STUDIES IN THE NAPHTHALENE SERIES

Part XII. The Preparation and Properties of 4-Stearyl-, 4-Palmithyl- and 4-Lauryl-1-naphthols

BY R. D. DESAI, F.A.SC., AND W. S. WARAVDEKAR

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

Received March 8, 1946

THE previous methods described by the authors[1] for the syntheses of 4-stearyl-, 4-palmityl and 4-lauryl-1-naphthols being unsatisfactory in giving the yields of the desired products, we repeated the conditions of condensing stearyl chloride with α-naphthol in presence of anhydrous zinc chloride, and have obtained nearly 30 per cent. yield of 4-stearyl-1-naphthol by following the details described in the experimental portion. As sufficient amount of this substance was available, we have studied some of its chemical properties in order to compare them with those of 4-acetyl-1-naphthol studied by Akram and Desai.[2]

4-Stearyl-1-naphthol can be easily methylated with dimethyl sulphate in presence of alkali. It can be smoothly reduced by amalgamated zinc to 4-octadecyl-1-naphthol, unaccompanied by even a trace of the neutral hydroxylic compound which was formed in good quantity in the reduction of 4-acetyl-1-naphthol. Bromination and nitration with one, two or three mols of bromine and nitric acid gave respectively 2-bromo-4-stearyl-1-naphthol and 2-nitro-4-stearyl-1-naphthol. These reactions are in direct contrast with those of 4-acetyl-1-naphthol which gave side-chain bromination products with excess of bromine, and 2:4-dinitro-1-naphthol with excess of nitric acid due to the displacement of the acetyl group by the nitro radical.

4-Stearyl-1-naphthol resembled 4-acetyl-1-naphthol in respect of the Pechmann and Nencki Reactions. Thus the condensation of 4-stearyl-1-naphthol with ethylacetoacetate in presence of concentrated sulphuric acid also gave 4-methyl-1:2-α-naphthapyrone, with the elimination of stearyl group, while on heating the solutions of this substance in glacial acetic and propionic acids in presence of anhydrous zinc chloride, 2-acetyl- and 2-propionyl-1-naphthols were obtained. Identical studies were made of 4-palmityl- and 4-lauryl 4-lauryl-1-naphthols and the results were similar to those of 4-stearyl-1-naphthol.

Experimental

Condensation of α-naphthol with stearyl chloride and the preparation of 4-stearyl-1-naphthol

A mixture of α-naphthol (15 gm.), anhydrous zinc chloride (14 gm.) and stearyl chloride (15 gm.) in nitrobenzene (80 c.c.) was kept for 48 hours at the room temperature, heated on water-bath for about 10 minutes and then decomposed by dilute hydrochloric acid in the cold. The nitrobenzene was steam-distilled when a brown product was obtained which on treating with 10% alkali gave alkali-soluble and alkali-insoluble products.

The alkali-soluble product (yield 30%) crystallised from alcohol in colourless, shining needles, m.p. 160–61° C., and was identified as 4-stearyl-1-naphthol (*cf.* previous paper.) Its alcoholic solution gave reddish violet colouration with aqueous ferric chloride. (Found: C, 81·8; H, 10·2; $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·2 per cent.)

The alkali-insoluble product which crystallised from alcohol in small needles, m.p. 82° C., was identified as 2-stearyl-1-naphthol (yield 40%).

p-*Nitrophenylhydrazone* of 4-stearyl-1-naphthol was obtained in yellowish red, short needles, m.p. 220°–21 C. (Found: N, 7·8; $C_{34}H_{47}O_3N_3$ requires N, 7·7 per cent.)

4-*Stearyl*-1-*methoxy-naphthalene.*—A mixture of 4-stearyl-1-naphthol (0·5 gm.), anhydrous potassium carbonate (1 gm.) and dimethyl sulphate (6 c.c.) in dry acetone (15 c.c.) was heated on water-bath under reflux per six hours. The alkali-insoluble product obtained was crystallised from alcohol in white, shining needles m.p. 125–26° C. undepressed by an authentic specimen prepared from α-naphthyl methyl ether and stearyl chloride by Desai and Waravdekar.[1] (Found: C, 81·8; H, 10·2; $C_{29}H_{44}O_2$ requires C, 82·1; H, 10·4 per cent.)

Clemmensen Reduction of 4-stearyl-1-naphthol and preparation of 4-octadecyl-1-naphthol.—The mixture of the ketone (1 gm.), amalgamated zinc (5 gm.) and hydrochloric acid (30 c.c.) was heated on sand-bath under reflux for six hours. The product crystallised from alcohol in white, shining needles m.p. 240–41° C. Its alcoholic solution did not give any colouration with ferric chloride. (Found: C, 84·7; H, 11·2; $C_{28}H_{44}O$ requires C, 84·4; H, 11·1 per cent.)

1-*Methoxy-4-octadecyl-naphthalene.*—The reduced product was methylated as before and crystallised from alcohol in white shining needles, m.p. 202–03° C., undepressed by the authentic specimen prepared by reducing

1-methoxy-4-stearyl-naphthalene. (Found: C, 84·6; H, 11·3; $C_{29}H_{46}O$ requires C, 84·9; H, 11·2 per cent.)

2-Bromo-4-stearyl-1-naphthaol.—Bromination of 4-stearyl-1-naphthol (3 gm.) with bromine (0·4 c.c.) in acetic acid (40 c.c.) gave pale-yellow, short needles, m.p. 180–81° C. (Found: Br, 16·2; $C_{28}H_{41}O_2$ Br, requires Br, 16·3 per cent.)

Further bromination with two and three mols of bromine gave the same product. The bromo product was treated with 10% alkali under reflux for four hours without any change.

2-Nitro-4-stearyl-1-naphthol.—Fuming nitric acid (0·3 c.c.) in acetic acid (10 c.c.) was added slowly to the solution of 4-stearyl-1-naphthol (3·3 gm.) in acetic acid (40 c.c.). The mixture was kept overnight and then poured in water, giving a deep-yellow coloured substance which crystallised from alcohol in fine, yellow needles, m.p. 175–76° C. (Found: N, 3·2; $C_{28}H_{41}O_4N$ requires N, 3·1 per cent.) Nitration with two and three mols of fuming nitric acid gave the same product.

Condensation of the ketone with ethyl acetoacetate.— A mixture of ethyl aceto acetate (1·5 c.c.) 4-stearyl-1-naphthol (0·5 gm.) in sulphuric acid (73% 15 c.c.) was kept overnight and then poured into water. The product obtained crystallised from alcohol in yellowish white small needles, m.p. 172° C. undepressed by the authentic sample of 4-methyl 1 : 2-α-naphtha-pyrone prepared from α-naphthol and ethyl aceto acetate.

Nencki Reaction with 4-stearyl-1-naphthol using acetic acid and propionic acid.—A mixture of zinc chloride (3 gm.), 4-stearyl-1-naphthol (0·5 gm.) in glacial acetic acid (15 c.c.) was heated on sand-bath under reflux for three hours and poured into water. The solid crystallised from alcohol in needles, m.p. 100° C., undepressed by 2-acetyl-1-naphthol. The experiment repeated with propionic acid gave the compound which crystallised from alcohol in small plates, m.p. 86° C., undepressed by 2-propionyl-1-naphthol.

Preparation of 4-palmityl-1-naphthol

Palmityl chloride (14 gm.) was added to a mixture of α-naphthol (15 gm.) zinc chloride (14 gm.) and nitrobenzene (80 c.c.) and the mixture after keeping for 48 hours at the ordinary temperature was heated on water-bath for 10 minutes, decomposed and steam-distilled. The product gave alkali-soluble and insoluble compounds. The alkali soluble compound crystallised from alcohol in colourless, shining, small flakes, m.p. 180–81° C. (yield 25%).

Its alcoholic solution gave reddish violet colouration with ferric chloride. It remained unchanged when treated with concentrated sulphuric acid. (Found: C, 81·5; H, 9·7; $C_{26}H_{38}O_2$ requires C, 81·7, H, 9·9 per cent.)

The alkali-insoluble product crystallised from alcohol in white shining flakes, m.p. 84° C., undepressed by the authentic specimen of 2-palmityl-1-naphthol.

p-*Nitrophenylhydrazone of* 4-1-*palmityl-naphthol* gave reddish, short needles, from alcohol m.p. 250–251° C. (Found: N, 8·2; $C_{32}H_{43}O_3N_3$ requires N, 8·1 per cent).

Methylation of 4-*palmityl*-1-*naphthol* gave white, shining, small needles, m.p. 129–30° C. The mixed m.p. with the authentic specimen of 4-palmityl-1-methoxy-naphthalene prepared from α-naphthyl methyl ether and palmityl chloride was unaltered.

4-*Hexadecyl*-1-*naphthol.*—A mixture of 4-palmityl-1-naphthol (1 gm.), amalgamated zinc (5 gm.) and hydrochloric acid (30 c.c.) was refluxed for 6 hours. The product crystallised from alcohol in white, shining plates, m.p. 250–51° C. (Found: C, 84·5; H, 10·5; $C_{26}H_{40}O$ requires C, 84·4; H, 10·9 per cent.)

Methylation of 4-*hexadecyl*-1-*naphthol* gave 1-methoxy-4-hexadecyl naphthalene which crystallised from alcohol in white, shining, flat needles, m.p. 224–25° C. undepressed by the authentic specimen prepared by reducing 1-methoxy-4-palmityl-naphthalene, obtained from α-naphthyl methyl ether and palmityl chloride. (Found: C, 84–6; H, 11·1. $C_{27}H_{42}O$ requires C, 84·8; H_2, 11·0 per cent.)

2-*Bromo*-4-*palmityl*-1-*naphthol.*—The ketone (3 gm.) was brominated with bromine (0·4 c.c.) in acetic acid (50 c.c.) and the product obtained was crystallised from alcohol in yellowish white shining plates, m.p. 230–31° C. It was unaffected by heating with 10% alkali. This was the only product obtained with 2 and 3 mols of bromine. (Found: Br, 17·4; $C_{26}H_{37}O_2$. Br, requires Br, 17·3 per cent.)

2-*Nitro*-4-*palmityl*-1-*naphthol.*—Nitration of the ketone (3 gm.) with fuming nitric acid (0·3 c.c.) in glacial acetic acid gave the nitro derivative which crystallised from alcohol in reddish white flat needles, m.p. 215–16° C. (Found: N, 3·1; $C_{26}H_{37}O_4N$ requires N, 3·3 per cent.)

The coumarin condensation of the ketone (0·59) with ethyl acetoacetate (1·5 c.c.) in presence of sulphuric acid (73%; 15 c.c.) gave 4-methyl-1:2-α-naphtha-pyrone identified by the mixed m.p. with an authentic specimen.

The action of acetic acid and propionic acid on 4-palmityl-1-naphthol in presence of zinc chloride gave 2-acetyl- and 2-propionyl-1-naphthols.

Preparation of 4-*lauryl*-1-*naphthol.*—A mixture of lauryl chloride (12 g.), α-naphthol (15 gm.) and zinc chloride (14 gm.) in nitrobenzene (80 c.c.) was kept for 48 hours at the room temperature and heated for 10 minutes on water-bath before decomposing. It was then steam-distilled, and the product was treated with alkali to separate the alkali soluble and insoluble components. The alkali-soluble compound crystallised from alcohol in white, shining flakes, m.p. 146–47° C. (yield 25%). Its alcoholic solution gave reddish violet colouration with ferric chloride. (Found: C, 80·8; H, 9·2; $C_{22}H_{30}O_2$ requires C, 80·9; H, 9·2 per cent.)

The alkali-insoluble product was identified as 2-lauryl-1-naphthol (yield 40%).

p-*nitrophenylhydroxone* of 4-lauryl-1-naphthol gave deep-red, shining, flat needles, m.p. 199–200° C. (Found: N, 9·2; $C_{28}H_{35}O_3N_3$ requires N, 9·1 per cent.)

1-*Methoxy*-4-*lauryl-naphthalene.*—The methylation of 4-lauryl-1-naphthol gave the methyl derivative which was identical with one prepared from α-naphthyl methyl ether and lauryl chloride. It crystallised from alcohol in white flakes, m.p. 111–12° C. (Found: C, 81·0; H, 9·3. $C_{23}H_{32}O_2$ requires C, 81·2, H, 9·4 per cent.)

4-*Dodecyl*-1-*naphthol.*—4-Lauryl-1-naphthol (1 g.) was reduced by amalgamated zinc (5 gm.) and hydrochloric acid (30 c.c.). The product crystallised from alcohol in white, shining, small flakes, m.p. 203–04° C. It did not give any colouration with ferric chloride. (Found: C, 84·4; H, 10·1; $C_{22}H_{32}O$ requires C, 84·5; H, 10·3 per cent.)

1-*Methoxy*-4-*dodecyl-naphthalene.*—The reduced product was methylated with dimethyl sulphate and proved to be identical with one prepared by reducing 1-methoxy-4-lauryl-naphthalene. It crystallised from alcohol in white, lustrous flakes, m.p. 166° C. (Found: C, 84·3; H, 10·3. $C_{23}H_{34}O$ requires C, 84·5; H, 10·4 per cent.)

2-*Bromo*-4-*lauryl*-1-*naphthol.*—4-Lauryl-1-naphthol (2·5 gm.) was treated with bromine (0·4 c.c.) in acetic acid (40 c.c.) and the product obtained was crystallised from alcohol in yellowish, shining plates, m.p. 170–71° C. (Found: Br, 19·8; $C_{22}H_{29}O_2Br$, requires Br., 19·7 per cent.)

2-*Nitro*-4-*lauryl*-1-*naphthol.*—Nitration of the ketone (2·5 gm.) with fuming nitric acid (0·3 c.c.) in acetic acid (50 c.c.) gave reddish, shining,

small flakes, m.p. 160–61° C. (Found: N, 3·7; $C_{32}H_{29}O_4N$ requires N, 3·8 per cent.)

The coumarin condensation of the ketone.—With ethyl-acetoacetate gave -4-methyl-1 : 2α-naphthapyrone.

Acetic acid and propionic acid.—When heated separately with 4-lauryl-1-naphthol in presence of zinc chloride gave 2-acetyl-1-naphthol and 2-propionyl-1-naphthol respectively.

We take this opportunity of thanking Rev. Father A. M. Coyne, S.J., for his kind interest and provision of facilities.

Summary

4-Stearyl, 4-palmityl, and 4-lauryl-1-naphthols were prepared in fairly good yield by the action of their respective acid chlorides on α-naphthol. Their properties have been studied, and compared with those of 4-acetyl-1-naphthol.

References

1. Desai and Waravdekar .. *Pro. Ind. Acad. Sci.*, 1941, **13**, 39. In press.
2. Akram and Desai .. *Ibid.*, 1940, **11**, 149.