

STUDIES IN NAPHTHALENE SERIES

Part V. The Properties of 2-Stearyl-, 2-Palmityl-, and 2-Lauryl-1-naphthols and Synthesis of 2-Octadecyl-, 2-Hexadecyl-, and 2-Dodecyl-1-naphthols

BY R. D. DESAI AND W. S. WARAVDEKAR

(From the Department of Chemistry, St. Xavier's College, Bombay)

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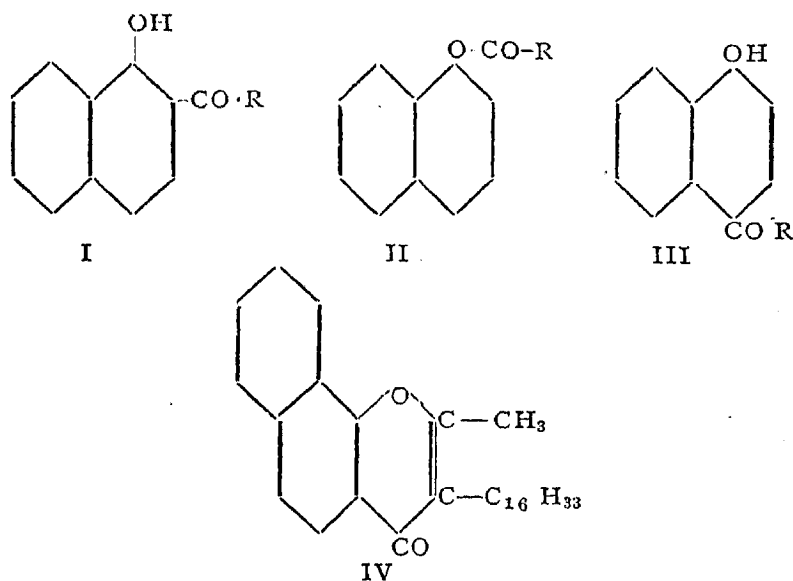
As some interesting properties of 2-acetyl- and 4-acetyl-1-naphthols have already been studied by the senior author (R. D. D.)¹ it was thought interesting to make a study of such derivatives of α -naphthol, where the acyl group consisted of long-chain alkyl groups like stearyl, palmityl and lauryl. Further interest attaches itself to such compounds as the presence of long-chain alkyl radicals in organic compounds has been recently exploited for the preparation of a number of technically important products. Though the investigations on the industrial potentialities of these compounds are not yet complete, we have decided to publish these results as very interesting differences in the chemical properties have been revealed by these hydroxy-ketones as compared with their lowest analogue.

2-Stearyl-1-naphthol (I, $R = C_{17}H_{35}$) was readily prepared from stearic acid and α -naphthol by the Nencki process² together with some α -naphthyl-stearate (II, $R = C_{17}H_{35}$). This ester was completely transformed into (1) by heating with anhydrous aluminium chloride, and no trace of the isomeric 4-stearyl-1-naphthol (III, $R = C_{17}H_{35}$) was formed. The ketone does not react with phenylhydrazine, but gives readily the *p*-nitro-phenylhydrazone. It can be methylated to 1-methoxy-2-stearyl-naphthalene by means of dimethyl sulphate and potassium carbonate. On Clemmensen Reduction, it gave exclusively 2-octadecyl-1-naphthol, whereas 2-acetyl-1-naphthol gave considerable quantities of 2-ethyl ac-tetrahydro-1-naphthol together with 2-ethyl-1-naphthol.

Bromination under all conditions gave only one mono-bromo derivative which was unaffected by boiling alkali. Therefore it must be 4-bromo-2-stearyl-1-naphthol. 2-acetyl-1-naphthol, under similar conditions, gave mono-, di- and tri-bromoderivatives. Similarly nitration with excess of fuming nitric acid gave 4-nitro-2-stearyl-1-naphthol, whereas 2-acetyl-1-naphthol under identical conditions gave only 2:4-dinitro-1-naphthol

with the displacement of the acetyl group. Vigorous acetylation according to the Kostanecki's method, gave 2-methyl-3-hexadecyl-1:4- α -naphthopyrone (IV) which was readily hydrolysed by dilute alkali to 2-stearyl-1-naphthol. This chromone (IV) thus differed from the one prepared from 2-acetyl-1-naphthol as it was hydrolysed to 1-hydroxy-2-naphtholic acid.³

The preparation and properties of 2-palmityl- and 2-lauryl-1-naphthols are similar to those of 2-stearyl-1-naphthol, and as they are fully described in the experimental portion, no further comment is necessary.



Experimental

2-Stearyl-1-naphthol.—An intimate mixture of α -naphthol (16 g.), stearic acid (32 g.) and powdered zinc chloride (20 g.) was heated in an oil-bath at 180° for three and half hours. The warm reaction mixture was poured into water acidulated with hydrochloric acid, the solid filtered off and washed thoroughly with water. Having removed most of the unreacted α -naphthol by extraction with boiling water, the residue was treated with 5 per cent. sodium bicarbonate solution to remove the stearic acid. The product was finally dissolved in alcohol when most of it dissolved leaving some residue. The alcoholic solution, on cooling deposited 2-stearyl-1-naphthol as white, small needles, m.p. 81–82 (depressed to 60–61° by α -naphthol). Its alcoholic solution gave green coloration with ferric chloride. It was insoluble in dilute sodium hydroxide solution, (but was) soluble in most of the organic solvents. (Yield = 55 per cent.)

(Found: C, 82.1; H, 10.3. $C_{28}H_{42}O_2$ requires C, 81.9; H, 10.2 per cent.)

The alcohol-insoluble portion crystallised from benzene in needles, m.p. 125°. It was insoluble in sodium hydroxide solution and its alcoholic solution did not give any coloration with ferric chloride. It was identified as *α*-naphthylstearate, as it was hydrolysed by alkali to stearic acid and *α*-naphthol. (Yield = 20 per cent.)

(Found: C, 81.8; H, 10.5. $C_{28}H_{42}O_2$ requires C, 81.9; H, 10.2 per cent.)

Fries transformation of α-naphthyl stearate to 2-stearyl-1-naphthol.—An intimate mixture of the ester (2 g.) and anhydrous aluminium chloride (5 g.) was slowly heated in an oil-bath at 140° for three hours. The solid obtained by decomposing the cold mixture with dilute, ice-cold hydrochloric acid crystallised from alcohol in needles m.p. 81–82°, and was identified as 2-stearyl-1-naphthol. (Yield = 70 per cent.)

The *p*-nitrophenylhydrazone was prepared by heating the solution of the ketone (0.5 g.) and 4-nitrophenylhydrazine (0.5 g.) in alcohol (20 c.c.) under reflux for six hours. The red liquid, on concentration, gave the hydrazone in small reddish flakes, m.p. 89–90° (depressed to 66–68° by the original ketone).

(Found: N, 7.6. $C_{34}H_{47}O_3N_3$ requires N, 7.7 per cent.)

1-Methoxy-2-stearyl-naphthalene.—A mixture of 2-stearyl-1-naphthol (1g.), anhydrous potassium carbonate (2 g.), dimethyl sulphate (3 c.c.) and dry acetone (20 c.c.) was refluxed on water-bath for 6 hours. The filtered solution, after the removal of acetone, gave a solid which crystallised from alcohol in white, lustrous, flat needles, m.p. 42–43°.

(Found: C, 82.0; H, 10.5. $C_{29}H_{44}O_2$ requires C, 82.1; H, 10.4 per cent.)

4-Bromo-2-stearyl-1-naphthol.—Bromine (0.2 c.c.) dissolved in glacial acetic acid (10 c.c.) was gradually added to the solution of 2-stearyl-1-naphthol (1.6 g.) in glacial acetic acid (25 c.c.). After 24 hours, the contents of the flask were added to much water, when a solid was slowly precipitated. It crystallised from alcohol in white, shining needles, m.p. 84–85° (depressed to 67–68° by the original ketone).

(Found: Br, 16.1; $C_{28}H_{41}O_2$ Br requires Br, 16.3 per cent.)

The bromo derivative was unaltered by boiling with 10 per cent. caustic soda solution for three hours. It could not be further brominated to dibromo- or tribromo-derivatives.

4-Nitro-2-stearyl-1-naphthol.—A solution of fuming nitric acid (*d.* = 1.5. 4 c.c.) diluted with glacial acetic acid (20 c.c.) was gradually added with

constant shaking to the solution of the ketone (1 g.) in glacial acetic acid (25 c.c.). The yellowish-white substance which separated out on adding the mixture to much water after 24 hours crystallised from hexane in pale-yellow needles, m.p. 71–72° (depressed to 53–54° by the original ketone).

(Found: N, 3.0. $C_{28}H_{41}O_4$ N requires N, 3.1 per cent.)

The nitro-derivative was soluble in the usual organic solvents, and was unaffected by boiling with alkali solution. It could not be further nitrated.

Clemmensen reduction of 2-stearyl-1-naphthol and preparation of 2-Octadecyl-1-naphthol.—Dilute hydrochloric acid (1:1) (50 c.c.) was added to a mixture containing amalgamated zinc (8 g.) and the ketone (2 g.) dissolved in alcohol (20 c.c.), and the contents refluxed on sand-bath for 8 hours. After diluting the cold mixture with water, the oily precipitate was extracted with ether, and the phenolic products removed with alkali solution, which on acidification gave 2-octadecyl-1-naphthol which was extracted with ether from the aqueous solution. It crystallised from hexane in small, brownish flakes, m.p. 119–20°, was soluble in the usual organic solvents, and its alcoholic solution did not give any coloration with ferric chloride.

(Found: C, 84.6; H, 11.2. $C_{28}H_{44}O$ requires C, 84.4; H, 11.1 per cent.)

Kostanecki reaction with 2-stearyl-1-naphthol and formation of 2-methyl-3-hexadecyl-1:4- α -naphthopyrone IV.—A mixture of the ketone (2 g.), anhydrous sodium acetate (2 g.) and acetic anhydride (15 c.c.) was heated at 175–80° in an oil-bath for 16 hours. A white, amorphous substance separated out slowly on adding the contents of the flask to water. It crystallised from hexane in white, lustrous, small needles, m.p. 73–74° (depressed to 59–60° by the original ketone), was insoluble in dilute alkali solution, but dissolved in concentrated sulphuric acid giving a pale-yellow colour. The chromone was very soluble in the usual organic solvents. (Yield = 70 per cent.)

(Found: C, 82.7; H, 9.5. $C_{30}H_{42}O_2$ requires C, 82.9; H, 9.7 per cent.)

Hydrolysis of the chromone to 2-stearyl-1-naphthol.—The above pyrone (0.5 g.) was boiled with 5 per cent. sodium hydroxide solution (10 c.c.) on a sand-bath under reflux for three hours. The cooled solution gave, on acidification with concentrated hydrochloric acid, a solid which after crystallisation melted at 81–82°, and was identified as 2-stearyl-1-naphthol by a mixed m.p.

N.B.—For the preparation of 2-palmityl- and 2-lauryl-1-naphthols, and their various derivatives we have adhered to the details followed in the case

of 2-stearyl analogues. Therefore, only the necessary information regarding their properties have been given, omitting all the preparative details.

2-Palmityl-1-naphthol was prepared as usual from α -naphthol (16 g.), palmatic acid (32 g.) and anhydrous zinc chloride (20 g.), and crystallised from alcohol in white, shining flakes m.p. 83–84° (depressed to 65–66° by α -naphthol). Its alcoholic solution gave green coloration with ferric chloride. (Yield = 70 per cent.)

(Found: C, 81.4; H, 10.1. $C_{26}H_{38}O_2$ requires C, 81.7; H, 9.9 per cent.)

The *p*-nitrophenylhydrazone of this ketone crystallised from alcohol in reddish-brown needles, m.p. 94–95°.

(Found: N, 8.2. $C_{32}H_{43}O_3N_3$ requires N, 8.1 per cent.)

1-Methoxy-2-palmityl-naphthalene prepared like the stearyl analogue crystallised from alcohol in white, shining needles, m.p. 41–42°.

(Found: C, 81.7; H, 10.0. $C_{27}H_{40}O_2$ requires C, 81.8; H, 10.1 per cent.)

4-Bromo-2-palmityl-1-naphthol crystallised from hexane in small, white lustrous needles, m.p. 86–87° (depressed to 69–70° by the original ketone). This bromo-derivative was unaltered by boiling with dilute alkali solution and could not be further brominated.

(Found: Br, 17.1. $C_{26}H_{37}O_2$ Br requires Br, 17.3 per cent.)

4-Nitro-2-palmityl-1-naphthol crystallised from hexane in fine, yellowish flakes, m.p. 76–77° (depressed to 61–62° by the original ketone). This nitro-derivative was unaffected by heating with alkali solution, and could not be further nitrated.

(Found: N, 3.1. $C_{26}H_{37}O_4N$ requires N, 3.3 per cent.)

2-Hexadecyl-1-naphthol crystallised from hexane in white, shining short needles, m.p. 124–25°. Its alcoholic solution did not give any coloration with ferric chloride.

(Found: C, 84.6; H, 11.0. $C_{26}H_{40}O$ requires C, 84.4; H, 10.9 per cent.)

2-Methyl-3-tetradecyl-1:4- α -naphthopyrone crystallised from hexane in white, lustrous needles, m.p. 89°, and was soluble in the usual organic solvents (yield = 75 per cent.). Its solution in concentrated sulphuric acid was brownish-yellow.

(Found: C, 82.6; H, 9.6. $C_{23}H_{38}O_2$ requires C, 82.8; H, 9.4 per cent.)

The chromone was hydrolysed by dilute alkali solution to 2-palmityl-1-naphthol.

2-Lauryl-1-naphthol prepared by using α -naphthol (14 g.), lauric acid (20 g.) and anhydrous zinc chloride (14 g.) crystallised from hexane in needles, m.p. 74–75°. Soluble in the usual organic solvents, its alcoholic solution gave green coloration with ferric chloride. (Yield = 65 per cent.)

(Found: C, 80.8; H, 9.1. $C_{23}H_{32}O_2$ requires C, 81.0; H, 9.2 per cent.)

The p-nitro-phenylhydrazone crystallised from alcohol in deep-red, shining needles, m.p. 135–36°.

(Found: N, 9.2. $C_{28}H_{35}O_3N_3$ requires N, 9.1 per cent.)

1-Methoxy-2-lauryl-naphthalene crystallised from alcohol in small, white flakes, m.p. 37–38°.

(Found: C, 80.9; H, 9.5. $C_{23}H_{32}O_2$ requires C, 81.2; H, 9.4 per cent.)

4-Bromo-2-lauryl-1-naphthol crystallised from hexane in yellowish, lustrous needles, m.p. 65–66° (depressed to 51–52° by the original ketone). The bromo-derivative was not affected by hot alkali solution and could not be further brominated.

(Found: Br, 19.6. $C_{22}H_{29}O_2$ Br requires Br, 19.7 per cent.)

2-Dodecyl-1-naphthol crystallised from hexane in white, lustrous, flat needles, m.p. 150–51°. It was soluble in the usual organic solvents, and its alcoholic solution did not give any coloration with ferric chloride.

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Summary

By the Nencki process, 2-stearyl-, 2-palmityl-, and 2-lauryl-1-naphthols have been prepared. These hydroxy ketones have been brominated, nitrated, reduced by the Clemmensen's method, and subjected to the Kostanecki Reaction, with a view to instituting a comparison with 2-acetyl-1-naphthol, the properties of which have been already studied and described.

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