. 86—88°. Addition of water to the mother-liquor precipitated a substance (B), m. p. 170—171°, which was crystallised and then had m. p. 173—174°. Water was added to the new mother-liquor and the precipitate obtained was crystallised from alcohol, giving a substance (1 g.), m. p. 133—154° (C). Repeated fractionation of the substance obtained by pouring the mother-liquor into water gave two substances, (D), m. p. 165° (minute quantity), and (E), m. p. 145°.

The substance of m. p. 173—174° was recrystallised, forming colourless needles, m. p. 174°, of 2-methyl-1 : 4-α-naphthapyrone (Wittig, Baugert, and Richter, *loc. cit.*, give m. p. 174—174·5°) (Found: C, 80·0; H, 4·6. Calc. for $C_{14}H_{10}O_2$: C, 80·0; H, 4·7%). It dissolved in sulphuric acid, giving a pale yellow solution with a weak green fluorescence. The solution in absolute alcohol gave a light yellow and a yellow coloration when treated with sodium amalgam and with magnesium and hydrochloric acid respectively. The almost colourless solution in boiling glacial acetic acid turned pale yellow on addition of a drop of concentrated sulphuric acid.

Fractional crystallisation of (C) yielded more of the substance (E), m. p. 145° (Found: C, 76·1; H, 4·9. Calc. for $C_{16}H_{12}O_3$: C, 76·2; H, 4·7%), which was 3-acetyl-2-methyl-1 : 4-α-naphthapyrone (Wittig, Baugert, and Richter give m. p. 143—144°). Its solution in sulphuric acid was pale yellow with a weak greenish fluorescence.

α-*Naphthaflavone* (I; R = Ph) *and* 3-*Benzoylnaphthaflavone* (II; R = Ph).—A dry mixture of 2-acetyl-1-naphthol (10 g.), benzoic anhydride (100 g.), and sodium benzoate (20 g.) was heated for 8 hours at 180—185° with mechanical stirring. The product was allowed to cool in a desiccator, powdered, and refluxed with 5% sodium carbonate solution (950 c.c.) for 2 hours. The solid obtained, after being washed with water, crystallised from alcohol in colourless needles (10·8 g.), m. p. 218° (Found : C, 82·9; H, 4·5. $C_{26}H_{16}O_3$ requires C, 83·0; H, 4·3%). It did not react with phenylhydrazine, was unaffected by boiling 10% alcoholic potassium hydroxide or concentrated hydrochloric acid, and is regarded as 3-*benzoyl*-α-*naphthaflavone*. The substance is insoluble in water, sparingly soluble in ethyl acetate, glacial acetic acid, benzene, and light petroleum, and rather more soluble in ethyl and methyl alcohol. In its colour reactions with sulphuric acid, sodium amalgam, and magnesium and hydrochloric acid it resembles the preceding methyl compound.

A mixture of 2-acetyl-1-naphthol (5 g.), benzoic anhydride (25 g.), and sodium benzoate (10 g.) was heated at 180—190° for 8 hours, moisture being excluded. The product, treated as described above, gave, after the sodium carbonate (200 c.c.) treatment, a solid which was crystallised from alcohol. The brownish-green crystals (3 g.), recrystallised from alcohol, gave needles (2·5 g.), m. p. 218°, identical with those obtained in the previous experiment. Water was added to the first alcoholic mother-liquor, and the yellow precipitate obtained was separated, by repeated fractional crystallisation from alcohol, into a less soluble substance, m. p. 218°, and a more soluble substance, m. p. 155°. The latter crystallised in yellow plates and was identified as α-naphthaflavone (I; R = Ph) (Found : C, 83·7; H, 4·6. Calc. for $C_{19}H_{12}O_2$: C, 83·8; H, 4·3%). The m. p. given by v. Kostanecki (*loc. cit.*) is 154—156°. In its colour reactions with sulphuric acid, sodium amalgam, magnesium and hydrochloric acid (pale orange colour), and boiling glacial acetic acid containing a drop of concentrated sulphuric acid, the naphthaflavone resembles the methyl analogue (in the last reaction a green fluorescence is also produced).

2-*Acetyl*-1-*naphthyl Benzoate*.—This substance was prepared, for comparison with the products of the action of benzoic anhydride on 2-acetyl-1-naphthol, by adding excess of benzoyl chloride (10 g.) gradually to the acetylnaphthol (3 g.) in warm 10% aqueous sodium hydroxide (20 c.c.). It crystallised from alcohol in colourless prisms (4·1 g.), m. p. 128° (Found : C, 78·5; H, 5·1. Calc. for $C_{19}H_{14}O_3$: C, 78·6; H, 4·8%). Ullmann (*Ber.*, 1897, **30**, 1466) gives m. p. 96·5°, and Hantzsch (*Ber.*, 1906, **39**, 3096) 131°.

4′-*Methoxy*-α-*naphthaflavone* (I; R = C_6H_4·OMe) *and* 3-*Anisoyl*-4′-*methoxy*-α-*naphthaflavone* (II; R = C_6H_4·OMe).—These were obtained, in the same way as the phenyl compound, from 2-acetyl-1-naphthol (5 g.), anisic anhydride (30 g.), and potassium anisate (9·8 g.). The product after sodium carbonate (200 c.c.) treatment was separated by repeated fractionation from alcohol into a substance, small yellow needles, m. p. 211—212° (Found: C, 76·7; H, 4·7. $C_{28}H_{20}O_5$ requires C, 77·1; H, 4·6%), which is considered to be the *anisoyl* derivative (II), and the less sparingly soluble 4′-methoxy-α-naphthaflavone (I), m. p. 181° (v. Kostanecki gives m. p. 181°) (Found: C, 79·4; H, 4·8. Calc. for $C_{20}H_{14}O_3$: C, 79·5; H, 4·6%). The two substances resemble the methyl compound (I; R = Me) in their colour reactions.

3′ : 4′-*Dihydroxynaphthaflavone* [I; R = $C_6H_3(OH)_2$].—A mixture of 1-acetoxy-2-naphthyl 3 : 4-dimethoxystyryl ketone (2 g.) and bromine (1 g.) in carbon disulphide (60 c.c.) was kept over-night and the white powder produced was crystallised from benzene–alcohol, giving pale yellow, slender, rectangular prisms (2·8 g.) of the *dibromide*, m. p. 161° (Found: Br, 29·7. $C_{23}H_{20}O_5Br_2$ requires Br, 29·9%). The dibromide (2·2 g.) was shaken with alcohol (10 c.c.), caustic potash (1 g.), and water (3 c.c.) for 3 hours, and the orange-coloured mixture poured into water (500 c.c.). The precipitate produced, after two crystallisations from alcohol, formed bright yellow needles (0·7 g.) of the *dimethoxynaphthaflavone*, m. p. 192° (after sintering at 184°) (Found: C, 75·6; H, 4·8. $C_{21}H_{16}O_4$ requires C, 75·9; H, 4·8%). This substance is insoluble in water, almost insoluble in ligroin, sparingly soluble in cold methyl and ethyl alcohol and glacial acetic acid but readily soluble in the hot solvents, and very soluble in hot ethyl acetate and benzene. The pale orange-yellow solution in sulphuric acid has a weak green fluorescence. The pale yellow solution in boiling glacial acetic acid turns pale orange on the addition of a drop of sulphuric acid.

The dimethoxynaphthaflavone (0·5 g.) was boiled with acetic anhydride (10 c.c.) and hydriodic acid (10 c.c.; *d* 1·7) during 2 hours, and the mixture poured into sulphurous acid; the brown flakes obtained crystallised from alcohol, containing a few drops of acetic acid, in pale yellow, woolly needles, m. p. 317—319°, of 3′ : 4′-*dihydroxynaphthaflavone* (Found: C, 75·2; H, 3·7. $C_{19}H_{12}O_4$ requires C, 75·0; H, 3·9%). The substance is insoluble in water and light petroleum, practically insoluble in benzene, insoluble in cold methyl alcohol and ethyl acetate and sparingly soluble when hot, and moderately easily soluble in hot ethyl alcohol and glacial acetic acid. The pale yellow solution in sulphuric acid has a weak green fluorescence, which becomes noticeably stronger on standing. The almost colourless solution in hot glacial acetic acid turns bright greenish-yellow on the addition of a drop of sulphuric acid. The alcoholic solution gives an emerald-green coloration with ferric chloride, a pale orange with magnesium and hydrochloric acid, and a greenish-orange with sodium amalgam. The addition of lead acetate, barium chloride, or potassium acetate solution to an alcoholic solution of the substance produced no precipitate. The dyeing properties will be recorded later together with those of other hydroxynaphthaflavones.

The *diacetate*, prepared in the usual manner, crystallised from alcohol in long silky needles, m. p. 204° (Found : C, 71·0; H, 4·2. $C_{23}H_{16}O_6$ requires C, 71·1 ; H, 4·1%).

FORMAN CHRISTIAN COLLEGE,
LAHORE.

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