

Reductive Methylation of 2-Naphthoic Acids

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Abstract

The successive action of lithium (2.5 equiv.) and methyl iodide on 2-naphthoic acids in ammonia gives 2-methyl-1,2-dihydro-2-naphthoic acids in fair yield.

As a continuation of our interest in the metal-ammonia reductions and reductive alkylations of carboxylic acids we now report our results on some 2-naphthoic acid derivatives.

Metal-ammonia reductions¹⁻⁵ and reductive alkylations^{2,5,6} of 1-naphthoic acids are well documented. We readily confirmed the loss of less than 5% methoxyl (g.l.c. analysis of the product) from 2-methoxy-1-naphthoic acid on reductive alkylation,² a surprising result in view of the 70% loss of OMe with 2-methoxybenzoic acid under these conditions.⁷ On the other hand 4-methoxy-1-naphthoic acid was shown to lose OMe completely. A significant proportion of the dialkylated product (1) (c. 30%), a product not observed with 1-naphthoic acid itself, appeared in this case; its formation is probably enhanced by the methoxide ion released into solution.

2-Naphthoic acids have been little examined^{8,9} and not under controlled conditions which might lead to isolation of the initially formed dihydro products. Compounds of this type have been reported with sodium amalgam in an indirect electroreduction process.¹⁰ We reasoned that, while in most reductions of aromatic acid derivatives the initial protonation is *para* to the carboxylate anion, in this case the preservation of one aromatic ring might favour *ortho* protonation at C 1. Further, the protonated product (2) should be protected by its charge from further reduction and be readily intercepted

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² Bachi, M. D., Epstein, J. W., Herzberg-Minzly, Y., and Loewenthal, H. J. E., *J. Org. Chem.*, 1969, **34**, 126.

³ Oommen, P. K., *Aust. J. Chem.*, 1975, **28**, 2095; 1976, **29**, 2087.

⁴ Marshall, J. L., Faehl, L. G., Ihrig, A. M., and Barfield, M., *J. Am. Chem. Soc.*, 1976, **98**, 3406, and references cited therein.

⁵ Grossel, M. C., and Hayward, R. C., *J. Chem. Soc., Perkin Trans. 2*, 1976, 851.

⁶ Slobbe, J., *J. Chem. Soc., Chem. Commun.*, 1977, 82.

⁷ Birch, A. J., and Slobbe, J., *Aust. J. Chem.*, 1977, **30**, 1045.

⁸ Eliel, E. L., and Hoover, T. E., *J. Org. Chem.*, 1959, **24**, 938.

⁹ Mander, L. N., Prager, R. H., and Turner, J. V., *Aust. J. Chem.*, 1974, **27**, 2645.

¹⁰ Przhivalgovskaya, N. M., Yares'ko, N. S., and Belov, V. N., *Zh. Org. Khim.*, 1968, **4**, 872, and references cited therein.

by an electrophile. This was verified by treating 2-naphthoic acid in the usual way with lithium (2.5 equiv.) and quenching with methyl iodide. The desired 2-methyl derivative (3) was obtained as the major product (Table 1) together with some of the further reduced (4). Several methoxy-substituted acids were also examined (Table 1). The products were easily separated (preparative g.l.c.) and characterized as their methyl esters.

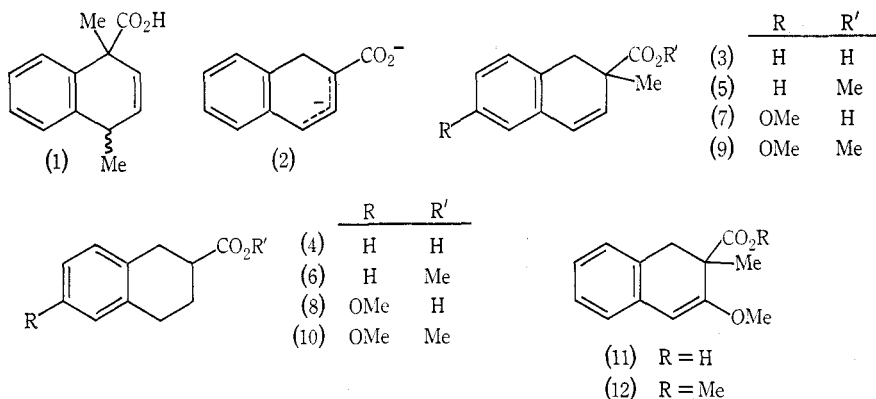


Table 1. Reductive methylation of 2-naphthoic acids

Substituent	Products ^A	Starting material	Total crude yield (%)
—	(3) (82%), (4) (18%)	trace	90
6-Methoxy	(7) (78%), (8) (22%)	trace	90
3-Methoxy	(11) (67%), (4) (20%)	10%	85
1-Methoxy	(3) (40%), (4) (16%), 2-naphthoic acid (9%)	35%	90

^A As determined by g.l.c. ratios of the methyl esters.

The further reduction products are readily explained by the partial protonation of (2) by ammonia (cf. dienic acids¹¹); the resulting styrene derivative would be expected to reduce rapidly. With 2-naphthoic acid, the alternative workup with ammonium chloride consistently gave a larger proportion of this overreduced compound (4) as well as some starting material. Of particular note (Table 1) is the total loss of 1-OMe in contrast to retention of 3-OMe. This highlights the uncertainty in trying to predict the loss of *o*-OMe. The factors governing this loss, a problem in a few cases only,^{7,12} are not well understood. In this case loss would be facilitated by the initial *ortho* protonation at the benzylic carbon. We feel protonation at this position is consistent with the results and favour it over the alternative mechanism of *para* protonation followed by isomerization.⁸

Experimental

The general details are described elsewhere.¹³ Gas-liquid chromatography was performed on a Pye 104 chromatograph; a glass column (8 ft by 0.375 in. o.d.) packed with 20% Apiezon L on

¹¹ Birch, A. J., and Slobbe, J., *Aust. J. Chem.*, 1976, **29**, 2737.

¹² House, H. O., Strickland, R. C., and Zaiko, E. J., *J. Org. Chem.*, 1976, **41**, 2401.

¹³ Slobbe, J., *Aust. J. Chem.*, 1976, **29**, 2553.

60/80 Chromosorb W was used. Reductive methylation procedures were as previously described;^{7,11} however, no more than 2.5 equiv. of lithium were used to give a maroon-to-brown rather than a blue solution. Known products were identified by physical and/or spectral data. Additional data are as follows.

Methyl 2-methyl-1,2-dihydro-2-naphthoate (5), b.p. 95–100°/1 mm (Found: C, 77.1; H, 7.1. $C_{13}H_{14}O_2$ requires C, 77.2; H, 7.0%). ν_{\max} 1730 cm^{-1} (methyl ester). N.m.r. δ ($CDCl_3$) 1.28, s, 3H, CH_3 ; 2.80, 3.28, ABq, J 16 Hz, 2H, C1–H₂; 3.65, s, 3H, CO_2CH_3 ; 5.95, 6.39, ABq, J 9 Hz, 2H, vinyl; 7.02, br s, 4H, aromatic. A small portion was hydrolysed with 20% KOH in aq. MeOH and worked up to give 2-methyl-1,2-dihydro-2-naphthoic acid (3), m.p. 92–93°, from light petroleum (lit.¹⁴ 93°, from aq. alcohol).

Methyl 6-methoxy-2-methyl-1,2-dihydro-2-naphthoate (9), b.p. 100–105°/1 mm (Found: C, 72.4; H, 6.7. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%). ν_{\max} 1730 cm^{-1} (methyl ester). N.m.r. δ ($CDCl_3$) 1.27, s, 3H, CH_3 ; 2.68, 3.20, ABq, J 15 Hz, 2H, C1–H₂; 3.62, s, 3H, CO_2CH_3 or OCH_3 ; 3.68, s, 3H, CO_2CH_3 or OCH_3 ; 5.98, 6.35, ABq, J 9 Hz, 2H, vinyl.

Methyl 3-methoxy-2-methyl-1,2-dihydro-2-naphthoate (12), b.p. 100–105°/1 mm, m.p. 51–55° (Found: C, 72.5; H, 7.1. $C_{14}H_{16}O_3$ requires C, 72.4; H, 6.9%). N.m.r. δ ($CDCl_3$) 1.30, s, 3H, CH_3 ; 2.67, 3.38, ABq, J 15 Hz, 2H, C1–H₂; 3.55, s, 3H, CO_2CH_3 or OCH_3 ; 3.58, s, 3H, CO_2CH_3 or OCH_3 ; 5.43, s, 1H, vinyl; 6.82, br s, 4H, aromatic.

Acknowledgments

Dr L. N. Mander provided a generous sample of 6-methoxy-2-naphthoic acid. M. Henry and L. L. Welling are warmly thanked for technical assistance.

Manuscript received 3 October 1977

¹⁴ Des Abbayes, H., *Bull. Soc. Chim. Fr.*, 1970, 3667.