# STUDIES IN NAPHTHALENE SERIES

## Part VII. Attempted Synthesis of 4-Stearyl-, 4-Palmityl-, and 4-Lauryl-1-naphthols

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In previous communications of this series, the synthesis of 4-acetyl, 2-stearyl-, 2-palmityl- and 2-lauryl-1-naphthols has been described,[1] and these have been found to be sufficiently interesting as intermediates for the preparation of azo-dyes and textile assistants. It appeared highly necessary to explore the methods of synthesising 4-stearyl-, 4-palmityl- and 4-lauryl-1-naphthols as these compounds are bound to be much more useful for the same purpose. Although our final objective has not been realised, we wish to place on record the interesting results so far obtained as it may be long before the interrupted work may be resumed.

The condensation of stearyl chloride with α-naphthol in the presence of anhydrous zinc chloride gave a very poor yield (5 per cent.) of 4-stearyl-1-naphthol, as the main product formed (80 per cent.) was its 2-stearyl-isomer, and the yield was not improved by using aluminium chloride, as it promoted the formation of 4:4′-dihydroxy-1:1′-dinaphthyl. This was surprising as 4-acetyl-1-naphthol was obtained in over 60 per cent. yield. When α-naphthol was replaced by its methyl ether, an excellent yield of the methyl ether of 4-stearyl-1-naphthol was obtained, but attempts to demethylate it in the presence of anhydrous aluminium chloride led to the simultaneous splitting off of the stearyl group as stearic acid. Its Clemmenson Reduction gave readily 1-methoxy-4-octadecyl-naphthalene, but its demethylation to 4-octadecyl-1-naphthol by anhydrous aluminium chloride did not lead to the encouraging results. As identical results are obtained by using palmityl and lauryl chlorides no further description of their products is necessary.

However, we have succeeded in preparing 4-stearyl-1-naphthol in good yield by condensing stearyl chloride with either 2-acetyl-1-naphthol, or 2-carbomethoxy-1-naphthol, and eliminating the acetyl and carboxyl groups from the resulting products, but the investigation is far from complete. This research as well as the condensation of long-chain unsaturated acids with α-naphthol will form the subjects of further communications.

### *Experimental*

*Condensation of stearyl chloride with α-naphthol and formation of* 4-*stearyl*-1-*naphthol*.—α-Naphthol (20 g.) and stearyl chloride (30 g.) were alternately added to a suspension of finely powdered anhydrous zinc chloride (20 g.) in nitrobenzene (120 c.c.). After keeping the mixture at the room temperature for 48 hours, the zinc chloride was dissolved by adding ice-cold, dilute, hydrochloric acid, and the nitrobenzene steam-distilled off. The dry reddish-brown solid was exhaustively extracted with petroleum ether (b.p. 40–60°), when 2-stearyl-1-naphthol (80 per cent. yield) went in solution, and the insoluble residue crystallised from alcohol when fine, white needles of 4-*stearyl*-1-*naphthol* (6 per cent. yield), m.p. 159–60° were obtained. It was soluble in alcohol, benzene, acetone, and acetic acid, but insoluble in hexane and petroleum ether. It was readily soluble in 5 per cent. caustic soda solution, thus differing fundamentally from its 2-isomer which is almost insoluble in the same medium. Its alcoholic solution gave violet coloration with ferric chloride.

(Found: C, 81·7; H, 10·1. $C_{28}H_{42}O_2$ requires C, 81·9; H, 10·2 per cent.)

*Condensation of α-naphthyl methyl ether with stearyl chloride and preparation of* 1-*methoxy*-4-*stearyl-naphthalene*.—Stearyl chloride (15 g.) dissolved in nitrobenzene (15 c.c.) was slowly added to a mixture of nitrobenzene (65 c.c.), powdered anhydrous zinc chloride (12 g.) and α-naphthyl methyl ether (8 c.c.). After keeping the mixture at the room temperature for 48 hours, it was worked up as usual. The dark-brown product that was obtained dissolved in alcohol on warming, leaving some residue (15 per cent.) which was identified as 4: 4′-dimethoxy-1: 1′-dinaphthyl.[2] The alcoholic solution, on cooling, deposited white, shining needles, m.p. 125–26° (yield = 70 per cent.).

1-*Methoxy*-4-*stearyl*-1-*naphthalene* was soluble in the usual organic solvents, and its alcoholic solution did not give any coloration with ferric chloride.

(Found: C, 81·8; H, 10·2. $C_{29}H_{44}O_2$ requires C, 82·1; H, 10·4 per cent.)

*Attempts to demethylate* 1-*methoxy*-4-*stearyl-naphthalene to* 4-*stearyl*-1-*naphthol*.—Finely powdered anhydrous aluminium chloride (3 g.) was gradually added to the solution of 4-stearyl-1-methoxy-naphthalene (2 g.) in dry benzene (60 c.c.) with thorough shaking, and warmed on water-bath for one hour and a half. After destroying aluminium chloride, the benzene was removed on the water-bath and the residue extracted with 5 per cent.

NaOH. The alkaline solution gave only stearic acid and α-naphthol on acidification with concentrated hydrochloric acid, and not a trace of 4-stearyl-1-naphthol.

*Clemmenson Reduction of* 1-*methoxy*-4-*stearyl-naphthalene to* 1-*methoxy* 4-*octadecyl-naphthalene.*—A solution of 1-methoxy-4-stearyl-naphthalene (2 g.) in alcohol (25 c.c.) was added to a flask containing amalgamated zinc (5 g.) and dilute hydrochloric acid (50 c.c.). After heating the mixture on sand-bath under reflux for 8 hours, the contents were decanted off into water, and extracted with ether. The residue left after the removal of ether crystallised from alcohol in small, white, lustrous needles, m.p. 202–03°.

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

1-*Methoxy*-4-*palmityl-naphthalene* was obtained in 65 per cent. yield using palmityl chloride. It was soluble in the usual organic solvents, and its alcoholic solution did not give any coloration with ferric chloride. Attempts to demethylate it by anhydrous aluminium chloride in dry benzene solution gave palmitic acid and α-naphthol.

(Found: C, 81·6; H, 10·2. $C_{27}H_{40}O_2$ requires C, 81·8; H, 10·1 per cent.)

1-*Methoxy*-4-*hexadecyl-naphthalene* obtained by the Clemmenson Reduction of the above product crystallised from alcohol in white needles, m.p. 224–25°. Soluble in the usual organic solvents, its alcoholic solution did not give any coloration with ferric chloride.

(Found: C, 84·6; H, 11·1. $C_{27}H_{42}O$ requires C, 84·8; H, 11·0 per cent.)

1-*Methoxy*-4-*lauryl-naphthalene* obtained in 70 per cent. yield using lauryl chloride crystallised from alcohol in small, lustrous flakes m.p. 111–12°. Soluble in the usual organic solvents, its alcoholic solution did not develop any colour with ferric chloride. It could not be demethylated to 4-lauryl-1-naphthol.

(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-*methoxy-naphthalene* obtained by the Clemmenson Reduction of the above product crystallised from alcohol in white, lustrous flakes m.p. 165–66°, and was soluble in usual organic solvents.

(Found: C, 84·3; H, 10·3. $C_{23}H_{34}O$ requires C, 84·5; H, 10·4 per cent.)

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## *Summary*

4-Stearyl-1-naphthol is obtained in a poor yield by the Friedel-Crafts Reaction between stearyl chloride and $\alpha$-naphthol as the main product is 2-stearyl-1-Naphthol. $\alpha$-naphthylmethyl ether, however, gave an excellent yield of 1-methoxy-4-stearyl-naphthalene, but its demethylation by anhydrous aluminium chloride led to the simultaneous removal of the stearyl group. Clemmenson Reduction gave readily 1-methoxy-4-octadecyl-naphthalene. Similar results were obtained by using palmityl and lauryl chlorides.

## REFERENCES

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