

## STUDIES IN NAPHTHALENE SERIES

### Part VI. Synthesis of 2-Propyl-1-Naphthol and Properties of 2-Propionyl-1-Naphthol

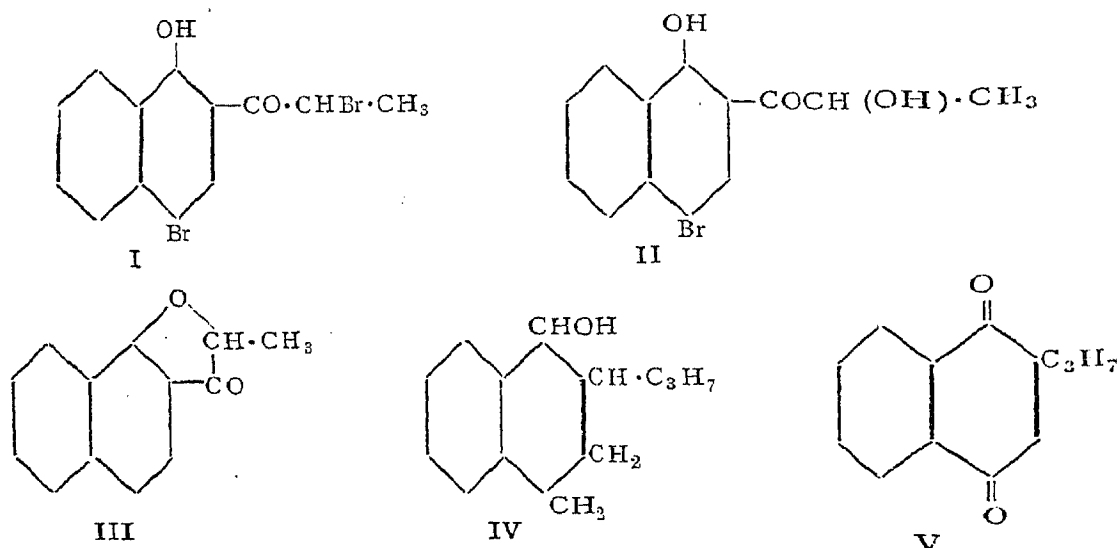
BY R. D. DESAI, ABDUL HAMID AND H. P. SHROFF

(From the Departments of Chemistry, Muslim University, Aligarh and St. Xavier's College, Bombay)

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As a continuation of the scheme outlined in Part I of this series,<sup>1</sup> we have prepared 2-Propyl-1-naphthol by the Clemmenson Reduction of 2-propionyl-1-naphthol which was prepared by a slight modification of Hantzsch's method.<sup>2</sup> As stated in Part I, it was impossible to avoid the formation of acidic as well as neutral by-products in small quantities. 2-Propionyl-1-naphthol gave readily the picrate, the semicarbozone, phenylhydrazone, the *p*-nitrophenylhydrazone, and the methyl ether (Robertson's method). It is not affected by heating with glacial acetic or propionic acids in the presence of anhydrous zinc chloride. Bromination gives mono- as well as dibromo-derivatives. The constitution of the mono-bromo-derivative which has also been prepared by Hantzsch is shown to be 4-bromo-2-propionyl-1-naphthol, as the chromone obtained by Kostanecki's method, gave 4-bromo-1-hydroxy-2-naphthoic acid on alkaline hydrolysis. The dibromo-derivative had the constitution represented by (1) as under the action of alkali solution it gave 2-lactyl-1-naphthol (II) as well as 5-bromo-2-methyl- $\alpha$ -naphtha-coumaranone (III). Nitration with one mol of fuming nitric acid gave 4-nitro-2-propionyl-1-naphthol, as its chromone gave 4-nitro-1-hydroxy-2-naphthoic acid on alkaline hydrolysis. However, two mols or excess of nitric acid gave exclusively 2:4-nitro-1-naphthol owing to the extrusion of the propionyl group.

A considerable amount of a neutral, hydroxylic compound was formed during the Clemmenson Reduction of 2-propionyl-1-naphthol to 2-propyl-1-naphthol. This has been provisionally assumed to be 2-propyl-ac-tetrahydro-1-naphthol (IV) from the analysis and general properties. 2-Propyl-1-naphthol which has been characterised by its picrate and methyl ether coupled readily with benzenediazonium chloride giving benzene-azo-3-propyl-4-naphthol, and an isomeric, neutral compound having the hydrazone structure (V) as its acid hydrolysis gave 2-propyl- $\alpha$ -naphthaquinone. Further work with the specific aim of preparing the azo dyes from 2-propionyl-1-naphthol is being continued.



### Experimental

2-Propionyl-1-naphthol- $\alpha$ -naphthol (75 g.) is slowly added to a warm solution of anhydrous zinc chloride (120 g.) in propionic acid (120 c.c.), and the solution heated to boiling on sand-bath for three hours. The warm solution is now poured into a large quantity of water (700 c.c.) containing some hydrochloric acid, when a coloured solid settles down. The supernatant liquid is decanted off, and the solid crystallised from alcohol when pale-yellow, square plates of 2-propionyl-1-naphthol crystallises out. The alcoholic mother-liquor is evaporated to dryness, and the coloured residue is purified through 10 per cent. caustic soda solution. The solid recovered on acidification gives further amount of the same ketone (yield = 65 per cent.). The recrystallised samples melt at  $85^{\circ}$ , and its alcoholic solution gives a dark-green colouration with ferric chloride.

*The Picrate* crystallised from hexane in long, red needles, m.p.  $88^{\circ}$  (depressed to  $74^{\circ}$  by the original ketone).

(Found: C, 53.0; H, 3.7.  $C_{19}H_{15}O_9N_3$  requires C, 53.1; H, 3.5 per cent.)

*The Semicarbozone* crystallised from glacial acetic acid in yellow, small plates, m.p.  $304^{\circ}$ .

(Found: C, 65.3; H, 5.8.  $C_{14}H_{13}O_2N_3$  requires C, 65.4; H, 5.8 per cent.)

*The Phenylhydrazone* crystallised from alcohol in lustrous, white plates, m.p.  $78^{\circ}$  (depressed to  $61^{\circ}$  by the original ketone).

(Found: C, 78.5; H, 6.1.  $C_{19}H_{18}ON_2$  requires C, 78.6; H, 6.2 per cent.)

The *p*-nitrophenylhydrazone crystallised from alcohol in red plates, m.p. 232°.

(Found: N, 12.2.  $C_{19}H_{17}N_3O_3$  requires N, 12.5 per cent.)

The methyl ether crystallised from hexane in white needles, m.p. 45°.

(Found: C, 78.2; H, 6.6.  $C_{14}H_{14}O_2$  requires C, 78.5; H, 6.5 per cent.)

2-Propionyl-1-naphthol remained unaffected when heated with glacial acetic acid or propionic acid in presence of anhydrous zinc chloride. Leaving it in contact with anhydrous aluminium chloride in nitrobenzene solution gave a product unmelted below 300° and giving a dark-green coloration with ferric chloride.

(Found: C, 79.4; H, 5.3.  $C_{28}H_{22}O_4$  requires C, 79.6; H, 5.2 per cent.)

*Kostanecki Reaction with 4-bromo-2-propionyl-1-naphthol and formation of 6-bromo-2:3-dimethyl-1:4- $\alpha$ -naphthopyrone.*—A mixture of 4-bromo-2-propionyl-1-naphthol (5 g.), anhydrous sodium acetate (15 g.) and acetic anhydride (25 c.c.) was heated in an oil-bath at 180–85° for ten hours with constant shaking. The solid obtained by pouring the mixture into water was triturated with 5 per cent. alkali in the cold to remove the unchanged material, and the residue crystallised from glacial acetic acid when the *pyrone* was obtained in white, long, silky needles, m.p. 225°.

(Found: Br, 26.4. Calc. for  $C_{15}H_{11}O_2$  Br. Br, 26.4 per cent.)

The chromone dissolves in concentrated sulphuric acid without giving any colour or fluorescence. Chakravarti and Bagchi<sup>3</sup> who have prepared this chromone by the application of Simonis Reaction between 4-bromo-1-naphthol and C-methyl-aceto-acetic ester record the m.p. as 211–12°.

*Hydrolysis of the above pyrone by alkali to 4-bromo-1-hydroxy-2-naphthoic acid.*—The *pyrone* (1 g.) was heated with 10 per cent. NaOH (20 c.c.) on the sand-bath under reflux for three hours. The filtered solution, on acidification with concentrated hydrochloric acid gave an acid, which after purification through sodium bicarbonate solution crystallised from alcohol in needles, m.p. 245–46°. This was identified as 4-bromo-1-hydroxy-2-naphthoic acid by comparison with an authentic specimen.

*4-Bromo-2- $\alpha$ -bromopropionyl-1-naphthol.*—The solution of bromine (1:1 c.c.) in glacial acetic acid (10 c.c.) was gradually added to the solution of 2-propionyl-1-naphthol (2 g.) in the same solvent (25 c.c.). After the addition of a trace of iodine, the solution is heated on water-bath for three hours

when copious evolution of hydrogen bromide takes place. The cooled solution deposited a solid which crystallised from glacial acetic acid in sulphur-yellow needles, m.p. 145°.

(Found: Br, 44.7.  $C_{13}H_{10}O_2Br_2$  requires Br, 44.7 per cent.)

The dibromoderivative is sparingly soluble in alcohol and cannot be further brominated.

*Action of caustic soda solution on the dibromoderivative.*—The solution of the dibromoderivative (1 g.) in 10 per cent. caustic alkali (15 c.c.) was heated on the water-bath under reflux for two hours. The cooled filtered solution gave a solid which crystallised from alcohol in yellow, micro-crystalline plates, m.p. 214°. There was practically no neutral product.

(Found: Br, 27.2.  $C_{13}H_{11}O_3$  Br requires Br, 27.1 per cent.)

*Action of sodium methoxide on the dibromoderivative, and formation of 4-bromo-2-acrylyl-1-naphthol, and 5-bromo-2-methyl-naphtha-coumaranone.*—A solution of the dibromoketone (2 g.) in sodium methoxide (2 g. Na; 50 c.c. methyl alcohol) was heated under reflux on water-bath for two hours. The residue left after the removal of alcohol was treated with hot water and dilute NaOH, and the insoluble portion filtered off. The neutral portion crystallised from alcohol in small, yellow plates, m.p. 252°.

(Found: Br, 28.7.  $C_{13}H_9O_2Br$  requires Br, 28.9 per cent.)

The alkaline, aqueous filtrate was acidified, when a yellow solid which crystallised from hexane as a micro-crystalline powder, m.p. 204° was obtained.

(Found: Br, 28.9.  $C_{13}H_9O_2$  Br requires Br, 28.9 per cent.)

*Nitration of 2-propionyl-1-naphthol and formation of 4-nitro-2-propionyl-1-naphthol.*—A solution of fuming nitric acid,  $d. = 1.5$  (0.7 c.c.) in glacial acetic acid (10 c.c.) is gradually added with constant shaking to a cooled solution of the ketone (3 g.) in glacial acetic acid (40 c.c.). A yellow solid begins to separate out at once, and the solid is filtered off after keeping the mixture for one hour. It crystallised from alcohol in long, yellow needles, m.p. 162°, and easily dissolved in alkali solution with a yellow colour (yield = 85 per cent.).

(Found: C, 63.4; H, 4.5.  $C_{13}H_{11}NO_4$  requires C, 63.7; H, 4.5 per cent.)

*Kostanecki Reaction with 4-nitro-2-propionyl-1-naphthol and formation of 6-nitro-2:3-dimethyl-1:4- $\alpha$ -naphthapyrone.*—A mixture of 4-nitro-2-propionyl-1-naphthol (5 g.), anhydrous sodium acetate (10 g.) and acetic anhydride (25 c.c.) was heated at 100° for two hours, then at 120° for three hours, and

finally at 140° for six hours. The solid obtained by pouring the mixture into water was triturated with dilute alkali and crystallised from glacial acetic acid when the *pyrone* was obtained in pale-yellow needles, m.p. 226°.

Its solution in concentrated sulphuric acid did not develop any colour or fluorescence.

(Found: C, 66.7; H, 4.2.  $C_{15}H_{11}O_4N$  requires C, 66.9; H, 4.1 per cent.)

*Hydrolysis of the above chromone to 4-nitro-1-hydroxy-2-naphthoic acid.*—The chromone (1 g.) was hydrolysed as usual by heating on sand-bath under reflux with 10 per cent. NaOH (20 c.c.). The acid obtained on acidifying the alkaline solution was purified through sodium bicarbonate solution and crystallised from alcohol in pale-yellow needles, m.p. 221°, undepressed by admixture with an authentic specimen of 4-nitro-1-hydroxy-2-naphthoic acid. During the nitration of 1-hydroxy-2-naphthoic acid with fuming nitric acid in glacial acetic acid, if sufficient care is not taken in cooling and shaking the mixture, the yield of the nitrated acid falls down considerably, and a large amount of 2-nitro-1-naphthol is formed.

*Nitration of 2-propionyl-1-naphthol with two or more mols of nitric acid.*—The nitration was carried out as usual using 0.5 c.c. of fuming nitric for 1 gm. of the ketone. The solid obtained by pouring the mixture into water after 12 hours was identified as 2:4-dinitro-1-naphthol.

*Clemmenson Reduction of 2-propionyl-1-naphthol and formation of 2-propyl-1-naphthol and 2-propyl-ac-tetrahydro-1-naphthol.*—A mixture of 2-propionyl-1-naphthol (20 g.), amalgamated zinc (30 gm.) and dilute hydrochloric acid (100 c.c.) was heated under reflux on sand-bath for 12 hours. The oily substance that floated on the surface of the cooled mixture was extracted with ether, and the acidic product was extracted with alkali. The alkaline solution on acidification gave an oil which was recovered by extraction with ether. 2-Propyl-1-naphthol was obtained as a thick, dark-brown oil, b.p. 165°/6 mm. (yield = 50 per cent.).

(Found: C, 83.8; H, 7.6.  $C_{13}H_{14}O$  requires C, 83.9; H, 7.5 per cent.)

*The Picrate* crystallised from benzene in red needles, m.p. 113° (depressed to 97° by picric acid).

(Found: C, 54.6; H, 4.3.  $C_{19}H_{17}O_8N_3$  requires C, 54.9; H, 4.1 per cent.)

The ethereal solution, from which 2-propyl-1-naphthol was extracted with alkali gave, on evaporation, an oil with a characteristic smell. It boiled

at 120–21°/7 mm. and did not form a picrate. Its ethereal solution slowly with sodium liberating hydrogen.

(Found: C, 81.8; H, 9.7.  $C_{13}H_{18}O$  requires C, 82.1; H, 9.5 per cent.)

The methyl ether of 2-propyl-1-naphthol, obtained by the alkali-dichromate sulphate method, was a thick-brown oil, b.p. 145°/6 mm.

(Found: C, 83.6; H, 8.1.  $C_{14}H_{16}O$  requires C, 84.0; H, 8.0 per cent.)

*Coupling of 2-propionyl-1-naphthol with benzene diazonium chloride and isolation of benzene-azo-3-propyl-4-naphthol and the phenyl hydrazones of 2-propionyl-1-naphthol and propyl- $\alpha$ -naphthaquinone.*—An ice-cold diazotised solution of aniline in hydrochloric acid was gradually added to the alkaline solution of 2-propionyl-1-naphthol (2 g.), and the red-dye that separated out was filtered off. The solid was treated with 5 per cent. NaOH solution and the alkali-insoluble portion was filtered off. The alkaline solution, on acidification, gave a red dye which crystallised from hexane in deep-red, small plates, m.p. 180°.

(Found: C, 78.5; H, 6.3.  $C_{19}H_{18}ON_2$  requires C, 78.6; H, 6.2 per cent.)

The alkali-insoluble product crystallised from alcohol in small, deep-red plates, m.p. 112°.

(Found: C, 78.2; H, 6.2.  $C_{19}H_{18}ON_2$  requires C, 78.6; H, 6.2 per cent.)

The neutral product was heated with dilute hydrochloric acid on a water-bath under reflux for four hours, and the solid that separated out on cooling was filtered off. It crystallised from alcohol in brown, small plates, m.p. 243°.

(Found: C, 77.6; H, 6.2.  $C_{13}H_{12}O_2$  requires C, 78.0; H, 6.0 per cent.)

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### Summary

2-Propyl-1-naphthol has been prepared by the Clemmenson Reduction of 2-propionyl-1-naphthol, the simple derivatives of which have been described. Bromination and nitration of 2-propionyl-1-naphthol under various conditions have been studied, and the constitution of the resulting products has been determined.

### REFERENCES

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