

STUDIES IN NAPHTHALENE SERIES

Part XIII. The Preparation and Properties of 6-Acy-2-naphthols containing Short and Long Chain Alkyl Groups

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

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

Received May 25, 1946

We have already described the synthesis of 1-stearyl-2-naphthol by Nenckis Method in a previous communication.¹ With the intention of preparing the acyl-2-naphthols having a free one position, we applied the method of Haworth and Sheldrick² to β -naphthol, but the resulting products were obtained in poor yields. Condensation of methyl β -naphthyl ether with the requisite acid chloride followed by the demethylation with hydrogen bromide or aluminium chloride gave the desired 6-acyl-2-naphthol, in many cases.

After studying the action of acetyl, propionyl, butyryl and benzoyl chlorides on methyl β -naphthyl ether, and converting the resulting methoxy into hydroxy derivatives, we condensed stearyl chloride with the above ether, 6-stearyl-2-methoxy-naphthalene was formed in good yield, but attempts to demethylate it with hydrogen bromide, hydrogen iodide or aluminium chloride led to the ejection of the stearyl group. Identical results were obtained with palmityl and lauryl chlorides. However other derivatives of 6-stearyl, 6-palmityl and 6-lauryl-2-methoxy-naphthalenes were studied.

EXPERIMENTAL

Condensation of β -naphthyl methyl ether with acetyl chloride by Friedel-Crafts method—Preparation of 2-methoxy-6-acetyl-naphthalene.

A mixture of β -naphthyl methyl ether (15 g.), anhydrous zinc chloride (13 g.) and acetyl chloride (8 c.c.) in nitro-benzene solution (70 c.c.) was kept for 48 hours and decomposed by dilute hydrochloric acid in cold. The nitrobenzene was steam-distilled and the product was purified and crystallised through alcohol in yellowish needles, m.p. 106–07° C. It was soluble in nearly all the organic solvents and its alcoholic solution did not give any colouration with ferric chloride (yield 70%). (Found: C, 78.1; H, 6.2; calculated for $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.1 per cent.)

The p-nitrophenylhydrazone crystallised from alcohol in reddish needles, m.p. 239–40° C. (Found: N, 12.3; $C_{19}H_{17}O_2N_3$ requires N, 12.5 per cent.)

Clemmensen Reduction of 2-methoxy-6-acetyl-naphthalene and formation of 2-methoxy-6-ethyl-naphthalene.

2-Methoxy-6-acetyl-naphthalene (1 g.) was heated with zinc amalgam (5 g.) and hydrochloric acid (30 c.c.) on the sand-bath under reflux for six hours. The product obtained was crystallised from alcohol in yellowish needles, m.p. 50–51° C. (Found: C, 83.9; H, 7.6; $C_{13}H_{14}O$ requires C, 83.8; H, 7.6 per cent.)

Demethylation of 2-methoxy-6-acetyl-naphthalene and preparation of 6-acetyl-2-naphthol.

The mixture of hydrobromic acid (15 c.c. of 48%) 2-methoxy-6-acetyl-naphthalene (5 g.) and acetic acid (35 c.c.) was heated on sand-bath for 6 hours. The solution was poured in a large quantity of water and the product obtained was purified through alkali. It crystallised from alcohol in yellowish flakes, m.p. 170–71° C. (yield 80%) and was soluble in the usual organic solvents. (Found: C, 77.2; H, 5.3; $C_{12}H_{10}O_2$ requires C, 77.4; H, 5.4 per cent.)

The *p*-nitrophenylhydrazone of 6-acetyl-2-naphthol gave reddish needles from alcohol, m.p. 254–53° C. (Found: N, 13.2; $C_{18}H_{15}O_3N_3$ requires N, 13.1 per cent.)

The Clemmensen Reduction of 6-acetyl-2-naphthol gave 6-ethyl-2-naphthol which crystallised from alcohol in white small flakes, m.p. 93–94° C. (Found: C, 83.5; H, 7.1; $C_{12}H_{12}O$ requires C, 83.7; H, 7.0 per cent.)

Condensation of β -naphthyl methyl ether with propionyl chloride preparation of 2-methoxy-6-propionyl-naphthalene.

Propionyl chloride (8 c.c.), anhydrous zinc chloride (13 g.) and β -naphthyl methyl ether (16 g.) in nitrobenzene solution (65 c.c.) were well mixed and kept for 48 hours. Nitrobenzene was then steam-distilled and the product formed was crystallised from alcohol in lustrous small plates, m.p. 108–09° C. (Yield 80%). It was slightly soluble in petroleum ether, but very soluble in all other organic solvents. (Found: C, 78.2; H, 6.4; $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.5 per cent.)

The *p*-nitrophenyl hydrazone of 2-methoxy-6-propionyl-naphthalene crystallised from alcohol in reddish, shining needles, m.p. 210–11° C. (Found: N, 11.9; $C_{20}H_{19}O_3N_3$ requires N, 12.0 per cent.)

2-Methoxy-6-propyl-naphthalene was obtained from 2-methoxy-6-propionyl-naphthalene (1 g.) on heating with amalgamated zinc (5 gm.) and hydrochloric acid (30 c.c.) for six hours, and crystallised from alcohol in

white, shining plates, m.p. 49–50° C. (Found: C, 84.2; H, 8.1; $C_{14}H_{15}O$ requires C, 84.0; H, 8.1 per cent.)

Demethylation of 2-methoxy-6-propionyl-naphthalene and preparation of 6-propionyl-2-naphthol.

By heating the mixture of 2-methoxy-6-propionyl-naphthalene (5 g.) and hydrobromic acid (15 c.c. of 48%) in acetic acid (40 c.c.) for four hours was obtained a brownish product which was purified through alkali and crystallised from alcohol in yellowish plates, m.p. 150–51° C. (yield 75%). Its alcoholic solution did not give any colouration with ferric chloride. (Found: C, 78.1; H, 6.2; $C_{13}H_{12}O_2$ requires C, 78.0; H, 6.0 per cent.)

The *p*-nitrophenylhydrazone of 6-propionyl-2-naphthol crystallised from alcohol in deep-red needles, m.p. 225–26° C. (Found: N, 12.3; $C_{19}H_{17}N_3O_3$ requires N, 12.5 per cent.)

6-Propyl-2-naphthol.—The mixture of the hydrochloric acid (35 c.c.), 6-propionyl-2-naphthol (1 g.) and amalgamated zinc (5 g.) was heated for six hours. The product was purified through alkali and crystallised from alcohol in white lustrous needles, m.p. 120–21° C. (Found: C, 83.9; H, 7.5; $C_{13}H_{14}O$ requires C, 83.8; H, 7.6 per cent.)

Condensation of β -naphthyl methyl ether with butyryl chloride and preparation of 2-methoxy-6-butyryl-naphthalene.

Condensation of β -naphthyl methyl ether (15 g.) with butyryl chloride (9 c.c.) in presence of anhydrous zinc chloride (13 g.) in nitrobenzene solution (70 c.c.) gave 2-methoxy-6-butyryl-naphthalene which crystallised from alcohol in white, lustrous flakes, m.p. 92–93° C. (yield 60%). (Found: C, 78.8; H, 7.1; $C_{15}H_{16}O_2$ requires C, 78.9; H, 7.1 per cent.)

The *p*-nitrophenyl hydrazone of 2-methoxy-6-butyryl-naphthalene crystallised from alcohol in reddish-brown plates, m.p. 200.01° C. (Found N, 11.5; $C_{21}H_{21}O_3N_3$ requires N, 11.6 per cent.)

The Clemmensen Reduction of 2-methoxy-6-butyryl-naphthalene (1 g.) with zinc amalgam (5 g.) and hydrochloric acid (35 c.c.) gave 2-methoxy-6-butyl-naphthalene which crystallised from alcohol in white, shining flakes, m.p. 52–53° C. (Found: C, 84.2; H, 8.3; $C_{15}H_{18}O$ requires C, 84.1; H, 8.5 per cent.)

The demethylation of 2-methoxy-6-butyryl-naphthalene (5 gm.) with hydrobromic acid (10 c.c. 48%) in glacial acetic acid (40 c.c.) gave 6-butyryl-2-naphthol which was purified through alkali and crystallised from alcohol in white, shining small needles, m.p. 155–56° C. (yield 75%). Its alcoholic

solution did not give any colouration with ferric chloride. (Found: C, 78.4; H, 6.4; $C_{14}H_{14}O_2$ requires C, 78.5; H, 6.6 per cent.)

The *p*-nitrophenyl hydrazone of 6-butyryl-2-naphthol crystallised from alcohol in deep-red shining needles m.p. 215–16° C. (Found: N, 12.1; $C_{20}H_{19}O_3N_3$ requires N, 12.0 per cent.)

6-Butyl-2-naphthol was obtained by reduction of 6-butyryl-2-naphthol (1 gm.) with zinc amalgam (5 gm.) and hydrochloric acid (35 c.c.). The product was crystallised from alcohol in white shining flakes, m.p. 97–98° C. (Found: C, 84.1; H, 8.3; $C_{14}H_{16}O$ requires C, 84.0; H, 8.1 per cent.)

Condensation of β -naphthyl methyl ether with benzoyl chloride and preparation of 2-methoxy-6-benzoyl-naphthalene

The mixture of β -naphthyl ether (15 g.), anhydrous zinc chloride (12 g.) and benzoyl chloride (14 c.c.) in nitrobenzene solution (70 c.c.) was kept for 48 hours and then steam-distilled. The product was crystallised from alcohol in yellowish needles, m.p. 120–21° C. (yield 75%). (Found: C, 82.5; H, 5.3; $C_{18}H_{14}O_2$ requires C, 82.4; H, 5.4 per cent.)

The *p*-nitrophenyl hydrazone of 2-methoxy-6-benzoyl-naphthalene crystallised from alcohol in reddish, shining flakes, m.p. 180–81° C. (Found: N, 10.5; $C_{24}H_{19}O_3N_3$ requires N, 10.6 per cent.)

2-Methoxy-6-benzoyl-naphthalene was prepared by the reaction of 2-methoxy-6-benzoyl-naphthalene (1 g.) with zinc amalgam (5 gm.) and hydrochloric acid (35 c.c.) and crystallised from alcohol in white, shining flakes, m.p. 81–82° C. (Found: C, 87.1; H, 6.3; $C_{18}H_{16}O$ requires C, 87.1; H, 6.5 per cent.)

Demethylation of 2-methoxy-6-benzoyl-naphthalene (8 g.) was carried out with hydrobromic acid (20 c.c.) in acetic acid (40 c.c.). The crude 6-benzoyl-2-naphthol was purified through alkali and crystallised from alcohol in yellowish needles, m.p. 145–46° C. (yield 80%). It was freely soluble in all organic solvents but less so in petroleum ether. Its alcoholic solution gave no colouration with ferric chloride. (Found: C, 82.4; H, 4.8; $C_{17}H_{12}O_2$ requires C, 82.2; H, 4.9 per cent.)

The *p*-nitrophenyl hydrazone of 6-benzoyl-2-naphthol crystallised from alcohol in reddish-brown, small needles, m.p. 200–01° C. (Found: N, 10.9; $C_{23}H_{17}O_3N_3$ requires N, 11.0 per cent.)

6-Benzyl-2-naphthol was prepared by reducing 6-benzoyl-2-naphthol (1 g.) with zinc amalgam (5 g.) and hydrochloric acid (30 c.c.) and

crystallised from alcohol in white, crystalline flakes, m.p. 112–13°C. (Found: C, 87.3; H, 6.2; $C_{17}H_{14}O$ requires C, 87.1; H, 6.0 per cent.)

Condensation of β -naphthyl methyl ether with stearyl chloride and preparation of 2-methoxy-6-stearyl-naphthalene

Stearyl chloride (30 g.) in nitrobenzene solution (30 c.c.) was slowly added to mixture of nitrobenzene (50 c.c.), powdered anhydrous zinc chloride (13 g.) and β -naphthyl methyl ether (16 g.). The mixture was kept for 48 hours at room temperature and decomposed in cold by dilute hydrochloric acid. The nitrobenzene was steam-distilled and the solid was crystallised from alcohol in white shining flakes, m.p. 116–17°C. (yield 75%). It was soluble in usual organic solvents and its alcoholic solution gave no colouration with ferric chloride. (Found: C, 82.1; H, 10.4; $C_{29}H_{44}O_2$ requires C, 82.0; H, 10.5 per cent.)

The *p*-nitrophenyl hydrazone of 2-methoxy-6-stearyl-naphthalene crystallised from alcohol in reddish shining flakes, m.p. 235–36°C. (Found: N, 7.3; $C_{35}H_{49}O_3N_3$ requires N, 7.5 per cent.)

Clemmensen reduction of 2-methoxy-6-stearyl-naphthalene and the formation of 2-methoxy-6-octadecyl-naphthalene

A mixture of 2-methoxy 6-stearyl-naphthalene (1 g.), zinc amalgam (5 g.) and hydrochloric acid (40 c.c.) was heated on sand-bath under reflux for eight hours. The product on crystallisation from alcohol gave white, shining plates, m.p. 60–61°C. (Found: C, 84.6; H, 11.2; $C_{29}H_{46}O$ requires C, 84.8; H, 11.3 per cent.)

Demethylation of 2-methoxy-6-stearyl-naphthalene by hydrobromic acid hydroiodic acid and anhydrous aluminium chloride

A solution of 2-methoxy-6-stearyl naphthalene (5 g.) and hydrobromic acid (20 c.c. of 48%) in glacial acetic acid (40 c.c.) was heated on sand-bath for five hours and then poured in water. The solid crystallised from alcohol in white, shining plates and was identified as stearic acid by a mixed m.p. 68–69°C. On keeping the 2-methoxy-6-stearyl-naphthalene with hydrobromic acid for 48 hours at room temperature with slight warming a mixture of stearic acid and the original substance was obtained. Even on keeping the methoxy ketone with hydrobromic acid for 12 hours, the demethylation did not succeed.

Demethylation of 2-methoxy-6-stearyl-naphthalene with hydroiodic acid in acetic acid gave only the stearic acid.

Lastly the demethylation was tried with anhydrous aluminium chloride in dry benzene but this also gave the stearic acid.

2-Methoxy-6-palmityl-naphthalene the condensation of β -naphthyl methyl ether (16 g.) with palmityl chloride (28 g.) in presence of zinc chloride (14 g.) in nitrobenzene solution (85 c.c.) gave 2-methoxy-6-palmityl naphthalene which crystallised from alcohol in white, shining plates, m.p. 105–06° C. (yield 65%). It was soluble in nearly all organic solvents and its alcoholic solution gave no colouration with ferric chloride. (Found: C, 81.7; H, 10.1; $C_{27}H_{43}O_2$ requires C, 81.8; H, 10.2 per cent.)

The p-nitrophenyl hydrazone of 2-methoxy-6-palmityl-naphthalene crystallised from alcohol in reddish, small flakes, m.p. 225–26° C. (Found: N, 7.8; $C_{33}H_{45}O_3N_3$ requires N, 7.9 per cent.)

2-Methoxy-6-hexadecyl-naphthalene was prepared by reducing 2-methoxy-6-palmityl naphthalene by zinc amalgam and the product was crystallised from alcohol in white, shining, soft needles, m.p. 54–55° C. (Found: C, 84.9; H, 11.0; $C_{27}H_{42}O$ requires C, 84.7; H, 11.1 per cent.)

Demethylation of 2-methoxy-6-palmityl naphthalene with HBr, HI or anhydrous aluminium chloride did not succeed but the palmityl group was split off.

2-Methoxy-6-lauryl-naphthalene was prepared by condensing lauryl chloride (28 g.) in nitrobenzene (35 c.c.) with β -naphthyl methyl ether (16 g.) and zinc chloride (14 g.) in nitrobenzene (50 c.c.). The reaction was kept for 48 hours at room temperature and steam-distilled. The solid crystallised from alcohol in white, lustrous flakes, m.p. 97–98° C. (yield 65%). (Found: C, 81.2; H, 9.4; $C_{23}H_{32}O_2$ requires C, 81.1; H, 9.5 per cent.)

The p-nitrophenyl hydrazone of 2-methoxy-6-lauryl-naphthalene crystallised from hot alcohol in reddish, small plates, m.p. 220–21° C. (Found: N, 8.6; $C_{29}H_{37}O_3N_3$ requires N, 8.8 per cent.)

2-Methoxy-6-dodecyl-naphthalene.—The Clemmensen reduction of 2-methoxy-6-lauryl-naphthalene with zinc amalgam and hydrochloric acid gave the reduced product which crystallised from alcohol in white shining plates, m.p. 47–48° C. (Found: C, 84.6; H, 10.4; $C_{23}H_{34}O$ requires C, 84.6; H, 10.5 per cent.)

Demethylation of 2-methoxy-6-lauryl naphthalene with HBr, HI or anhydrous aluminium chloride did not proceed but the lauryl group was split off.

SUMMARY

Some 6-acyl-2-naphthols such as 6-acetyl; 6-propionyl-6-butyryl; and 6-benzoyl-2-naphthols have been prepared by the demethylation 2-methoxy-6-acetyl; 2-methoxy-6-propionyl-; 2-methoxy-6-butyryl and 2-methoxy-6-benzoyl-naphthalenes. In the case of 2-methoxy-6-stearyl-; 2-methoxy-6-palmityl and 2-methoxy-6-lauryl-naphthalenes, an attempt was made to demethylate them to get the hydroxy ketones, but the stearyl, palmityl and lauryl groups were split off. The properties of all the methoxy- and hydroxy-ketones have been studied.

We have great pleasure in expressing our thanks to Rev. Father A. M. Coyne, S.J., for the provision of the facilities.

REFERENCES

1. Desai and Waravdekar .. *Proc. Acad. Ind. Sci.*, 1946.
2. Haworth and Sheldrick .. *J.*, 1934, 864.