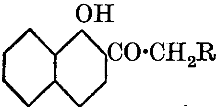
121. *Synthetical Experiments in the Chromone Group. Part V. Chromones derived from 2-Phenylacetyl-*1-*naphthol and 2-β-Phenylpropionyl-*1-*naphthol.*

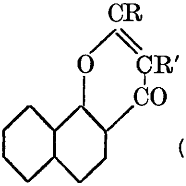
By Ujagar Singh Cheema and Krishnasami Venkataraman.

The action of acid anhydrides on 2-acetyl-1-naphthol (Bhullar and Venkataraman, J., 1931, 1165) and on 1-acetyl-2-naphthol (Menon and Venkataraman, *ibid.*, p. 2591) has already been reported. The investigation has now been extended to ω-substituted 2-acetyl-1-naphthols. 2-*Phenylacetyl*-1-*naphthol* (I; R = Ph) and 2-β-*phenylpropionyl*-1-*naphthol* (I; R = CH_2Ph) have each been treated with acetic anhydride and with benzoic anhydride under the usual conditions for chromone synthesis; the normal γ-pyrones, 3-*phenyl*-2-*methyl*-1 : 4-α-*naphthapyrone* (II; R = Me, R′ = Ph), 2 : 3-*di*-

phenyl-1 : 4-*α-naphthapyrone* (II; R = R′ = Ph), 3-benzyl-2-methyl-1 : 4-α-naphthapyrone (II; R = Me, R′ = CH_2Ph), and 3-benzyl-α-naphthaflavone (II; R = Ph, R′ = CH_2Ph), have been produced. The reactions proceeded smoothly, the products requiring scarcely any purification. It would thus appear that the Allan–Robinson condensation is more applicable to ω-substituted ketones, such as ω-methoxyphloracetophenone and the ketones concerned in the present work, than to methyl ketones, such as resacetophenone, phloracetophenone, and gallacetophenone.

(I.)





(II.)

2-Phenylacetyl-1-naphthol is a new substance, prepared by the Nencki reaction. Witt and Braun (*Ber.*, 1914, **47**, 3216) noticed that the preparation of 2-acetyl-1-naphthol by the Nencki reaction is greatly facilitated by the addition of acetic anhydride. We have found this to be very generally applicable and have thus been able to obtain greatly improved yields of resacetophenone and gallacetophenone; in the preparation of (I; R = Ph or CH_2Ph) also, the use of the appropriate acid anhydride led to higher yields. We have made 2-β-phenylpropionyl-1-naphthol by heating α-naphthol with β-phenylpropionic acid and zinc chloride; it has previously been prepared by catalytic reduction of 2-cinnamoyl-1-naphthol (Pfeiffer, Kalckbrenner, Kunze, and Levin, *J. pr. Chem.*, 1928, **119**, 109).

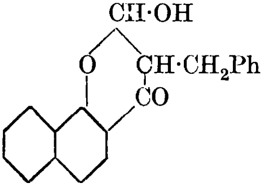
In the Nencki reaction with α-naphthol, differences were disclosed according to the nature of the acid constituent. Of the four acids used, β-phenylpropionic acid gave the best results, a good yield of a readily crystallisable material being obtained even in the absence of anhydride; phenylacetic acid was second in order; the ketone obtained from acetic acid in the absence of anhydride was dark-coloured and required tedious purification and the yield was unsatisfactory; benzoic acid gave extremely poor yields of 2-benzoyl-1-naphthol and addition of anhydride proved no advantage.

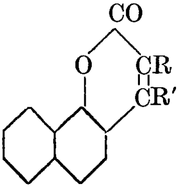
2-Phenylacetyl-1-naphthol did not react with ethyl formate and sodium, but 2-β-phenylpropionyl-1-naphthol gave two products, (A), m. p. 172°, and (B), m. p. 149°. (B) proved to be 3-*benzyl*-1 : 4-*α-naphthapyrone* (II; R = H, R′ = CH_2Ph). When (A) was heated with alcoholic sulphuric acid or acetic anhydride, (B) was obtained. (A), however, could not be the oxymethylene derivative of the phenylpropionylnaphthol, as it had no ferric chloride reaction;

on the basis of its properties it may be formulated as *2-hydroxy-3-benzyl-2 : 3-dihydro-1 : 4-α-naphthapyrone* (III).

The structures 3-phenyl-2-methyl-1 : 4-α-naphthapyrone, 3-benzyl-2-methyl-1 : 4-α-naphthapyrone, and 3-benzyl-α-naphthaflavone were assigned by Jacobson and Ghosh (J., 1915, **107**, 1055, 432, 964) to substances obtained by condensing α-naphthol with ethyl α-phenylacetoacetate, ethyl α-benzylacetoacetate, and ethyl α-benzoyl-β-phenylpropionate respectively. Baker and Robinson (J., 1925, **127**, 1981) and Baker (*ibid.*, p. 2349) having conclusively demonstrated that all such condensations lead to α-pyrones, there is little doubt that the three products of Jacobson and Ghosh are really the isomeric 1 : 2-naphthapyrones. The m. p.'s of two of them are quite different from those of the true chromones prepared by us. The third substance, 3-phenyl-4-methyl-1 : 2-α-naphthapyrone (IV; R = Ph, R′ = Me), m. p. 215—216°, has been made by Bargellini (*Atti R. Accad. Lincei*, 1925, **2**, 261) by heating 2-acetyl-1-naphthol with sodium phenylacetate and acetic anhydride; the isomeric γ-pyrone prepared by us melted at 204°; Jacobson and Ghosh's compound had m. p. 209°. We repeated their experiment and found the product difficult to purify. Under the conditions of the Hoesch reaction, however, α-naphthol and α-acetylphenylacetonitrile gave a substance, m. p. 212°, identical with Bargellini's product.

(III.)





(IV.)

2-Acetyl-1-naphthol and 2-benzoyl-1-naphthol, heated with acetic anhydride and sodium β-phenylpropionate as in the Bargellini reaction (*loc. cit.*), gave respectively 3-acetyl-2-methyl-1 : 4-α-naphthapyrone (Bhullar and Venkataraman, *loc. cit.*) and the acetyl derivative of 2-benzoyl-1-naphthol; the latter was also the only product of the action of acetic anhydride and sodium acetate on 2-benzoyl-1-naphthol under the conditions of the Bargellini reaction. When, however, sodium phenylacetate was used, coumarin formation took place normally, 3-phenyl-4-methyl-1 : 2-α-naphthapyrone being formed from 2-acetyl-1-naphthol (Bargellini, *loc. cit.*) and 3 : 4-*diphenyl*-1 : 2-α-*naphthapyrone* (IV; R = R′ = Ph) from 2-benzoyl-1-naphthol.

EXPERIMENTAL.

2-Phenylacetyl-1-naphthol (I; R = Ph).—A solution of anhydrous zinc chloride (10 g.) in phenylacetic acid (24 g.) was heated together with phenylacetic anhydride (38 g.) and α-naphthol (20 g.) for 1 hour (oil-bath at 150°) and the mixture was then cooled and poured into water. The semi-solid precipitate was collected, washed with sodium carbonate solution and with water, and crystallised twice from alcohol, giving very pale yellow, irregular plates (17 g.), m. p. 96° (Found: C, 82·4; H, 5·8. $C_{18}H_{14}O_2$ requires C, 82·4; H, 5·4%). In the absence of the acid anhydride, the yield of *ketone* was only 11 g. The ketone gives a bright chlorophyll-green coloration with alcoholic ferric chloride.

The *acetyl* derivative, prepared by heating the ketone with acetic anhydride (2 parts) and a drop of pyridine, formed colourless needles, m. p. 109°, from alcohol (Found: C, 78·6; H, 5·3. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%). The *benzoyl* derivative crystallised from alcohol in prismatic needles, m. p. 161° (Found: C, 81·7; H, 5·0. $C_{25}H_{18}O_3$ requires C, 82·0; H, 4·9%). The 2 : 4-*dinitrophenylhydrazone* crystallised from alcohol–chloroform in bright orange needles, m. p. 252° (Found: N, 12·4. $C_{24}H_{18}O_5N_4$ requires N, 12·7%).

2-β-*Phenylpropionyl*-1-*naphthol* (I; R = CH_2Ph).—The preparation was carried out as in the previous case with zinc chloride (11 g.), β-phenylpropionic acid (30 g.), β-phenylpropionic anhydride (Robinson and Shinoda, J., 1925, **127**, 1976) (49 g.), and α-naphthol (23 g.). The *ketone* (25 g.) crystallised from alcohol (in which it is almost insoluble in the cold) in bright yellow leaflets, m. p. 99° (Found: C, 82·4; H, 5·7. $C_{19}H_{16}O_2$ requires C, 82·6; H, 5·8%). In the absence of the anhydride the yield was 19 g. The ketone gives a dark green coloration with alcoholic ferric chloride.

The *acetate*, m. p. 91° (Found: C, 79·1; H, 5·9. $C_{21}H_{18}O_3$ requires C, 79·2; H, 5·7%), and the *benzoate*, m. p. 88° (Found: C, 81·8; H, 5·4. $C_{26}H_{20}O_3$ requires C, 82·1; H, 5·3%), crystallised from alcohol in colourless needles, and the 2 : 4-*dinitrophenylhydrazone* from alcohol–chloroform in deep orange needles, m. p. 223—224° (Found: N, 12·1. $C_{25}H_{20}O_5N_4$ requires N, 12·3%).

3-*Benzyl*-1 : 4-α-*naphthapyrone* (II; R = H, R′ = CH_2Ph).—To an ice-cooled mixture of finely divided sodium (1 g.) and 2-β-phenylpropionyl-1-naphthol (5 g.) in dry ether (20 c.c.), ethyl formate (15 g.) was added in small portions with vigorous shaking, and after 12 hours the brown semi-solid mass was shaken with ether and ice-water. The aqueous layer was filtered, an insoluble substance (A) and the filtrate being examined separately. (A), after being washed with acetic acid and with water, crystallised from alcohol in colourless needles (2·7 g.), m. p. 172° (Found: C, 79·2, 78·8; H, 5·4, 5·4. Calc. for $C_{20}H_{14}O_2$: C, 83·9; H, 4·9%. Calc. for $C_{20}H_{16}O_3$: C, 78·9; H, 5·3%). The pale yellow solution of the substance in concentrated sulphuric acid has a bright blue fluorescence. The alcoholic solution gives no coloration with ferric chloride. The colourless solution in boiling glacial acetic acid is unaffected by the addition of a drop of sulphuric acid. When the substance was heated with acetic anhydride and poured into water, the product obtained, after one crystallisation from alcohol, melted at 149°; the same product (B) was obtained by treatment of (A) with boiling 20% alcoholic sulphuric acid and precipitation with water. The substance (A) is insoluble in aqueous caustic soda, but develops a yellow coloration after a long time. Fusion with 50% caustic potash led to a practically quantitative yield of 2-β-phenylpropionyl-1-naphthol. The only structure consistent with these observations appears to be that of 2-*hydroxy*-3-*benzyl*-2 : 3-*dihydro*-1 : 4-*α*-*naphthapyrone* (III).

The aqueous filtrate after removal of (A) was acidified and the precipitate (0·5 g.) was boiled with absolute alcohol (10 c.c.) and concentrated sulphuric acid (1 c.c.) during 2 hours and poured into water. The product crystallised from alcohol in colourless stout needles, m. p. 149°, identical with (B).

The reaction was repeated under the following conditions. Sodium dust (0·6 g.) was added to a solution of 2-β-phenylpropionyl-1-naphthol (3 g.) in ethyl formate (12 c.c.). After the reaction had moderated, the mixture was heated on the water-bath for 15 minutes and cooled, and absolute alcohol (14 c.c.) added. When all the sodium had dissolved, concentrated hydrochloric acid (28 c.c.) was introduced, and the whole heated on the water-bath for 3 hours and poured into water. The precipitate was collected, dissolved in warm alcohol, and poured into 1% aqueous caustic soda. The separated solid was washed and crystallised from alcohol. The substance, m. p. 149°, was identical with (B), which must, therefore, be 3-*benzyl*-1 : 4-*α*-*naphthapyrone* (Found : C, 83·6; H, 5·0. $C_{20}H_{14}O_2$ requires C, 83·9; H, 4·9%). The almost colourless solution in sulphuric acid has a bright bluish-green fluorescence. The colourless solution in boiling glacial acetic acid develops a blue fluorescence, but no coloration on the addition of a drop of sulphuric acid. The solution in absolute alcohol turns greenish-yellow on the addition of sodium amalgam.

3-*Phenyl*-2-*methyl*-1 : 4-*α*-*naphthapyrone* (II; R = Me, R′ = Ph).—2-Phenylacetyl-1-naphthol (5 g.) and fused sodium acetate (7 g.) were refluxed with acetic anhydride (54 g.) for 8 hours (oil-bath at 160—165°). After cooling, the excess of acetic anhydride was hydrolysed by means of hot 5% aqueous caustic potash (500 c.c.). The undissolved residue crystallised from alcohol in colourless needles, m. p. 203—204° (Found: C, 84·2; H, 5·2. $C_{20}H_{14}O_2$

requires C, 83·9; H, 4·9%). The colourless solution in sulphuric acid exhibits a blue fluorescence.

2 : 3 - *Diphenyl*-1 : 4 - α - *naphthapyrone* (II; R = R′ = Ph).—An intimate mixture of 2-phenylacetyl-1-naphthol (5 g.), benzoic anhydride (40 g.), and sodium benzoate (10 g.) was heated at 180—185° for 6 hours. The cooled and powdered product was taken up in boiling alcohol (165 c.c.), and a solution of caustic potash (21 g.) in water (40 c.c.) added. After 30 minutes' heating, the solution was cooled and poured into a large volume of water. The precipitate obtained crystallised from alcohol in cream-coloured needles (2·5 g.), m. p. 206—207° (Found: C, 86·3; H, 4·8. $C_{25}H_{16}O_2$ requires C, 86·2; H, 4·6%). The yellow solution of the substance in sulphuric acid has a green fluorescence.

3-*Benzyl*-2-*methyl*-1 : 4-α-*naphthapyrone* (II; R = Me, R′ = CH_2Ph).—A mixture of 2-β-phenylpropionyl-1-naphthol (2·8 g.), acetic anhydride (30 g.), and fused sodium acetate (6 g.) was heated at 160—170° for 8 hours. Hydrolysis of the excess of acetic anhydride was effected by means of 10% alcoholic caustic potash (350 c.c.). The major portion of the alcohol was removed under reduced pressure, and the residue poured into much water. The precipitate crystallised from alcohol in large colourless prisms and curved needles (1·2 g.), m. p. 139° (Jacobson and Ghosh, 187°). The colourless solution in sulphuric acid shows a bright blue fluorescence (Found: C, 84·1; H, 5·6. Calc. for $C_{21}H_{16}O_2$: C, 84·0; H, 5·3%).

3-*Benzyl*-α-*naphthaflavone* (II; R = Ph, R′ = CH_2Ph).—The synthesis was carried out, with 2-β-phenylpropionyl-1-naphthol (3 g.), benzoic anhydride (24 g.), and sodium benzoate (6 g.), as in the preceding experiment. The product crystallised from glacial acetic acid in very pale cream-coloured, stout, prismatic needles (1·7 g.), m. p. 187° (Jacobson and Ghosh, 72°) (Found: C, 85·9; H, 5·0. Calc. for $C_{26}H_{18}O_2$: C, 86·2; H, 5·0%). The pale yellow solution in sulphuric acid has a bluish-green fluorescence. The colourless solution in boiling glacial acetic acid turns bright yellow on the addition of a drop of sulphuric acid.

3-*Phenyl*-2-*styryl*-1 : 4-α-*naphthapyrone* (II; R = CH:CHPh, R′= Ph).—A mixture of 2-phenylacetyl-1-naphthol (3 g.), cinnamic anhydride (35 g.), and sodium cinnamate (8 g.) was heated at 180—185° for 8 hours. The precipitate obtained after the usual treatment crystallised from glacial acetic acid in very pale cream-coloured, silky needles (2·7 g.), m. p. 262—263° (Found: C, 86·4; H, 4·8. $C_{27}H_{18}O_2$ requires C, 86·6; H, 4·8%). The reactions of the substance are described in the following paper.

3-*Benzyl*-2-*styryl*-1 : 4-α-*naphthapyrone* (II; R = CH:CHPh, R′ =

CH_2Ph).—The product similarly obtained from 2-β-phenylpropionyl-1-naphthol (3 g.), cinnamic anhydride (35 g.), and sodium cinnamate (10 g.) crystallised from glacial acetic acid in colourless needles (2·8 g.), m. p. 223° (Found : C, 86·3 ; H, 5·3. $C_{28}H_{20}O_2$ requires C, 86·6 ; H, 5·1%).

3-*Phenyl*-4-*methyl*-1 : 2-*α-naphthapyrone* (IV ; R = Ph, R′ = Me).—A rapid stream of dry hydrogen chloride was passed into an ice-cooled mixture of α-naphthol (6·2 g.), α-acetylphenylacetonitrile (6·9 g.), fused powdered zinc chloride (2 g.), and dry ether (50 c.c.) during several hours. After being kept for 3 days in the ice-chest, the ether was decanted from the reddish-brown semi-solid mass, and this was washed with dry ether and boiled with water (400 c.c.) for 2 hours. The solid, collected after cooling, crystallised from glacial acetic acid in colourless needles (0·6 g.), m. p. 212° (Found : C, 83·6 ; H, 4·9. Calc. for $C_{20}H_{14}O_2$: C, 83·9 ; H, 4·9%). The melting point was much depressed by admixture with 3-phenyl-2-methyl-1 : 4-α-naphthapyrone. The pale yellow solution in sulphuric acid has a bright greenish-blue fluorescence.

An identical substance, m. p. 212° (Found : C, 83·5 ; H, 4·9%), was prepared by Bargellini's method (*loc. cit.*).

3-*Acetyl*-2-*methyl*-1 : 4-*α-naphthapyrone.*—2-Acetyl-1-naphthol (5 g.), sodium β-phenylpropionate (4·7 g.), and acetic anhydride (48 g.) were heated together under reflux for 30 hours on a sand-bath and the mixture was poured into much water; after 12 hours, the precipitate was collected and crystallised from glacial acetic acid. Recrystallisation from alcohol gave long colourless needles, m. p. 147°, identified as 3-acetyl-2-methyl-1 : 4-α-naphthapyrone (Bhullar and Venkataraman, *loc. cit.*, m. p. 145°) (Found : C, 76·0 ; H, 4·7. Calc. for $C_{16}H_{12}O_3$: C, 76·2 ; H, 4·8%).

The Action of Acetic Anhydride on 2-*Benzoyl*-1-*naphthol.*—Bargellini's coumarin synthesis was carried out with 2-benzoyl-1-naphthol (Edminson and Hilditch, J., 1910, **97**, 226) (1·5 g.), sodium acetate (0·7 g.), and acetic anhydride (12 g.), and the product isolated in the usual way. Two crystallisations from aqueous acetic acid gave very pale yellow, stout, rectangular needles (0·7 g.), m. p. 118° (Found : C, 78·3, 78·4 ; H, 5·1, 4·9. Calc. for $C_{19}H_{14}O_3$: C, 78·6 ; H, 4·8%). The substance gave 2-benzoyl-1-naphthol on hydrolysis with hydrochloric acid and was identified as the acetate of the ketone.

3 : 4-*Diphenyl*-1 : 2-*α-naphthapyrone* (IV ; R = R′ = Ph).—As in the two preceding reactions, 2-benzoyl-1-naphthol (3·4 g.), sodium phenylacetate (2·5 g.), and acetic anhydride (29 g.) were heated together on a sand-bath for 30 hours and the mixture was poured into water. The product crystallised from glacial acetic acid in

pale yellow needles (1·5 g.), m. p. 237° (Found: C, 86·0; H, 4·7. $C_{25}H_{16}O_2$ requires C, 86·2; H, 4·6%). The yellow solution in sulphuric acid has a bright green fluorescence.

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[*Received, September 28th,* 1931.]