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Birch Reduction of 2-Methoxy-1-naphthoic Acids

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Abstract

The reduction of 2-methoxy-1-naphthoic acids (1) with 2·4 equiv. of sodium in liquid ammonia leads to the formation of the 1,4-dihydro compounds (2). These reduction products on esterification with diazomethane followed by hydrolysis with dilute mineral acids yield methyl 2-oxotetralin-1-carboxylates (5). This constitutes a satisfactory general method of synthesis of (5).

Introduction

Some methyl 2-oxotetralin-1-carboxylates (5) were required for synthesis.[1] Pelletier[2,3] has shown that carboxymethylation of 5-methoxytetral-2-one occurs in the 3-position, not in the 1-position. Birch reduction of 1-naphthoic acid gave[4] the 1,4-dihydro compound, and of 1-methoxy-2-naphthoic acid, with loss of methoxyl group, the 1,2,3,4-tetrahydro- or 1,2,3,4,5,8-hexahydro-2-naphthoic acid.[5] Under similar conditions 2-methoxy-1-naphthoic acid gave 1,4,5,8-tetrahydro-2-methoxy-1-naphthoic acid.[5] Extent of reduction of an alkoxynaphthalene depends on conditions,[6,7] notably the ratio of alkali metal employed. Carefully controlled conditions might be expected to convert 2-alkoxy-1-naphthoic acids into the 1,4-dihydro derivatives as sources of (5) after acid hydrolysis.

Discussion and Results

The optimum condition for reduction of 1-naphthoic acids to dihydro compounds was found to involve 2·4 equiv. of sodium. The presence of the electron-attracting carboxylic group[8] has a powerful orientating influence on the course of the reduction. If the aromatic ring of (2) were to be reduced the loss in resonance energy involved will be 151 kJ compared to only 105 kJ for the first ring. The fact that the intermediate carbanion (6) must be considerably stable, owing to the high degree of conjugation,

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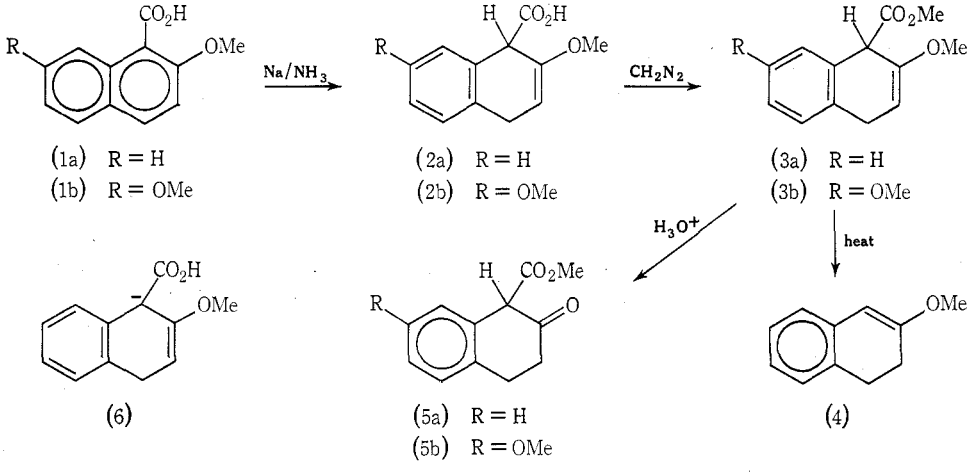
[3] Pelletier, S. W., Chapel, R. L., Parthasarathy, P. C., and Lewin, N., *J. Org. Chem.*, 1966, **31**, 1747.
[4] Birch, A. J., *J. Chem. Soc.*, 1944, 430.
[5] Eliel, E. L., and Hoover, T. E., *J. Org. Chem.*, 1959, **24**, 938.
[6] Marshall, J. A., and Anderson, N. H., *J. Org. Chem.*, 1965, **30**, 1292.
[7] Stork, G., and Schulenberg, J. W., *J. Amer. Chem. Soc.*, 1956, **78**, 250.
[8] Birch, A. J., Murray, A. R., and Smith, H., *J. Chem. Soc.*, 1951, 1945.

makes the decrease in resonance stabilization in going from the naphthalene system to the dihydro compound much less than 105 kJ. Hence the reduction of the second ring becomes much more difficult than that of the first. Probably the longer time of equilibration employed in the present experiments helps the equilibrium to be shifted in favour of the more stable species like (6) which have little tendency for further reduction. However, large quantities of sodium[5] would reduce both the rings.



To protect the carboxylic group, the dihydro acid (2a) was esterified with diazomethane. In the purification of the enol-ether ester (3a) by vacuum distillation 3,4-dihydro-2-methoxynaphthalene (4) was obtained as a low-boiling fraction (25%). This might have arisen by the pyrolytic decomposition of the ester group of (3a) followed by rearrangement. The acid hydrolysis of (3a) resulted in the β-keto ester (5a) in an overall yield of 71% from the naphthoic acid (1a). In a similar way (5b) was made from (1b).

The use of compounds like (5a) and (5b) in the total synthesis of natural products will be discussed in a future communication.

Experimental

2-Methoxy-1-naphthoic acid was obtained by the reaction of 2-hydroxy-1-naphthoic acid with methyl sulphate and sodium hydroxide followed by basic hydrolysis of the resultant ester, m.p. 178–179° (lit.[9] 176–177°).

Methyl 1,4-Dihydro-2-methoxynaphthalene-1-carboxylate (3a)

To a well-stirred solution of 2·02 g of (1a) in an anhydrous solvent mixture of ethanol (8 ml), tetrahydrofuran (50 ml) and liquid ammonia (200–250 ml) was added clean metallic sodium (552 mg) in small pieces at a time. The reaction mixture was kept overnight in an atmosphere of nitrogen. The residue was dissolved in water (200 ml), acidified to pH 5 with sodium dihydrogen phosphate solution and extracted with ether to yield 2·1 g of the dihydronaphthoic acid (2a).

An ethereal solution of this acid (2a) was esterified with an excess of a solution of diazomethane in ether. The product was fractionated by vacuum distillation. The first fraction (0·5 g), b.p. 90–95° (0·6 mm), was 3,4-dihydro-2-methoxynaphthalene (4). The second fraction (1·5 g), b.p. 125–130°/0·6 mm, was (3a): i.r. ($CHCl_3$) 1668, 1725 (ester carbonyl) cm^{-1}; λ_{max} (MeOH) 264 (ε

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1090), 272 nm (1190); n.m.r. δ ($CDCl_3$) 3·38, s, 6H, OCH_3 and CO_2CH_3; 3·4, m, 2H, C4–H; 4·27, t, $J_{1,4}$ 3·5 Hz, 1H, C1–H; 4·81, m, $J_{3,4}$ 4·5 Hz, $J_{3,4}$ 3·5 Hz, 1H, C3–H; 7, m, aromatic H.

Methyl 2-Oxotetralin-1-carboxylate (5a)

A solution of 1·5 g of (3a) in acetone (25 ml) and 3N hydrochloric acid (5 ml) was refluxed for 15 min in an atmosphere of nitrogen. The reaction mixture was cooled to room temperature, diluted with 100 ml of water and extracted with ether. The ether solution on usual workup and vacuum distillation yielded 1·45 g of the keto ester (5a), b.p. 115–120°/0·15 mm (lit.[10] b.p. 126°/0·6 mm); i.r. ($CHCl_3$) 1630, 1719 cm^{-1} (enolic β-keto ester); λ_{max} (MeOH): 225 (ε 15460), 275 (16300), 302 nm (8700); n.m.r. δ ($CDCl_3$) 2·4, m, 4H, C3–H and C4–H, A_2B_2 system; 3·64, s, 3H, CO_2CH_3; 6·92, m, 3H, C5–H, C6–H and C7–H; 7·45, m, 1H, C8–H; 12·3, s, 1H, C2 enolic H.

Methyl 1,4-Dihydro-2,7-dimethoxynaphthalene-1-carboxylate (3b)

The Birch reduction of 2,7-dimethoxy-1-naphthoic acid (1b) (4·64 g) was carried out by the procedure adopted in the reduction of (1a) described earlier. The dihydro compound (2b) thus obtained was esterified with diazomethane. The crude product on distillation under reduced pressure afforded 3·72 g (73·75%) of (3b), b.p. 140–150° (0·6 mm). Three recrystallizations from ether yielded an analytical sample, m.p. 91–92°; i.r. ($CHCl_3$) 1610, 1680, 1725 cm^{-1}; λ_{max} (MeOH) 278 (ε 2400), 287 nm (2200); n.m.r. δ ($CDCl_3$) 3·49, s, 3H, C7–OCH_3; 3·51, m, 2H, C4–H; 3·55, s, 3H, C2–OCH_3; 3·63, s, 3H, CO_2CH_3; 4·16, t, $J_{1,4}$ 3·5 Hz, 1H, C1–H; 4·87, q, $J_{3,4}$ 5 Hz, $J_{3,4}$ 3·5 Hz, 1H, C3–H; 6·63, d, $J_{5,6}$ 8 Hz, 1H, C6–H; 6·67, s, 1H, C8–H; 6·93, d, $J_{5,6}$ 8 Hz, 1H, C5–H.

Methyl 7-Methoxy-2-oxotetralin-1-carboxylate (5b)

The hydrolysis of (3b) was effected under mild acid conditions as in the preparation of (5a). The reaction proceeded in 66·3% yield to give the keto ester (5b), b.p. 130–140°/0·15 mm; i.r. ($CHCl_3$) 1600, 1635, 1715 cm^{-1}; λ_{max} (MeOH) 217 (ε 29000), 232 (20800), 258 (13900), 270 (15200), 297 nm (14300); n.m.r. δ ($CDCl_3$) 2·36, m, 4H, C3–H and C4–H, A_2B_2 system; 3·51, s, 3H, OCH_3; 3·63, s, 3H, CO_2CH_3; 6·33, q, $J_{5,6}$ 8 Hz, $J_{6,8}$ 2·5 Hz, 1H, C6–H; 6·74, d, $J_{5,6}$ 8 Hz, 1H, C5–H; 7·1, d, $J_{6,8}$ 2·5 Hz, 1H, C8–H (Found: C, 66·6; H, 6·1. Calc. for $C_{13}H_{14}O_4$: C, 66·7; H, 6·0%).

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