

STUDIES IN NAPHTHALENE SERIES

Part VIII. The Preparation and Properties of 2:4-Dipropionyl-1-Naphthol and 4-Acetyl-2-Propionyl-1-Naphthol

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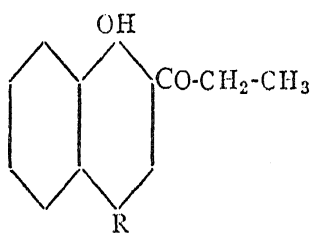
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As the study of the chemical properties of 2:4-diacetyl-1-naphthol and (2-acetyl-4-propionyl-1-naphthol by Akram and Desai¹ revealed some interesting properties of this class of compounds, we thought it necessary to prepare some more compounds of this type for further investigation. 2:4-dipropionyl-1-naphthol (I, R = Propionyl) which can be most conveniently prepared by the condensation of propionyl chloride with 2-propionyl-1-naphthol in the presence of anhydrous zinc chloride does not form a picrate. This seems to be the general property of 2:4-diacyl-1-naphthols, whilst 2-acyl- and 4-acyl-1-naphthols readily form this derivative. Bromination with one mol. of bromine gave a monobromo-derivative which was presumably 2- α -bromopropionyl-4-propionyl-1-naphthol (II) as the action of hot 5 per cent. NaOH gave bromine-free, neutral, as well as acidic products. Its dibromo- as well as tribromo-derivatives could not be obtained in a state of purity.

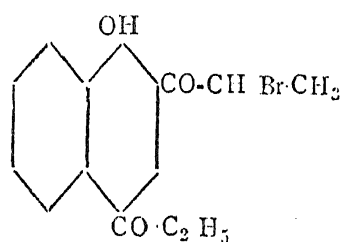
Nitration of 2:4-dipropionyl-1-naphthol with one mol. of fuming nitric acid gave mainly 4-nitro-2-propionyl-1-naphthol, together with small amounts of 2-nitro-4-propionyl-1-naphthol and 2:4-dinitro-1-naphthol, while 2:4-dinitro-1-naphthol and 2-nitro-4-propionyl-1-naphthol were formed when two mols. of nitric acid were used. It was not possible to isolate a nitro derivative containing both the propionyl groups intact. The lability of the propionyl group in either 2- or 4-position, and especially in the latter was further revealed by heating 2:4-dipropionyl-1-naphthol with either propionic or acetic acid in presence of anhydrous zinc chloride, when 2-propionyl-1-naphthol was formed in each case. Vigorous acetylation of 2:4-dipropionyl-1-naphthol gave 2:3-dimethyl-6-propionyl-1:4- α -naphthopyrone (III, R = propionyl) the alkaline hydrolysis of which gave 4-propionyl-1-hydroxy-2-naphthoic acid, as on heating it was quantitatively converted into 4-propionyl-1-naphthol.

Clemmenson Reduction of the acid gave 4-propyl-1-hydroxy-2-naphthoic acid.

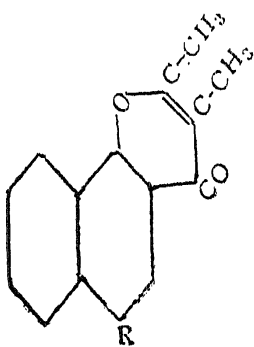
4-acetyl-2-propionyl-1-naphthol (I, R = acetyl) was obtained either by the action of acetyl chloride on 2-propionyl-1-naphthol or of propionyl chloride on 4-acetyl-1-naphthol, and as the same product was formed in each case, its constitution was beyond doubt. It did not form a picrate as usual, but gave a monobromo-derivative readily. As the bromine is removed by the action of 5 per cent. alkali with the formation of a halogen-free acidic product, the halogen must be present in the side-chain away from the hydroxyl group. The action of sodium methoxide did not give any neutral coumaranone derivative. Therefore, it must presumably be 2-propionyl-4-bromoacetyl-1-naphthol (IV). Nitration with one mol. of fuming nitric acid gave mainly 4-nitro-2-propionyl-1-naphthol and small amounts of 2-nitro-1-naphthol and 2 : 4-dinitro-1-naphthol. The Nencki Reaction using either acetic or propionic acid gave 2-propionyl-1-naphthol. Vigorous acetylation gave 2 : 3-dimethyl-6-acetyl-1 : 4- α -naphtha-pyrone (III, R = acetyl) which was hydrolysed by dilute alkali to 4-acetyl-1-hydroxy-2-naphthoic acid, the decarboxylation of which gave 4-acetyl-1-naphthol.



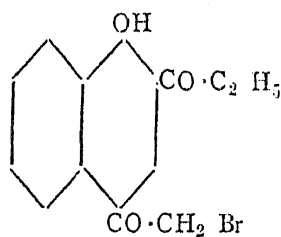
(I)



(II)



(III)



(IV)

Experimental

2 : 4-Dipropionyl-1-naphthol.—(a) To a mixture of powdered anhydrous Zinc chloride (15 g.), 2-propionyl-1-naphthol (20 g.) and nitrobenzene (150 c.c.), propionyl chloride (11 g.) was gradually added with constant shaking and cooling. The mixture was worked up as usual after 48 hours and the resulting solid product purified through dilute alkali. It crystallised from hexane in white needles m.p. 103° (yield is almost quantitative).

(b) Propionyl chloride (11 g.) was slowly added to a solution of 4-propionyl-1-naphthol (20 g.), and anhydrous aluminium chloride (15 g.) in

nitrobenzene (125 c.c.). The solid obtained by working up the product as usual after 48 hours was exhaustively extracted with hexane which dissolved 2 : 4-dipropionyl-1-naphthol (yield 45 per cent.). The hexane-insoluble portion consisted of unreacted 4-propionyl-1-naphthol and a high-melting compound of the dinaphthol type.

2 : 4-dipropionyl-1-naphthol is soluble in the usual organic solvents, but almost insoluble in concentrated caustic soda solution (over 5 per cent.) as the sodium salt is precipitated. Its alcoholic solution gives a prussian-blue coloration with ferric chloride. It does not form a picrate. (Found : C, 74.7; H, 6.4. $C_{16}H_{16}O_3$ requires C, 75.0; H, 6.3 per cent.)

2- α -bromo-propionyl-4-propionyl-1-naphthol.—Bromine (0.4 c.c.) dissolved in glacial acetic acid (10 c.c.) was gradually added to a solution of the ketone (2 g.) in acetic acid (25 c.c.). The solid obtained by pouring the solution into a large quantity of water after 24 hours crystallised from hexane in yellow needles m.p. 100° (depressed to 75° by the original ketone, as well as 4-bromo-2-propionyl-1-naphthol m.p. 98°). Its alcoholic solution gave greenish-black coloration with ferric chloride. (Found : Br, 24.0; $C_{16}H_{15}O_3$ Br, requires Br, 23.9 per cent.)

Action of 5 per cent. alkali on the monobromo derivative.—A solution of the monobromo derivative (1 g.) in 5 per cent. NaOH (25 c.c.) was heated on water-bath under reflux for three hours. The solid that separated out was filtered off, washed with water, and crystallised from alcohol when small plates m.p. 254° were obtained. (Found : C, 75.3; H, 5.6. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5 per cent.)

The alkaline solution was acidified with concentrated hydrochloric acid when a solid which crystallised from alcohol in small needles m.p. 133° was obtained. (Found : C, 75.2; H, 5.7. $C_{16}H_{14}O_3$ requires C, 75.6; H, 5.5 per cent.)

Nitration of 2 : 4-dipropionyl-1-naphthol with one mol. of fuming nitric acid and formation of 4-nitro-2-propionyl-1-naphthol, 2-nitro-4-propionyl-1-naphthol and 2 : 4-dinitro-1-naphthol.—A solution of fuming nitric acid (0.4 c.c. ; $d = 1.5$) in glacial acetic acid (5 c.c.) was slowly added to cooled solution of 2 : 4-dipropionyl-1-naphthol (2 g.) in glacial acetic acid (50 c.c.). The solid that separated out after one hour was filtered off, and crystallised from alcohol when pale-yellow needles of 4-nitro-2-propionyl-1-naphthol m.p. 162° were obtained. The acetic acid mother-liquor, on pouring into much water furnished a solid which was treated with 5 per cent. NaOH solution. The alkali-insoluble salt furnished 2-nitro-4-propionyl-1-naphthol

m.p. 100° (next paper) while the soluble salt gave 2 : 4-dinitro-1-naphthol m.p. 138°.

Nitration of 2 : 4-dipropionyl-1-naphthol with two mols. of nitric acid.—Fuming nitric acid (0.4 c.c.) was slowly added to a cooled solution of the naphthol (1 g.) in glacial acetic acid (30 c.c.). As nothing separated out the mixture was poured into a large quantity of water after four hours. An oil, slowly solidifying to a yellow mass was obtained, and this was treated with 5 per cent. caustic soda solution. The alkali-insoluble sodium salt gave 2-nitro-4-propionyl-1-naphthol, while the soluble salt gave 2 : 4-dinitro-1-naphthol.

Nencki Reaction with 2 : 4-dipropionyl-1-naphthol using acetic and propionic acids.—A solution of anhydrous zinc chloride (1 g.) ; 2 : 4-dipropionyl-1-naphthol (1 g.) and glacial acetic or propionic acid (10 c.c.) was heated on sand-bath under reflux for three hours, and poured into water. The solid was crystallised from alcohol, and identified as 2-propionyl-1-naphthol by mixed m.p. with an authentic specimen.

Kostanecki Reaction with 2 : 4-dipropionyl-1-naphthol and formation of 2 : 3-dimethyl-6-propionyl-1 : 4- α -naphtha-pyrone.—A mixture of 2 : 4-dipropionyl-1-naphthol (3 g.), anhydrous sodium acetate (6 g.) and acetic anhydride (15 c.c.) was heated in an oil-bath at 170–80° for eight hours, and poured into water. The solid, after being triturated with 5 per cent. caustic soda solution crystallised from alcohol in white needles m.p. 168°. The chromone dissolved in concentrated sulphuric acid with a greenish-yellow colour and fluorescence. (Found: C, 77.0; H, 5.6. $C_{18}H_{16}O_3$ requires C, 77.1; H, 5.7 per cent.)

Hydrolysis of the Chromone to 1-hydroxy-4-propionyl-2-naphthoic acid.—The chromone (2 g.) suspended in 5 per cent. caustic soda solution (25 c.c.) was heated under reflux on sand-bath for three hours. The cooled, filtered solution, on acidification with concentrated hydrochloric acid gave an acid which crystallised from alcohol in slender, white needles m.p. 205°. Its alcoholic solution gave prussian-blue colour with ferric chloride. (Found: C, 68.6; H, 5.2. $C_{14}H_{12}O_4$ requires C, 68.9; H, 5.0 per cent.)

When heated above its melting point for nearly half an hour, it decomposed into 4-propionyl-1-naphthol m.p. 188°, identified by comparing it with an authentic specimen (next paper). The reduction of 1-hydroxy-4-propionyl-2-naphthoic acid by amalgamated zinc gave 1-hydroxy-4-propyl-2-naphthoic acid which crystallised from hexane in white plates m.p. 174°. (Found: C, 72.8; H, 6.2. $C_{14}H_{14}O_3$ requires C, 73.0; H, 6.1 per cent.)

This acid gave 4-propyl-1-naphthol on heating above its m.p. for half an hour.

4-acetyl-2-propionyl-1-naphthol.—(a) Acetyl chloride (12 g.) was slowly added to a mixture of 2-propionyl-1-naphthol (30 g.), powdered zinc chloride (20 g.) and nitrobenzene (200 c.c.). After forty-eight hours, the mixture was worked up as usual, and the solid, purified through five per cent. alkali, crystallised from dilute alcohol in slender needles m.p. 142° (yield = 80 per cent.)

(b) The same substance can be obtained in 75 per cent. yield by the action of propionyl chloride on 4-acetyl-1-naphthol in presence of anhydrous aluminium chloride. The alcoholic solution of the naphthol gave prussian-blue colour with ferric chloride, and did not form a picrate. (Found : C, 74.2; H, 5.9. $C_{15}H_{14}O_3$ requires C, 74.4; H, 5.8 per cent.)

When heated with a solution of zinc chloride in either acetic or propionic acid, it was converted into 2-propionyl-1-naphthol, with the loss of the acetyl group.

2-propionyl-4-bromoacetyl-1-naphthol, was obtained by adding a five per cent. solution of Bromine in chloroform (50 c.c.) to a solution of 4-acetyl-2-propionyl-1-naphthol (2 g.) in chloroform (50 c.c.). After the removal of chloroform, the solid crystallised from alcohol in brownish-yellow needles m.p. 158°. (Found: Br, 24.8. $C_{15}H_{13}O_3$ Br requires Br, 24.9 per cent.)

Action of 5 per cent. caustic soda on the monobromo derivative.—This has done as usual, and the halogen-free acidic product crystallised from alcohol in small needles m.p. 108°. The same result was obtained by the action of alcoholic sodium methoxide. (Found: C, 69.5; H, 5.5. $C_{15}H_{14}O_4$ requires C, 69.8; H, 5.4 per cent.)

Nitration of 2-propionyl-4-acetyl-1-naphthol with one mol. of fuming nitric acid.—To a solution of the naphthol (1 g.) in glacial acetic acid (20 c.c.), fuming nitric acid (0.1 c.c.) dissolved in the same solvent (5 c.c.) was gradually added with sufficient stirring and cooling. The solid that separated out after half an hour was filtered off and was identified as 4-nitro-2-propionyl-1-naphthol by a mixed m.p. with an authentic specimen. The glacial acetic acid mother-liquor gave a solid on pouring into water. On treating this with 5 per cent. caustic soda solution, the orange-red sodium salt that separated out was identified as that of 2-nitro-1-naphthol (m. p. 128°) while the soluble salt gave 2 : 4-dinitro-1-naphthol (m.p. 138°).

The Kostanecki Reaction with 4-acetyl-2-propionyl-1-naphthol gave 2 : 3-dimethyl-6-acetyl-1 : 4- α -naphthopyrone which crystallised from alcohol in slender, white needles m.p. 189°. It dissolved in concentrated sulphuric acid with a yellowish-green colour and fluorescence. (Found: C, 76.3; H, 5.1. $C_{17}H_{14}O_3$ requires C, 76.7; H, 5.3 per cent.)

The Chromone gave 1-hydroxy-4-acetyl-2-naphthoic acid, on alkaline hydrolysis, and the alcoholic solution of this acid gave prussian-blue colour with ferric chloride. It crystallised from alcohol in needles m.p. 219–220°. (Found : C, 67.6 ; H, 4.5. $C_{13}H_{10}O_4$ requires C, 67.8 ; H, 4.3 per cent.)

When this acid was heated at 200° for one hour, the residue, after trituration through sodium bicarbonate solution crystallised from alcohol in needles m.p. 200°, and was identified as 4-acetyl-1-naphthol by a mixed m.p.

We express our grateful thanks to Capt. M. Haider Khan, M.A., B.Sc., for his kind interest in this work and provision of facilities.

Summary

2 : 4-dipropionyl-1-naphthol, and 4-acetyl-2-propionyl-1-naphthol have been prepared, and have been subjected to bromination, nitration and vigorous acetylation. The constitution of the resulting products in each case has been determined. The acyl groups in 2 as well as 4 positions are found to be labile during nitration, and it is observed that the 4-acyl group, whatever its character, is found to be more labile than the 2-acyl group as the latter is unaffected during the course of the Nencki Reaction.

REFERENCE

1. Akram and Desai . . . *Proc. Ind. Acad. Sci.*, (A), 1940, 11, 156.