STUDIES IN NAPHTHALENE SERIES

Part XIV. The Preparation and Properties of 2: 4-Distearyl-; 2: 4-Dipalmityl- and 2: 4-Dilauryl-1-naphthols

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

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

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THE preparation and properties of 2:4-diacetyl-1-naphthol have been described by Akram and Desai.[1] The present authors[2] have also studied the behaviour of 2-stearyl- and 4-stearyl-1-naphthols. It was thought interesting to study the properties of 2:4-distearyl-, 2:4-dipalmityl- and 2:4-dilauryl-1-naphthols with a view to comparing their properties with those of 2:4-diacetyl-1-naphthol.

2:4-Distearyl-1-naphthol did not give a colouration with ferric chloride. Neither did it react with bromine under any condition. Nitration with excess of fuming nitric acid gave 4-nitro-2-stearyl-1-naphthol. When its solution in glacial acetic acid or propionic acid was heated in the presence of anhydrous zinc chloride, only 2-stearyl-1-naphthol was obtained, as the 4-stearyl group was eliminated. Vigorous acetylation by Kostanecki's method gave 2-methyl-3-hexadecyl-6-stearyl-1:4-α-naphthapyrone, which, on alkaline hydrolysis, regenerated the original ketone.

Akram and Desai (*ibid.*) found that 2:4-diacetyl-1-naphthol gave green colouration with ferric chloride, and reacted with bromine giving mono and tribromo derivatives. Nitration of this ketone gave mixture of 4-nitro-2-acetyl-1-naphthol and 2:4-dinitro-1-naphthol. With regard to the Nencki and Kostanecki Reactions both the ketones behaved similarly. Thus it was interesting to find the long-chain ketone differing from the short-chain analogue in some of its properties,

2:4-Palmityl- and 2:4-dilauryl-1-naphthols which were prepared simulated the behaviour of 2:4-distearyl-1-naphthol.

EXPERIMENTAL

Condensation of 2-stearyl-1-naphthol with stearyl chloride by Friedel-Crafts method—Preparation of 2:4-distearyl-1-naphthol.

A solution of 2-stearyl-1-naphthol (8 g.) in nitrobenzene (50 c.c.) was added to a mixture of stearyl chloride (6 g.) and anhydrous zinc chloride

(4 g.) in nitrobenzene solution (20 c.c.). The mixture was kept for 48 hours at room temperature and then decomposed by dilute hydrochloric acid in the cold. The solid obtained on steam-distilling nitrobenzene, was purified and crystallised from alcohol in pale-yellow, shining, soft needles, m.p. 110–11° C. (yield 75%). Its alcoholic solution gave no colouration with ferric chloride. It was soluble in usual organic solvents but less so in petroleum ether. (Found: C, 81·4; H, 11·4; $C_{46}H_{76}O_3$ requires C, 81·6; H, 11·3 per cent.)

The p-*nitrophenyl hydrazone* of 2:4-distearyl-1-naphthol crystallised from alcohol in red, shining, short needles, m.p. 180–81° C. (Found: N, 5·1; $C_{52}H_{81}N_3O_3$ requires N, 5·2 per cent.)

Nitration of 2:4 *distearyl-*1*-naphthol with excess of fuming nitric acid.*

When the ketone was nitrated with one, two and three moles of fuming nitric acid the original ketone was obtained in all the cases. Therefore, the excess of fuming nitric acid (5 c.c. of d. = 1·5) in acetic acid (20 c.c.) was added to the solution of 2:4 distearyl-1-naphthol (1 g.) in acetic acid (30 c.c.). The mixture was heated on water-bath for one hour and kept overnight at room temperature. On pouring in water a yellowish mass separated out which was crystallised from petroleum ether in pale yellow shining needles, m.p. 72° C., undepressed by the authentic sample of 4-nitro-2-stearyl-1-naphthol.

Action of acetic acid and propionic acid on 2: 4-*distearyl-*1*-naphthol.*

A mixture of glacial acetic acid (15 c.c.), anhydrous zinc chloride (3 g.) and 2:4-distearyl-1-naphthol (1 g.) was heated on sand-bath under reflux for three hours. The product obtained was crystallised from alcohol in white shining small needles, m.p. 82° C., undepressed by an authentic specimen of 2-stearyl-1-naphthol and no trace of 2-acetyl-1-naphthol was observed. When the reaction was repeated with propionic acid instead of acetic acid only 2-stearyl-1-naphthol and no trace of 2-propionyl-1-naphthol was obtained.

Kostanecki Reaction of 2: 4-*distearyl-*1*-naphthol and preparation of* 2-*methyl-*3-*hexadecyl-*6-*stearyl-*1 : 4-*α-naphthapyrone.*

A mixture of 2:4 distearyl-1-naphthol (2 g.), powdered anhydrous sodium acetate (2 g.) and acetic anhydride (20 c.c.) was heated at 175–80° C. for 12 hours. The solid separated on pouring the mixture in water was crystallised from alcohol in white, lustrous flat needles, m.p. 85–86° C. It dissolved in concentrated sulphuric acid giving a brownish-yellow solution. (Found: C, 82·1; H, 10·8; $C_{48}H_{76}O_3$ requires C, 82·3; H, 10·9 per cent.)

Hydrolysis of the above pyrone with 10% alkali on water-bath for three hours gave the original ketone, m.p. 110–11° C., undepressed by a pure sample of 2 : 4 distearyl-1-naphthol.

Condensation of 2-palmityl-1-naphthol with palmityl chloride and preparation of 2 : 4-dipalmityl-1-naphthol.

2-Palmityl-1-naphthol (9·0 g.) was condensed with palmityl chloride (6·5 g.) in presence of zinc chloride (4 g.) in nitrobenzene solution (70 c.c.). The reaction was kept for 48 hours and then decomposed by hydrochloric acid. On steam-distilling nitrobenzene, the solid obtained was purified and crystallised from alcohol in fine yellow lustrous flakes, m.p. 115–16° C. (yield 72 per cent.). Its alcoholic solution did not give any colouration with ferric chloride. (Found: C, 81·4; H, 11·1; $C_{42}H_{68}O_3$ requires C, 81·2; H, 11·0 per cent.)

The p-*nitrophenylhydrazone* of 2 : 4-dipalmityl-1-naphthol crystallised from alcohol in yellowish-red, shining flat needles, m.p. 188-89° C. (Found: N, 5·4; $C_{48}H_{73}O_4N_3$ requires N, 5·5 per cent.)

Bromination of 2 : 4-dipalmityl-1-naphthol did not give any bromo-product and the nitration with excess of fuming nitric acid gave 4-nitro-2-palmityl-1-naphthol.

The Nencki Reaction with 2 : 4-dipalmityl-1-naphthol (1 g.) using acetic acid (15 c.c.) or propionic acid gave 2-palmityl-1-naphthol.

Kostanecki Reaction with 2 : 4-dipalmityl-1-naphthol—Preparation of 2-methyl-3-tetradecyl-6-palmityl-1 : 4-α-naphthapyrone.

A mixture of 2 : 4-dipalmityl-1-naphthol (2 g.), powdered anhydrous sodium acetate (2 g.) and acetic anhydride (20 c.c.) was heated at 175–80° C. for 12 hours. The product obtained was crystallised from alcohol in white, shining plates, m.p. 91–92° C. It was soluble in usual organic solvents with sulphuric acid and gave a brownish-yellow coloured solution. (Found: C, 81·8; H, 10·7; $C_{44}H_{68}O_3$ requires C, 81·9; H, 10·6 per cent.)

The above pyrone was hydrolysed with 10% caustic soda and gave back the original 2 : 4-distearyl-1-naphthol.

2 : 4-*Dilauryl-1-naphthol.*

The condensation of 2-lauryl-1-naphthol (9 g.) with lauryl chloride (6 g.) in presence of zinc chloride (4 g.) in nitrobenzene solution (70 c.c.) gave 2 : 4-dilauryl-1-naphthol which was crystallised from alcohol in fine, white, shining flakes, m.p. 92–93° C. (yield 70%). It was soluble in usual

organic solvents but less soluble in petroleum ether. (Found: C, 80·5; H, 10·2; $C_{34}H_{52}O_3$ requires C, 80·3; H, 10·3 per cent.)

The p-*nitrophenylhydrazone* of 2:4-dilauryl-1-naphthol gave from alcohol yellowish red, shining, flat needles, m.p. 170–71° C. (Found: N, 6·3; $C_{40}H_{45}O_4N_3$ requires N, 6·5 per cent.) The nitration of 2:4-dilauryl-1-naphthol with excess of fuming nitric acid gave 4-nitro-2-lauryl-1-naphthol.

The action of acetic and propionic acids on 2:4-dilauryl-1-naphthol in presence of anhydrous zinc chloride gave 2-lauryl-1-naphthol only.

Kostanecki Reaction with 2:4-*dilauryl*-1-*naphthol and preparation of* 2-*methyl*-3-*decyl*-6-*lauryl*-1:4-α-*naphthapyrone.*

2:4-Dilauryl-1-naphthol (2 g.), sodium acetate (2 g.) and acetic anhydride (20 c.c.) were heated at 175–80° C. for 12 hours and then poured in water. The solid which separated out was crystallised from alcohol in white shining small plates, m.p. 62–63° C. It dissolved in concentrated sulphuric acid giving a pale-brown colour. (Found: C, 81·4; H, 9·4; $C_{36}H_{52}O_3$ requires C, 81·2; H, 9·8 per cent.)

The pyrone on heating with 10 per cent. sodium hydroxide for three hours gave 2:4-dilauryl-1-naphthol.

Summary

We have synthesised 2:4-distearyl-, 2:4-dipalmityl; and 2:4-dilauryl-1-naphthols from 2-stearyl; 2-palmityl; 2-lauryl-1-naphthols and stearyl, palmityl and lauryl chlorides.

The properties of these diacetyl ketones have also been studied and compared with those of diacetyl-1-naphthol.

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References

1. Akram and Desai .. *Proc. Ind. Acad. Sci.*, 1940, **11**, 154.
2. Desai and Waravdekar .. *Ibid.*, 1940, **12**, 507; in the press.

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