tassium hydroxide, the solution was then diluted with water, acidified and the precipitate thus formed extracted with sodium carbonate solution. The alkaline extract contained sodium benzoate, while the insoluble part was compound IIa, if the starting material was the acid Ia, or compound IIb, if one had started from the acid Ib. In some of the runs the reaction with peroxybenzoic acid was carried out in ether, but yields were very poor. In others, 0.5 g. of trichloroacetic acid were added to the chloroform solution for each gram of stilbene-2-carboxylic acid. Table II summarizes the results of several reactions conducted under different conditions. The yields were evaluated on the basis of accurate fractional crystallizations, and, in the case of inseparable mixtures, from melting-point diagrams. They should be accurate within ±5%.

(c) *With peroxyformic acid.* A suspension of 1 g. of the acid Ia in 10 ml. of 98% formic acid was treated with 0.5 ml. of 35% hydrogen peroxide and heated during 20 min. on a steam bath. After 6 hr. at room temperature, the formic acid was distilled off under reduced pressure, the residue was dissolved in ether, washed with sodium carbonate solution and dried over magnesium sulfate. After elimination of the ether and crystallization from benzene-ligroin, 0.45 g. of the lactone IIIa were obtained. The mother-liquor was evaporated to dryness and the residue refluxed for 5 min. with 10 ml. of 5% ethanolic potassium hydroxide, diluted with water and acidified with sulfuric acid: 0.3 g. of the lactone IIa separated out. The filtrate gave a formic acid containing distillate.

When the same reaction was carried out with 1 g. of the acid Ib, 0.30 g. of IIIb and, after saponification, 0.45 g. of IIb were obtained. The methyl ester of the acid Ia gave similarly IIIa (50% yield) and IIa (30%); the methyl ester of Ib yielded IIIb (40%) and IIb (40%).

Reactions of other unsaturated acids with peroxybenzoic acid. Table I summarizes the results obtained with other unsaturated acids, which were left with peroxybenzoic acid in chloroform at room temperature, until a starch-iodide test showed that the peroxyacid had disappeared. The products were isolated as described above and obtained pure after one crystallization from benzene or from a benzene-ligroin mixture.

Saponification of the lactones. A solution of 0.1 g. of each of the lactones in 2 ml. of methanol was treated with 2 ml. of 10% methanolic potassium hydroxide and left at room temperature until a clear solution was obtained upon dilution with water. The aqueous solution was acidified with concentrated hydrochloric acid and the precipitate was collected, or, if the lactone did not precipitate, it was extracted with ether. The following results were obtained: the lactones IIa and IIb, and all those of Table I, were recovered unchanged. The lactones IIIa and IIIb were transformed into those IIa and IIb, respectively. When 3-phenyl-3-(α-hydroxyethyl)-phthalide was refluxed for 15 min. with 10% ethanolic potassium hydroxide the solution became brown. Dilution with water produced some precipitate, which was extracted with ether. Acidification of the aqueous layer gave a solid, which, after crystallization from carbon tetrachloride, yielded needles, m.p. and mixed m.p. with 3-phenylphthalide[18] 115°.

3-Phenyl-4-chloro-3,4-dihydroisocoumarins (IVa and IVb). The lactone IIIa (0.3 g.) was treated with 2 ml. of thionyl chloride and refluxed for 10 min. The excess thionyl chloride was then evaporated under reduced pressure and the residue, after crystallization from benzene–petroleum ether, gave 0.1 g. of prisms, m.p. 108–110°, of IVa.[2]

The same reaction, starting from the lactone IIIb, led to the chlorolactone IVb, m.p. 146–147°.[2]

3-Benzoylphthalide. A solution of the lactone IIa (0.2 g.) in 5 ml. of glacial acetic acid was treated with 0.2 g. of chromium trioxide and heated for 30 min. on a steam bath. On cooling a precipitate separated out, which, after crystallization from ethanol, gave prisms, m.p. 148° (0.1 g.). This product did not depress the melting point of the compound prepared by the treatment of 2,3-diphenyl-1,4-diketo-1,2,3,4-tetrahydroisoquinoline with hydrochloric acid, which, according to Wanag and Walbe[4] should be 3-phenylisochroman-1,4-dione.

A solution of 0.5 g. of 3-benzoylphthalide in 30 ml. of glacial acetic acid was shaken with hydrogen in the presence of 0.3 g. of 5% palladium on charcoal, until the absorption of hydrogen stopped (1 hr.). After filtration and dilution with 200 ml. of water, the solution was extracted with ether, the ether extract was washed with sodium carbonate solution, dried over magnesium sulfate and evaporated. The residue, after crystallization from benzene-ligroin, gave 0,25 g. of IIa, m.p. 148–149°. When the reduction was carried out according to Wanag and Walbe,[2] with tin powder and hydrochloric acid in ethanol, the product was an acid, m.p. 162° with decomposition, whose melting-point was not depressed in a mixture with *o*-phenacylbenzoic acid.[5]

PISA, ITALY

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[18] F. Ullmann, *Ann.*, **291**, 17 (1896).

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Birch Reduction of 2-Naphthoic and of *ortho*-Methoxynaphthoic Acids

ERNEST L. ELIEL AND TROY E. HOOVER

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The Birch reduction of 2-naphthoic acid and its 1- and 3-methoxy derivative gives mainly 1,2,3,4-tetrahydro-2-naphthoic acid or 1,2,3,4,5,8-hexahydronaphthoic acid, depending on conditions and proportions of reagents. The methoxyl group, where present, is lost in these reductions. 2-Methoxy-1-naphthoic acid, on the other hand, gives mainly 2-methoxy-1,4,5,8-tetrahydro-1-naphthoic acid without loss of the methoxyl group.

In connection with another problem we were interested to find out whether an *o*-methoxybenzoic acid could be submitted to the Birch reduction[1] without loss of either the carboxyl or the methoxyl function. By "Birch reduction" is meant the reduction of an aromatic compound, usually to a 1,4-cyclohexadiene derivative, by means of an alkali metal–liquid ammonia–alcohol combination. The reaction was originally discovered by Wooster[2]

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[1] (a) A. J. Birch, *Quart. Revs.*, **4**, 69 (1950). (b) See also G. W. Watt, *Chem. Revs.*, **46**, 317 (1950).

[2] C. B. Wooster, U. S. Patent, **2,182,242** (Dec. 5, 1939); *Chem. Abstr.*, **34**, 1993 (1940); C. B. Wooster and K. L. Godfrey, *J. Am. Chem. Soc.*, **59**, 596 (1937).

but has been investigated particularly extensively by Birch in the period 1944–55; a very useful experimental modification was described by Wilds and Nelson in 1953.[3] The reduction of anisole[1a,3] is one of the classical examples of the Birch reduction and leads to 1-methoxy-1,4-cyclohexadiene, addition of hydrogen taking place at positions other than that occupied by the methoxyl substituent. The reduction of benzoic acids has also been studied;[4] in this case the hydrogen seeks the position occupied by the electron-withdrawing group and a 1-carboxy-2,5-cyclohexadiene results. The sodium salt of 1-naphthoic acid has similarly been reduced to 1,4-dihydro-1-naphthoic acid,[5] but the reduction is atypical in that no proton donor such as alcohol was present during the reduction.

A few examples of the reduction of methoxybenzoic acids are on record.[6] To the extent that one may generalize from these few instances, it seems that a methoxyl group *para*- to the carboxyl group is eliminated in the Birch reduction, but a methoxyl group *meta*- to the carboxyl group is preserved. Thus, veratric acid (3,4-dimethoxybenzoic acid) yields, after hydrolysis of the intermediate enol ether, cyclohexanone-3-carboxylic acid. Surprisingly enough, the same product is obtained from *m*-methoxybenzoic acid, indicating that the intermediate reduction product was a methoxytetrahydrobenzoic acid instead of the expected methoxydihydrobenzoic acid. 3,4,5-Trimethoxybenzoic acid upon reduction and hydrolysis yields 1,3-cyclohexanedione-5-carboxylic acid, presumably *via* 1,4-dihydro-3,5-dimethoxybenzoic acid; the *p*-methoxyl group is eliminated.

The significance of these observations is not, however, entirely unambiguous; for previously[7] it had been found that the central methoxyl group in pyrogallol trimethyl ether (1,2,3-trimethoxybenzene) is completely lost in the Birch reduction and one of the two methoxyl groups in veratrole (1,2-dimethoxybenzene) is partly lost. Thus, it is possible that similar loss of methoxyl functions in polymethoxybenzoic acids is caused mainly by the adjacent methoxyl group rather than by the carboxyl group in the *para*- position. The reduction of 5,6,7,8-tetrahydro-3-methoxy-2-naphthoic acid and 5,6,7,8-tetrahydro-1-methoxy-2-naphthoic acid[8] might have settled this question; but in the former case the (major) acidic product was not characterized, and in the latter case it was identified only tentatively as 2,5,6,7,8,10-hexahydro-2-naphthoic acid, since chromic acid oxidation of the crude acidic product gave 5,6,7,8-tetrahydro-2-naphthoic acid. The reduction of *o*- and *p*-methoxybenzoic acid has been mentioned without experimental details in several papers by Birch[6,8] as involving loss of the methoxyl function. Recently, however, the reduction of *o*-methoxybenzoic acid with sodium and methanol in liquid ammonia has been found[9] to give 2-methoxy-1,4-dihydrobenzoic acid (isolated in the form of derivatives) *without* loss of the methoxyl function.

The present work is concerned with the reduction of 2-naphthoic acid (I), 1-methoxy-2-naphthoic acid (II), 3-methoxy-2-naphthoic acid (III), and 2-methoxy-1-naphthoic acid (IV). The method of reduction was that of Wilds and Nelson,[3] using liquid ammonia with ether as a co-solvent, lithium as the reducing metal and anhydrous ethanol as the proton source. In most instances, 10 g.-atoms of lithium were employed per mole of compound to be reduced, but in some runs the amount of reducing agent was deliberately limited.

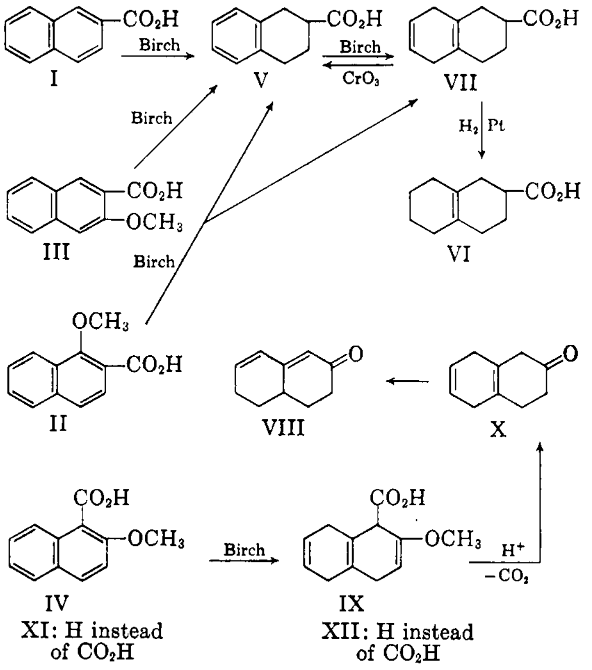

Figure 1

The reduction of 2-naphthoic acid (I) with an excess of lithium gave a hexahydro-2-naphthoic acid which was transparent in the ultraviolet region of the spectrum and did not react with maleic anhydride, indicating that the double bonds were nonconjugated. Oxidation of this material with chromium trioxide yielded 1,2,3,4-tetrahydro-2-naphthoic acid (V), suggesting that the two double bonds in the hexahydro acid were in the unsub-

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(3) A. Wilds and N. Nelson, *J. Am. Chem. Soc.*, **75**, 5360 (1953).

(4) Unpublished results by A. J. Birch quoted in ref. 1. The reduction of *o*-toluic acid to 1,4-dihydro-2-methylbenzoic acid has been described by A. J. Birch, *J. Chem. Soc.*, 1551 (1950).

(5) A. J. Birch, *J. Chem. Soc.*, 430 (1944).

(6) A. J. Birch, P. Hextall, and S. Sternhell, *Aust. J. Chem.*, **7**, 256 (1954).

(7) A. J. Birch, *J. Chem. Soc.*, 102 (1947).

(8) A. J. Birch, A. R. Murray, and H. Smith, *J. Chem. Soc.*, 1945 (1951).

(9) M. E. McEntee and A. R. Pinder, *J. Chem. Soc.*, 4419 (1957). This report appeared after the present work was completed.

stituted ring. Hydrogenation of the hexahydro acid with platinum in ethanol yielded an octahydro-2-naphthoic acid, characterized by its blue nitroso chloride derivative. Bedause of failue of this material to undergo further hydrogenation and because it formed a nitroso chloride rather than an oxime upon treatment with nitrosyl chloride,[5] it was assigned the structure 1,2,3,4,5,6,7,8-octahydro-2-naphthoic acid (VI) and the original reduction product is therefore 1,2,3,4,5,8-hexahydro-2-naphthoic acid (VII).

Reduction of 2-naphthoic acid with a limited amount of lithium (4 g.-atoms per mole) gave the known 1,2,3,4-tetrahydro-2-naphthoic acid (V). Compound V is probably an intermediate in the reduction of I to VII, since it could, in turn, be reduced to VII by means of the Birch procedure.

The reduction of 1-methoxy-2-naphthoic acid (II) with excess lithium gave, on one occasion, 1,2,3,4-tetrahydro-2-naphthoic acid (V) and on another 1,2,3,4,5,8-hexahydro-2-naphthoic acid (VII). Since the yields were not very high, it is possible that in both instances mixtures were obtained. It seems that here, again, the tetrahydroacid (V) is the primary product and is then further reduced to the hexahydroacid (VII).

From the reduction of 3-methoxy-2-naphthoic acid (III) with excess lithium, only the tetrahydroacid V was isolated, though in poor yield. The concomitant formation of some hexahydroacid VII is not excluded.

Whereas the reduction of the 1- and 3-methoxy-2-naphthoic acids thus proceeded with elimination of the methoxyl function, a different result was observed in the reaction of 2-methoxy-1-naphthoic acid (IV). Reduction of this material produced, in respectable yield, an acidic tetrahydro derivative which still contained the methoxyl function. The ultraviolet spectrum of this material indicated the absence of conjugated double bonds, although a moderately strong maximum was found at 209 mμ, possibly due to an enol ether function. The infrared spectrum showed a carbonyl band (carboxylic acid) at 5.90μ and a doublet at 6.01 and 6.11μ, as is to be expected for an enol ether.[3] Treatment of this material with 2,4-dinitrophenylhydrazine in acid produced, depending on conditions, either an unconjugated or a conjugated 2,4-dinitrophenylhydrazone. The melting point of the conjugated derivative agreed with that reported[7] for the 2,4-dinitrophenylhydrazone of 2-keto-2,3,4,5,6,10-hexahydronaphthalene (VIII). On this basis, the reduction-product was assigned structure IX, 1,4,5,8-tetrahydro-2-methoxy-1-naphthoic acid. The unconjugated dinitrophenylhydrazone is probably a derivative of 2-keto-1,2,3,4,5,8-hexahydronaphthalene (X), even though it melted slightly lower than the known derivative of this ketone,[8] possibly because of geometric isomerism.

The fact that the derivatives of 2-naphthoic acid (II and III) lose their methoxyl substituent upon Birch reduction whereas the derivative of 1-naphthoic acid (IV) does not is of interest. An explanation for the loss of methoxyl is suggested in Fig. 2. This explanation is based on the following known facts: (1) The metal (lithium) in the Birch reduction adds most readily to the carboxyl-substituted carbon and the carbon *para*- to its[6]; (2) if the primary reduction product is a methylenecyclohexadiene, it rearranges readily to a benzene derivative[10]; (3) a methoxyl group in a β-methoxystyrene and in a benzyl ether is readily hydrogenolyzed,[11] whereas other types of methoxyl groups evidently survive the conditions of the Birch reduction.

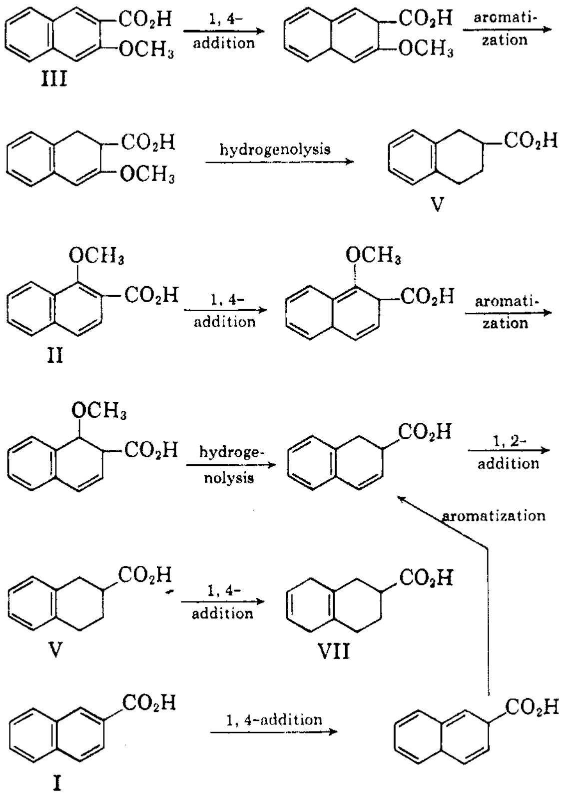

Figure 2

The reduction of 2-methoxy-1-naphthoic acid (IV) to the tetrahydroderivative IX is in close analogy with the known reduction of 2-naphthyl methyl ether (XI) to 1,4,5,8-tetrahydro-2-naphthyl methyl ether (XII).[8] In this case, as in the case of anisole[1a,3,5] and *o*-methoxybenzoic acid,[9] there is no obvious reason why the methoxy group should be

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(10) *Cf.* W. J. Bailey and J. Rosenberg, *J. Am. Chem. Soc.*, **77**, 73 (1955).

(11) R. Stoermer and Th. Biesenbach, *Ber.*, **38**, 1964 (1905) have described the hydrogenolysis of phenyl β-styryl ether, $C_6H_5OCH{=}CHC_6H_5$ to phenol and ethylbenzene by means of sodium and ethanol; and A. Klages, *Ber.*, **39**, 2587 (1906) has described the hydrogenolysis of benzyl alcohol to toluene under the same conditions; benzyl alkyl ethers would probably be reduced similarly.

lost. Upon treatment with acid, XII is known to give rise first to 1,2,3,4,5,8-hexahydro-2-ketonaphthalene (X) and then to 2,3,4,5,6,10-hexahydro-2-ketonaphthalene (VIII).[8]

Also shown in Fig. 2 is what we believe to be the sequence of events in the reduction of 2-naphthoic acid. 1,4-Addition in the carboxyl-substituted 2- and the 10-position gives 2,10-dihydro-2-naphthoic acid which rearomatizes itself to 1,2-dihydro-2-naphthoic acid. The latter then undergoes reduction at the styrene-type double bond[1b] to give the isolated product 1,2,3,4-tetrahydro-2-naphthoic acid (V).[12] Further 1,4-addition may then proceed in the second benzene ring to give the hexahydroacid VII. There are several analogies in the literature suggesting that such addition will avoid the alkyl-substituted positions, the most closely similar case being the reduction of tetralin to 1,2,3,4,5,8-hexahydronaphthalene.[5]

EXPERIMENTAL

Melting points are uncorrected. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill.

Reduction of 2-naphthoic acid. (I) (a) *Using excess lithium.* To a suspension of 8.6 g. (0.05 mole) of 2-naphthoic acid and 2.42 g. (0.35 g.-atom) of lithium wire in 200-ml. liquid ammonia and 40-ml. anhydrous ethyl ether contained in a three necked flask was added 25 ml. of anhydrous ethanol over a 20-min. period with good mechanical stirring. The ammonia was allowed to evaporate and more ether was added. The reaction mixture was cooled in an ice bath and 35 ml. water was added, followed by 120 ml. of $3N$ hydrochloric acid. The ether layer was separated and the acid layer extracted with two more portions of ether. The combined ether layers were washed with water and brine, dried over sodium sulfate, and concentrated until crystallization commenced. The solution was chilled and filtered to yield a first crop of crystals weighing 4.84 g., m.p. 77–79° and a second crop weighing 2.49 g., m.p. 67–73°. Two recrystallizations of the first crop from petroleum ether (b.p. 90–120°) returned 3.52 g. of 1,2,3,4,5,8-hexahydro-2-naphthoic acid (VII) melting at 80–81°. Two further recrystallizations from aqueous methanol raised the melting point to 81–82°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.18; H, 7.92; neut. equiv., 178.2. Found: C, 74.40; H, 8.06; neut. equiv., 178.6.

The ultraviolet spectrum of this material showed only a very low maximum at 273 mμ (ethanol), $\epsilon = 15$. The substance was recovered from an attempted reaction with maleic anhydride.

Further material was recovered from the second crop. A second reduction produced essentially the same result.

(b) *Using four equivalents of lithium.* This reduction was carried out using 0.34 g. (0.002 mole) of 2-naphthoic acid, 7 ml. ether, 25 ml. ammonia, 0.06 g. (0.008 g.-atom) lithium and enough anhydrous ethanol to decolorize the solution. The isolation procedure was as described above and there was obtained 0.24 g. of product which, after recrystallization from petroleum ether (b.p. 60–65°) weighed 0.11 g. and melted at 95.5–96.5°. This material was 1,2,3,4-tetrahydro-2-naphthoic acid (V) since its melting point was undepressed by admixture of an authentic sample of V kindly made available by Professor Melvin S. Newman of Ohio State University.

Reduction of 1,2,3,4-tetrahydro-2-naphthoic acid (V). This reduction was carried out as described for 2-naphthoic acid using 0.60 g. (0.0033 mole) of V, 10 ml. of anhydrous ether, 50 ml. of liquid ammonia, 0.21 g. (0.03 g.-atom) of lithium, and sufficient ethanol to produce decolorization. The residue of this reaction, worked up as described before, weighed 0.53 g. Two recrystallizations from petroleum ether (b.p 60–65°) returned 0.20 g. of 1,2,3,4,5,8-hexahydro-2-naphthoic acid (VII), m.p. 82–83° undepressed by admixture of the analytical sample described earlier.

Chromic acid oxidation of 1,2,3,4,5,8-hexahydro-2-naphthoic acid (VII). A 1-g. sample (0.006 mole) of VII obtained in the Birch reduction of I was oxidized by means of 0.6 g. chromium trioxide in 5 ml. glacial acetic acid using the method of Birch.[5] After the exothermic reaction was over, the reaction mixture was diluted with 15 ml. of water and the solid product was collected and crystallized twice from aqueous ethanol to give 0.40 g. of 1,2,3,4-tetrahydro-2-naphthoic acid (V), m.p. 96–97°, undepressed by admixture of the authentic specimen described above

Catalytic hydrogenation of 1,2,3,4,5,8-hexahydro-2-naphthoic acid (VII). A 3.50-g. sample (0.0195 mole) of VII, m.p. 80–81° in 60 ml. anhydrous ethanol was hydrogenated for 8 hr. using 0.15 g. of platinum oxide as catalyst at an initial hydrogen pressure of 40 p.s.i. The catalyst was removed by filtration and the residue concentrated under reduced pressure to give 3.28 g. of a sticky, pleasant-smelling solid. Four recrystallizations from petroleum ether (b.p. 60–90°) returned 0.58 g. melting at 111.5–113°. Further recrystallization from aqueous methanol raised the melting point to 114–115°. The mixed melting point with a sample of the all-*cis*-decahydro-2-naphthoic acid, m.p. 105–106° (kindly provided by Professor William G. Dauben of the University of California) was depressed to 88–97°. The analysis of the material indicated it to be an octahydronaphthoic acid (VI).

Anal. Calcd. for $C_{11}H_{16}O_2$: C, 73.29; H, 8.95 Found: C, 73.53; H, 8.82.

Essentially the same result was obtained in a second hydrogenation extended to 40 hr., except that an increased amount of a nonacidic, pleasant-smelling oil was obtained. The acid is apparently partially esterified under the conditions of the reduction. When the hydrogenation was carried out in glacial acetic acid, the product (perhaps a mixture of diastereoisomeric decahydroacids?) did not crystallize.

Nitroso chloride of VI. To 9.5 g. of sodium nitrite in 37 ml. water was added dropwise, at 0°, a mixture of 2.5 ml. water, 3.4 ml. of concentrated sulfuric acid, and 11 g. of amyl alcohol. The aqueous layer was separated and the amyl nitrite washed with 2.5 ml. of sodium bicarbonate–sodium chloride solution. To a mixture of 0.154 g. (0.00085 mole) of VI and 0.25 g. (0.00175 mole) of amyl nitrite at $-15°$ was added 0.15 ml. of concentrated hydrochloric acid. A small amount of acetone was added and the solvent removed by vacuum evaporation. This left a blue solid, m.p 108–111°. Two recrystallizations from acetone returned 0.038 g. of blue material, m.p. 127–128°.

Anal. Calcd. for $C_{11}H_{16}ClNO_3$: C, 63.68; H, 6.60. Found: C, 63.76; H, 6.80.

1-Methoxy-2-naphthoic acid (II). This acid was prepared as previously described.[13] Distillation of the crude product (m.p. 115–118°) in a sausage flask through a short column at reduced pressure followed by crystallization from benzene gave material melting at 127.0–127.5° (lit.[13] 126–127°).

Reduction of 1-methoxy-2-naphthoic acid (II). (a) To a well stirred suspension of 9.26 g. (0.046 mole) of II in 20 ml. ether

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(12) The scheme proposed here is not unique. Alternative means of reducing the substituted ring in 2-naphthoic acid and its 1- and 3-methoxy derivatives, possibly without disturbing the aromatic character of the unsubstituted ring even temporarily, can be envisaged. The loss of the methoxyl function in II and III might involve β-elimination of methanol from the 1,2,3,4-tetrahydro acid corresponding to II and III.

(13) E. Bretscher, H. G. Rule, and J. Spence, *J. Chem. Soc.*, 1493 (1928).

and 225 ml. liquid ammonia was added 3.2 g. (0.46 g.-atom) of lithium wire over a 15-min. period. After stirring for 15 more min., another 50 ml. of liquid ammonia was added, followed by the slow addition of 22 ml. anhydrous ethanol. The product was isolated as described for the reduction of 2-naphthoic acid, using 105 ml. 4*N* hydrochloric acid in the extraction. The residue weighed 9.08 g. Recrystallization from aqueous ethanol returned 7.02 g., m.p. 71–76°. Recrystallization of 6 g. of this material from petroleum ether (b.p. 39–45°) and from aqueous ethanol gave a total of 2.25 g., m.p. 93–94° and 94–95°. This material did not depress the melting point of a sample of 1,2,3,4-tetrahydro-2-naphthoic acid (V) obtained in the reduction of 3-methoxy-2-naphthoic acid (see below). The literature[14] gives 96.0–96.6° as the melting point of V.

Anal Calcd. for $C_{11}H_{12}O_2$: C, 75.04; H, 6.87; neut. equiv., 176.2. Found: C, 75.32, 75.22; H, 6.89, 7.01; neut. equiv., 176.7.

The ultraviolet spectrum of this material, λ_{max} 266 mμ, ϵ_{max} 450; λ_{max} 273.5 mμ, ϵ_{max} 500 (ethanol) closely resembles the spectrum of tetralin.[15]

The amide of this product melted at 135–136° (lit.[14] 138.0–138.8°).

(b) The above experiment was repeated under apparently similar conditions, using 8.22 g. (0.041 mole) of II, 35 ml. ether, 225 ml. liquid ammonia, 2.8 g. (0.4 g.-atom) lithium wire, and 20 ml. anhydrous ethanol. The residue this time weighed 6.46 g. and melted at 56–74°. Three recrystallizations from petroleum ether (b.p. 60–65°) returned 3.08 g., m.p. 79–81°. Further recrystallizations from the same solvent failed to raise the melting point beyond 80.5–81°. This material was 1,2,3,4,5,8-hexahydro-2-naphthoic acid (VII), since it did not depress the melting point of the analytically pure sample of VII obtained in the reduction of 2-naphthoic acid (see above).

Reduction of 3-methoxy-2-naphthoic acid (III). A sample of 3.03 g. (0.015 mole) of III[16] was reduced using 20 ml. anhydrous ether, 100 ml. liquid ammonia, 1.04 g. (0.15 g.-atom) lithium wire, and *ca.* 3 ml. anhydrous ethanol. Acidification was effected using 18 ml. of 6*N* hydrochloric acid and the red, semisolid residue after ether extraction and concentration weighed 2.53 g. Recrystallization of this material from petroleum ether gave 0.475 g., m.p. 95–97°, 0 381 g., m.p. 89–91° and 0.117 g. (after sublimation), m.p. 87–91°. Further recrystallization from petroleum ether (b.p. 39–45°), petroleum ether–acetone and aqueous methanol gave material melting at 96.5–97.5° whose melting point was undepressed by admixture of an authentic sample of 1,2,3,4-tetrahydro-2-naphthoic acid (V) (see above), lit.[14] m.p. 96.0–96.6°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 75.04; H, 6.87. Found: C, 74.93; H, 6.92.

The reduction was repeated with essentially the same result.

The amide of V obtained in the above reduction melted at 137.5–138° (lit.[14] 138.0–138.8°) and, upon admixture, did not depress the melting point of an authentic sample kindly provided by Professor M. S. Newman.

2-Methoxy-1-naphthoic acid (IV). 2-Hydroxy-1-naphthaldehyde was methylated by the published procedure.[17] The product, m.p. 83.5–84.5° (lit.[17] 84°) was oxidized as previously described[18] to IV, m.p. 174–176° (lit.[18] 176–177°).

Reduction of 2-methoxy-1-naphthoic acid (IV). The reduction of 12.95 g. (0.064 mole) of IV in 90 ml. anhydrous ether and 300 ml. liquid ammonia was effected using 4.5 g. (0.65 g.-atom) lithium wire and sufficient anhydrous ethanol to decolorize the solution. The reaction and isolation were effected as described for 2-naphthoic acid, 125 ml. of 4*N* hydrochloric acid being employed in the acidification step.[19] The residue from the reaction weighed 11.4 g. Treatment of this material with diethyl ether and filtration gave 6.7 g. of 1,4,5,8-tetrahydro-2-methoxy-1-naphthoic acid (IX), m.p. 133.5–134.5°. Low-temperature crystallization from absolute ethanol did not change the melting point.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; neut. equiv., 206. Found: C, 70.09; H, 6.80; neut. equiv., 210.

The ultraviolet spectrum of the material showed a maximum in ethanol at 209 mμ, $\epsilon = 2000$ and was otherwise transparent except for a slight shoulder at 250–255 mμ.

A 208-mg. sample (0.001 mole) of the above acid dissolved in 100 ml. 95% ethanol was treated with 4 ml. of a 0.25*M* 2,4-dinitrophenylhydrazine reagent in phosphoric acid. After 40 hr. the precipitated derivative was collected; it weighed 289 mg., m.p. 138–141°. After two recrystallizations from ethanol–ethyl acetate the material melted at 162–163° (lit.[8] m.p. 171° for the dinitrophenylhydrazone of X).

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91. Found: C, 58.56; H, 4.99.

The material was orange in color and absorbed in the ultraviolet at 230 mμ, $\epsilon = 17,000$ and at 360 mμ, $\epsilon = 20,000$ (ethanol).

When the derivative was prepared from a 50-mg. sample of IX by heating with 2 ml. of a 2,4-dinitrophenylhydrazine–sulfuric acid solution in 95% ethanol,[20] the originally orange precipitate changed in color to red and melted at 189–191° (59 mg.). Two recrystallizations from ethanol–ethyl acetate raised the melting point to 202–204° (lit.[8] m.p. 202° for the dinitrophenylhydrazone of VIII).

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91. Found: C, 58.72; H, 4.99.

The material absorbed in the ultraviolet at 267 mμ, $\epsilon = 17,500$ and at 302 mμ, $\epsilon = 15,000$ and in the visible at 405 mμ, $\epsilon = 49,000$.

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