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## The Hydrogenation of Hydroxynaphthoic Acids<sup>1</sup>

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The hydrogenation of 6-hydroxy-1-naphthoic acid in alkaline solution with Raney nickel at 75° yielded 40% of 6-hydroxy-1,2,3,4-tetrahydro-1-naphthoic acid and 9% of the corresponding 5,6,7,8-tetrahydro isomer. When the hydrogenation was conducted at 150°, 6-hydroxydecahydro-1-naphthoic acid was obtained in a yield of 64% (44% of solid isomers and 20% of liquid isomers). The hydrogenation of 6-hydroxy-2-naphthoic acid under similar conditions at 100° yielded 40% of 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid and 10% of the corresponding 1,2,3,4-tetrahydro compound. At 150°, a sharp melting 6-hydroxydecahydro-2-naphthoic acid was isolated in 15% yield and a mixture of liquid perhydrohydroxy acids in 20%. The effect of acidity on the course of tetrahydrogenation also has been investigated.

The preparation of substituted decalins containing an oxygenated function in one ring and a reactive group in the other has been of interest in connection with the synthesis of completely alicyclic steroidal compounds. Toward this end the hydrogenation of appropriate naphthalene derivatives has been investigated as a convenient source of the corresponding decalins. All reported attempted reductions of such disubstituted naphthalenes, however, have been unsuccessful because of the difficulty of retaining the oxygenated function; in each case saturation of the naphthalene nucleus was accompanied by hydrogenolysis of this group. Robinson and Weygand<sup>3</sup> obtained 2-decalol from the platinum and acetic acid hydrogenation of 2,6-dihydroxynaphthalene. Similarly, when the hydroxyl groups were protected by methylation or acetylation, the corresponding 2-methoxy or 2-acetoxydecalin was formed. Also 5-methyl-6-methoxy-2-naphthoic acid suffered hydrogenolysis of the methoxyl group under the same conditions. Long and Burger<sup>4</sup> attempted to prepare 6-hydroxydecahydro-1-naphthoic acid, but the only product isolated was a mixture of decahydro-1-naphthoic acids. Price, Enos and Kaplan<sup>5</sup> also have studied the perhydrogenation of 6-hydroxy-1,2,3,4-tetrahydro-1-naphthoic acid under various conditions with platinum and Raney nickel catalysts, but again only hydrogenolysis products were obtained.

During the past few years, however, several methods have been reported by which the retention of a hydroxyl group in the hydrogenation of a phenolic compound can be achieved. For example, the following methods have been employed: (a) Raney nickel at high pressure in alkaline solution<sup>6</sup>; (b) platinum at atmospheric pressure in alkaline solution<sup>7</sup>; (c) pallidized strontium carbonate at high pressure in neutral solution.<sup>8</sup> The tetrahydrogenation and the perhydrogenation of 6-hydroxy-1-naphthoic acid (Ia) and 6-hydroxy-2-naphthoic acid (Ib) has now been accomplished by the reduction of the acid in aqueous alkaline solution over Raney nickel at 2500 p.s.i.<sup>9</sup>

The perhydrogenation of 6-hydroxy-1-naphthoic acid (Ia) was carried out under the above conditions at 150°. The product was separated into a crystalline mixture of isomeric 6-hydroxy-decahydro-1-naphthoic acids (IVa, 44%), m.p. 165–180°, and a sirupy acidic fraction. Attempts to obtain a pure isomer from the crystalline mixture were unsuccessful.

The sirupy mixture of acids was esterified and acetylated and the resulting product separated by distillation into its two principal components, the hydrogenolysis product ester (Va) and the perhy-

(6) P. Mastagli and M. Meteyer, *Compt. rend.*, **224**, 1779 (1947); L. F. Fieser, *et al.*, *THIS JOURNAL*, **70**, 3196 (1948); W. G. Dauben and R. E. Adams, *ibid.*, **70**, 1759 (1948); H. E. Ungnade and F. V. Morriss *ibid.*, **70**, 1898 (1948).

(7) R. H. Levin and J. H. Pendergrass, *ibid.*, **69**, 2436 (1947).

(8) R. H. Martin and R. Robinson, *J. Chem. Soc.*, 491 (1943).

(9) Since this work was completed and reported, H. E. Ungnade and F. V. Morriss (*THIS JOURNAL*, **72**, 2112 (1950)) have reported that these isomeric hydroxynaphthoic acids also can be hydrogenated successfully by reduction of their esters in the presence of a trace of alkali.

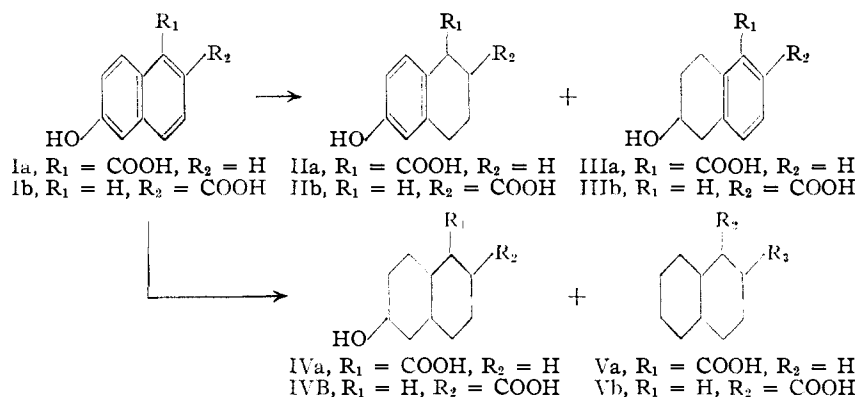
(1) This paper was presented in part before the Organic Division of the American Chemical Society, San Francisco Meeting, March, 1949.

(2) A.E.C. Predoctoral Fellow, 1948–1949.

(3) R. Robinson and E. Weygand, *J. Chem. Soc.*, 386 (1941).

(4) L. Long and A. Burger, *J. Org. Chem.*, **6**, 852 (1941).

(5) C. C. Price, H. I. Enos and W. Kaplan, *THIS JOURNAL*, **69**, 2261 (1947).



drogenated hydroxy acid ester (IVa). Liquid acid (IVa) recovered in this manner amounted to 20% based on the starting hydroxynaphthoic acid. The total yield of perhydro acid (IVa) thus was 64%. Although the yield of hydrogenolysis ester (Va) was only 3.7%, it is probable that the actual quantity was slightly greater than this.

The methyl 6-acetoxydecahydro-1-naphthoate so obtained was saponified and the resulting solution fractionally acidified. A crystalline 6-hydroxydecahydro-1-naphthoic acid was isolated in 15% yield (based on ester) which after recrystallization melts from 151.0–154.5°. Ungnade and Morriss<sup>9</sup> have reported two pure isomers melting 220.5–221.5° and 219–220°. Saponification of the hydrogenolysis ester likewise yielded a mixture of solid decahydro-1-naphthoic acids similar in properties to those reported by previous workers.<sup>4,5</sup>

When 6-hydroxy-2-naphthoic acid (Ib) was perhydrogenated under similar conditions, the product was a viscous sirup from which could be separated, in 15–20% yield, a crystalline 6-hydroxydecahydro-2-naphthoic acid (IVb), m.p. 196–197°. The residual sirup was separated by distillation and was found to consist of 6-hydroxydecahydro-2-naphthoic acid (IVb) and the hydrogenolysis product, decahydro-2-naphthoic acid (Vb). The yields were 14 and 19%, respectively. The total over-all yield of perhydro acid (IVb) thus was 35–40%. Ungnade and Morriss<sup>9</sup> have reported a product melting from 198–200° which appears to be identical with the solid perhydro acid obtained above.

An attempt was made to relate the solid hydroxy perhydro acid (IVb) with the known perhydro-2-naphthoic acids.<sup>10</sup> The removal of the hydroxyl group was accomplished by conversion to the corresponding bromo compound and subsequent removal of the halogen by hydrogenolysis by hydrogenation over Raney nickel in alcoholic sodium methoxide solution. The degradation product evidently consists of a mixture of decahydro-2-naphthoic acids since it failed to yield a single isomer on recrystallization.<sup>10</sup> Consequently, providing that no inversion of an asymmetric center occurred in the process of removal of the hydroxyl group, the crystalline hydroxy acid is also an isomeric mixture. In view of the work of Prelog and Zalan,<sup>11</sup> who obtained *l*-3-methyl-4-ethylhexane from *d*-1,5-dibromo-2,3-diethylpentane by hydro-

genolysis of the bromine atoms in methanolic sodium methoxide, it seems reasonable that the same procedure applied to 6-bromodecahydro-2-naphthoic acid would likewise cause no inversions at the various centers not concerned with this reaction. To establish this point conclusively, however, *cis*-2-bromodecalin, prepared from *cis*-2-decalol (m.p. 105°), was subjected to hydrogenation under the conditions de-

scribed above. Since pure *cis*-decalin was obtained, it is evident that the hydrogenolysis procedure does not affect the configuration of the ring juncture. On the other hand, in this series the effect of hydrogen bromide in acetic acid and of alcoholic sodium methoxide upon the configuration of the carboxyl group cannot be readily evaluated since not all of the four possible *dl*-acid are known. It has been found, however, that each of the two pure *cis*-decahydro-2-naphthoic acid are stable toward these reagents.<sup>12</sup> Consequently, it appears that the solid perhydro acid (IVb) is of doubtful stereochemical purity.

When 6-hydroxy-1-naphthoic acid (Ia) was hydrogenated under the same conditions but at only 75°, tetrahydrogenation occurred and the two isomeric 6-hydroxytetrahydro-1-naphthoic acids (IIa and IIIa) were isolated. The mixture was separated by fractional acidification of the alkaline reaction mixture. The 1,2,3,4-tetrahydro acid (IIa) was isolated in a yield of 40% and the isomeric 5,6,7,8-tetrahydro compound (IIIa) in a yield of only 8.7%. The ultraviolet spectra of these two acids, together with the spectra of several analogous compounds, are shown in Fig. 1. It can be seen that the spectrum of the 1,2,3,4-tetrahydro acid (IIa) compares favorably with that of *p*-hydroxyphenylacetic acid whereas the spectrum of the 5,6,7,8-isomer agrees closely with that of 5,6,7,8-tetrahydro-1-naphthoic acid.

When 6-hydroxy-2-naphthoic acid was hydrogenated at 100° and the same pressure as above, the two isomeric hydroxytetrahydro acids (IIb and IIIb) were also formed. These acids were separated by extraction of an ethereal solution of their esters with 5% sodium hydroxide. The phenolic material yielded 6-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid (IIb), m.p. 145–146° (8%), and the non-phenolic material, 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid (IIIb), m.p. 180–181° (39%). The 1,2,3,4-tetrahydro isomer was also obtained in 25% yield by the sodium and alcohol reduction of the starting acid. Methylation of acid (IIb) with dimethyl sulfate yielded a 6-methoxy derivative which was identical with that previously reported by Price and Kaplan.<sup>13</sup> The ultraviolet spectra (Fig. 2) of the two hydroxytetrahydro acids show the expected bands as compared with *ar*-2-tetralol and 5,6,7,8-tetrahydro-2-naphthoic acid.

(10) G. Tsatsas, *Ann. chim.*, **19**, 217 (1944).

(11) V. Prelog and E. Zalan, *Helv. Chim. Acta.*, **27**, 535 (1944).

(12) W. G. Dauben and E. Hoerger, unpublished results.

(13) C. C. Price and W. Kaplan, *This Journal*, **66**, 477 (1944).

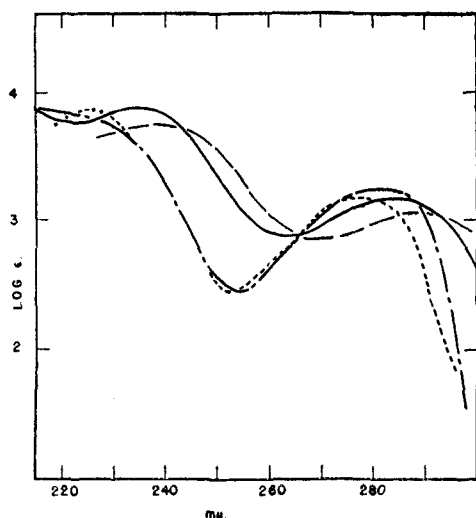
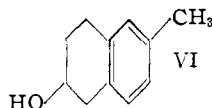


Fig. 1.—6-Hydroxy-5,6,7,8-tetrahydro-1-naphthoic acid, —; 5,6,7,8-tetrahydro-1-naphthoic acid, ----; 6-hydroxy-1,2,3,4-tetrahydro-1-naphthoic acid, - · - ·; *p*-hydroxyphenylacetic acid, · · · ·.

Perhydrogenation of 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid either with platinum in acetic acid or Raney nickel in alkaline solution produced the same mixture of perhydro hydroxy acids as the one step process. Similar results were obtained by the Raney nickel reduction of the sodium salt of the 1,2,3,4-tetrahydro acid (I).

Various other conditions for the reduction of 6-hydroxy-2-naphthoic acid were tried in order to compare the above method with the others discussed earlier but in no case were the desired results obtained. In each of the three methods employing the use of a platinum catalyst<sup>4,7,14</sup> hydrogenolysis of the hydroxyl group occurred.

A copper chromite hydrogenation of ethyl 6-hydroxy-2-naphthoate was also studied. While no reaction occurred at 160° and 2500 p.s.i., when the temperature was raised to 200° reduction proceeded slowly. After separation of the small amount of acidic material, the reaction mixture was saponified and yielded 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid in 12% yield and a non-saponifiable, neutral solid (C<sub>11</sub>H<sub>14</sub>O) in 40% which formed a crystalline *p*-phenylbenzoate. This compound has been shown to be 6-hydroxy-5,6,7,8-tetrahydro-2-methylnaphthalene (VI) by comparison with an authentic sample. This latter material was prepared from 6-hydroxy-5,6,7,8-tetrahydro-2-naph-



thoic acid by reduction with lithium aluminum hydride and hydrogenolysis of the resulting carbinol group with palladium on charcoal.

It is of interest to compare the tetrahydrogenation results obtained by Ungnade and Morriss<sup>9</sup> employing the esters of these hydroxynaphthoic acids with those obtained in the present research

(14) R. H. Baker and R. D. Schuetz, *THIS JOURNAL*, **69**, 1250 (1947).

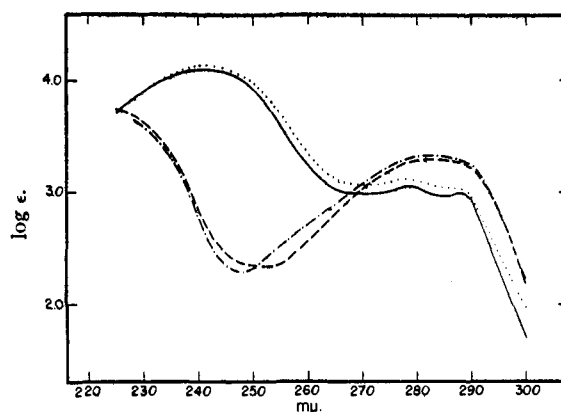


Fig. 2.—6-Hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid, ---; *ar*-2-tetralol, - · - ·; 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid, —; 5,6,7,8-tetrahydro-2-naphthoic acid, · · · ·.

using an aqueous alkaline solution of the salt. The former workers found that in each case, the 5,6,7,8-tetrahydro isomer could be isolated in 40–50% yield but they did not report any results pertaining to the 1,2,3,4-tetrahydro acid. Under aqueous alkaline conditions, it has been found that whereas the 6-hydroxy-1-naphthoic acid (Ia) yielded mostly the 1,2,3,4-tetrahydro compound (ratio 4/1), the 6-hydroxy-2-naphthoic acid (Ib) gave predominately the 5,6,7,8-tetrahydro acid (ratio 4/1). From such differing results, it is apparent that in the tetrahydrogenation both the relative positions occupied by the substituents and the hydrogenation conditions employed are of critical importance.

Various theories have been postulated in order to explain the products obtained when a polynuclear hydrocarbon substituted with a hydroxyl or carboxyl group is partially hydrogenated. For example, Ungnade and McLaren<sup>15</sup> have reported that alkali will promote the reduction of a phenolic ring in the presence of another aromatic nucleus (or function) whose reduction is not activated by alkali. In line with this idea, Stork<sup>16</sup> has postulated a more exact role for the base in such an activation and, in addition, his work indicates that, in the presence of alkali, carboxyl substituted rings are less readily hydrogenated than unsubstituted aromatic rings. These ideas, coupled together, adequately explain the results obtained on tetrahydrogenation of methyl 6-hydroxy-1 (and 2)-naphthoate and on 6-hydroxy-2-naphthoic acid. The direct antithesis appears to hold, however, with the 6-hydroxy-1-naphthoic acid.

Since it would appear that the role of a carboxylate anion in the 1-position of the naphthalene nucleus exerts a much different effect than when it is in the 2-position or when it is esterified, the tetrahydrogenation of 1-naphthoic acid has been examined. Adkins and Burgoyne<sup>17</sup> recently reported that when ethyl 1-naphthoate was hydrogenated in alcoholic solution over W-6 Raney nickel at 2–3 atmospheres pressure, the ratio of 5,6,7,8- to 1,2,3,4-tetrahydro acid was about 5 to 3, whereas with the 2-ester the ratio was 15 to 1. In

(15) H. E. Ungnade and A. D. McLaren, *ibid.*, **66**, 118 (1944).

(16) G. Stork, *ibid.*, **69**, 576 (1947).

(17) H. Adkins and E. E. Burgoyne, *ibid.*, **71**, 3528 (1949).

the present work, it was found that when 1-naphthoic acid was hydrogenated in alkaline solution over W-2 Raney nickel at 75° and 2500 p.s.i. the above ratio was 3 to 4 and in neutral solution it was 3 to 1. Tetrahydrogenation over platinum at atmospheric pressure in acetic acid yielded practically pure 5,6,7,8-tetrahydro-1-naphthoic acid (ratio 6 to 1). It has been found previously that 2-naphthoic acid yields exclusively the 5,6,7,8-tetrahydro acid regardless of the conditions of hydrogenation. Thus it appears that the generalization of Stork,<sup>16</sup> "that in a polycyclic aromatic system that ring will become reduced, the reduction of which will result in the smallest loss of resonance energy by the system," is an oversimplification of the process. At the present time, it is not clear exactly what effect the carboxyl group exerts when in the 1 position and further work is in process in this respect.

In addition to the above tetrahydrogenation of the 6-hydroxy-2-naphthoic acid (Ib) in alkaline solution, the reaction has also been investigated in alcoholic solution acidified with acetic acid and similar results to the alkaline experiment were obtained. Also, it is of passing interest to note that under these mild acidic conditions, hydrogenolysis is not the main reaction.

For a further comparison with the results of Stork on the hydrogenation of 2-naphthol and its methyl ether, the hydrogenation of 6-methoxy-2-naphthoic acid was studied. It was found that when the reduction was conducted in basic medium, the hydrogenolysis compound, 5,6,7,8-tetrahydro-2-naphthoic acid, was the only identifiable product (22%). In the presence of acid, again only one pure product could be isolated and the resulting 6-methoxy-1,2,3,4-tetrahydro-2-naphthoic acid was obtained in 16% yield.

Although several methods of preparation of the 6-hydroxy-2-naphthoic acid (Ib) have been reported previously,<sup>18</sup> a more convenient method based upon the work of Curd and Raison<sup>19</sup> was adapted in this present investigation. These latter workers obtained a mixture of 6-hydroxy- and 6-acetoxy-2-cyanonaphthalene by the action of cuprous cyanide on 6-acetoxy-2-bromonaphthalene but did not hydrolyze the resulting nitrile. This hydrolysis has been found to proceed smoothly in the presence of aqueous sodium hydroxide giving 6-hydroxy-2-naphthoic acid in 79% over-all yield from the bromide.

**Acknowledgment.**—We wish to express our appreciation to the Office of Naval Research for support of this work and to Mr. Edward R. Nelson for assistance given during the progress of this study.

#### Experimental<sup>20</sup>

**6-Hydroxy-1-naphthoic Acid.**—This acid was prepared from 1-acetylamino-6-hydroxynaphthalene following the procedure of Long and Burger,<sup>6</sup> m.p. 207–210°.

(18) C. Butler and F. A. Royle, *J. Chem. Soc.*, **123**, 1649 (1923); J. Cason, *This Journal*, **63**, 828 (1941); W. S. Knowles, J. A. Kuck and R. C. Elderfield, *J. Org. Chem.*, **7**, 374 (1942).

(19) F. H. S. Curd and C. G. Raison, *J. Chem. Soc.*, 160 (1947).

(20) Analyses by the Microanalytical Laboratory of the Department of Chemistry, University of California. All melting points are corrected. The absorption spectra were taken in 95% ethanol using a Beckman model DU spectrophotometer.

**6-Hydroxy-2-naphthoic Acid.**—6-Acetoxy-2-bromonaphthalene (107 g., 0.404 mole, m.p. 96–105°) was heated with cuprous cyanide (41.4 g., 0.461 mole) and pyridine (35.4 cc.) in a manner similar to that described by Curd and Raison.<sup>19</sup> The crude reaction product was distilled, b.p. 210–230° (0.5 mm.), and yielded 54.5 g. of a yellow solid which has previously been shown<sup>19</sup> to be a mixture of 6-acetoxy- and 6-hydroxy-2-cyanonaphthalene. The nitrile (42 g.) was then refluxed with a solution of 42 g. of sodium hydroxide in 200 cc. of water and 50 cc. of methanol for 24 hours. The methanol was removed by distillation and the solution acidified with concentrated hydrochloric acid. The precipitate was then boiled for a few minutes in the acidic solution, cooled and filtered, yield 46 g. (78.8% based on 6-acetoxy-2-bromonaphthalene) of a white solid, m.p. 245–247° (lit. 245–248°<sup>18</sup>).

**Tetrahydrogenation of 6-Hydroxy-1-naphthoic Acid.**—A solution of 4.73 g. (0.025 mole) of 6-hydroxy-1-naphthoic acid and 1.56 g. (0.013 mole) of sodium carbonate monohydrate in 31 ml. of water was hydrogenated at 75° over W-2 Raney nickel catalyst (3 ml.) at an initial pressure of 2500 p.s.i. at 25°. The hydrogenation ceased after 1 hour and an uptake amounting to two mole equivalents of hydrogen. After cooling and filtering, the solution was fractionally acidified with concentrated hydrochloric acid. The addition of 1.25 ml. of acid deposited 2.31 g. of crude 6-hydroxy-1,2,3,4-tetrahydro-1-naphthoic acid, m.p. 122–131°, which after several recrystallizations from toluene melts from 130–132°; yield 2.05 g. (42.4%). No melting point depression was observed when this product was mixed with a sample of the same tetrahydro acid (m.p. 129–130°) prepared by the sodium and alcohol reduction method of Price, *et al.*<sup>5</sup>

Upon addition of 0.5 ml. of acid to the filtrate from the first precipitation, a second crop of solid acid (0.97 g., m.p. 105–120°) was obtained which was probably a mixture of the two tetrahydro isomers. Further acidification of the mother liquor from the second precipitation with 0.5 ml. of acid deposited 0.42 g. of crude 6-hydroxy-5,6,7,8-tetrahydro-1-naphthoic acid, m.p. 145–155°. Recrystallization from nitroethane gave 0.42 g. (8.7%) of the pure isomer, m.p. 157–159°. Ungnade and Morriss<sup>9</sup> report 157.5–158.5°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>: C, 68.73; H, 6.30. Found: C, 69.16; H, 6.45.

**Tetrahydrogenation of 6-Hydroxy-2-naphthoic Acid.** (a) *In Alkaline Solution.*—A solution of 5.0 g. (0.026 mole) of 6-hydroxy-2-naphthoic acid and 1.4 g. (0.013 mole) of sodium carbonate in 31 cc. of water was hydrogenated over Raney nickel (3 cc.) at 100° and an initial pressure of 2500 p.s.i. at 25°. The hydrogenation ceased after two hours and an uptake amounting to two mole equivalents of hydrogen. The bomb was opened while still warm and the catalyst filtered. It is advantageous to filter the warm solution in order to prevent the precipitation of the insoluble sodium salt of the 5,6,7,8-tetrahydro isomer. Upon acidification of the filtrate an oil separated which soon solidified. This crude mixture of solid tetrahydroisomers (4.64 g.) was esterified with methanol (46 cc.) and concentrated sulfuric acid (4.6 cc.). An ethereal solution of the esters was separated into phenolic and non-phenolic fractions by extraction with 5% sodium hydroxide, and the corresponding acids were recovered by saponification. The non-phenolic fraction yielded 2.5 g. of crude 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid which after recrystallization from acetone-hexane gave 2.0 g. (39%) of white needles, m.p. 180.3–180.9°. Ungnade and Morriss<sup>9</sup> report 178.5–179.0°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>: C, 68.73; H, 6.30. Found: C, 68.56; H, 6.36.

The phenolic fraction yielded 1.13 g. of a mixture consisting of the starting acid and 6-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid. The latter was separated by dissolving the mixture in 13.5 cc. of 1 N NaOH and acidifying with 12.0 cc. of 1 N HCl. The precipitate was recrystallized from toluene and yielded 0.40 g. (8%) of white needles, m.p. 145.6–146.2°.

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>3</sub>: C, 68.73; H, 6.30. Found: C, 68.90; H, 6.31.

The same yields were obtained with five times the amount of starting material. Also in experiments conducted exactly as described above except that one and two equivalents of sodium hydroxide were used in place of sodium carbonate, identical results were obtained.

(b) *In Acidic Solution.*—A solution of 2.0 g. (0.011 mole) of 6-hydroxy-2-naphthoic acid in 10 cc. of warm absolute ethanol was acidified with two drops (0.1 cc.) of glacial acetic acid. Raney nickel (2 cc.) was added and the mixture hydrogenated under an initial pressure of 2500 p.s.i. The temperature was 130–165° and the reduction ceased after 2 hours and an uptake of two mole equivalents of hydrogen. The catalyst was filtered and the solvent removed under reduced pressure. The residue, 1.9 g., was esterified and separated as above. From the non-phenolic fraction there was obtained 0.85 g. (41%) of 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid, m.p. 179.2–180.6°, which showed no depression of melting point with the afore prepared isomer. The phenolic ester yielded 0.30 g. of acid which required only one recrystallization from toluene for purification; yield 0.23 g. (11%), m.p. 143.4–145.7°, mixed melting point with 6-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid obtained from basic hydrogenation, m.p. 143.8–145.7°.

**6-Acetoxy-5,6,7,8-tetrahydro-2-naphthoic Acid.**—The hydroxy acid (20.0 g., 0.104 mole) was dissolved in 50 cc. of hot acetic anhydride containing 0.1 g. of freshly fused sodium acetate and the solution heated on a steam-bath for 1.5 hours. After processing in the usual manner, 22.8 g. (93.5%) of 6-acetoxy-5,6,7,8-tetrahydro-2-naphthoic acid was obtained, m.p. 156–160°. An analytical sample was prepared by recrystallization from benzene–hexane followed by sublimation, m.p. 158.5–161.3°.

*Anal.* Calcd. for  $C_{13}H_{14}O_4$ : C, 66.65; H, 6.02. Found: C, 66.77; H, 6.08.

**6-Methoxy-1,2,3,4-tetrahydro-2-naphthoic Acid.**—The tetrahydro isomer (1.0 g., 5 mmoles) was heated with an aqueous solution of 0.42 g. (0.01 mole) of sodium hydroxide and 1.5 cc. (0.016 mole) of dimethyl sulfate for 2 hours. The oil which separated and solidified on cooling was esterified with methanol and concentrated sulfuric acid and separated from phenolic material by extraction with alkali. Saponification yielded 0.79 g. of crude 6-methoxy-1,2,3,4-tetrahydro-2-naphthoic acid which was purified by recrystallization from dilute aqueous ethanol, yield 0.065 g. (60.5%), m.p. 147.8–151.1°. Price<sup>18</sup> reports a melting point of 151° of the same compound.

*Anal.* Calcd. for  $C_{12}H_{14}O_3$ : C, 69.88; H, 6.84. Found: C, 69.83; H, 6.83.

**Perhydrogenation of 6-Hydroxy-1-naphthoic Acid.**—A solution of 5.0 g. (0.027 mole) of 6-hydroxy-1-naphthoic acid and 1.65 g. (0.013 mole) of sodium carbonate monohydrate in 29 ml. of water was hydrogenated at 150° over W-2 Raney nickel catalyst (3 ml.) at an initial pressure of 2500 p.s.i. at 25°. After 16 hours, approximately five mole equivalents of hydrogen had been absorbed. The catalyst was removed by filtration of the cooled reaction mixture and the filtrate partially acidified with 0.4 ml. of concentrated hydrochloric acid. A flocculent precipitate formed which was removed by filtration of the cooled mixture. After drying, this solid was quite hard and melts above 250°; weight 0.12 g. It was not characterized further. The filtrate was acidified with excess concentrated hydrochloric acid and a mixture of a solid and an oil separated. The mixture was extracted with ether and the ethereal solution evaporated to dryness. The resultant sticky solid was extracted with cold ether, leaving 1.60 g. (30.4%) of insoluble white crystalline 6-hydroxydecahydro-1-naphthoic acid, m.p. 160–180. After recrystallization from water, this mixture melts from 165–180°. Numerous attempts were made to obtain a single isomer from this mixture by means of fractional acidification and crystallization from various solvents but with no success.

*Anal.* Calcd. for  $C_{11}H_{18}O_3$ : C, 66.64; H, 9.15. Found: C, 66.41; H, 9.21.

Evaporation of the ethereal extract yielded 2.75 g. (52.1%) of sirupy acids. Upon standing, some solid material formed in this sirup and was found to melt over approximately the same range as the original solid fraction. This solid (0.71 g.) was removed after diluting the mixture with ether.

The combined liquid acids (24.0 g.) from the hydrogenation of 60 g. of starting acid were esterified with diazomethane, acetylated by heating with acetic anhydride and sodium acetate and the resulting product was distilled through a 30-plate column. The lower boiling fraction consisted of methyl decahydro-1-naphthoate (IV), 2.29 g. (3.7% based

on 6-hydroxy-1-naphthoic acid), b.p. 97–104° (3 mm.),  $n_D^{25}$  1.4833.

*Anal.* Calcd. for  $C_{12}H_{20}O_2$ : C, 73.43; H, 10.27. Found: C, 73.59; H, 10.13.

The higher boiling fraction gave 16.2 g. (19.9%) of methyl 6-acetoxydecahydro-1-naphthoate, b.p. 145–148° (3 mm.),  $n_D^{25}$  1.4802.

*Anal.* Calcd. for  $C_{14}H_{22}O_4$ : C, 66.61; H, 8.72. Found: C, 66.40; H, 8.59.

A sample of methyl decahydro-1-naphthoate (0.82 g.) was saponified with aqueous sodium hydroxide and 0.60 g. of a semi-solid acid was obtained. After several recrystallizations from 50% aqueous ethanol, this solid still melts over a range of 117–123° and is probably a mixture of stereoisomers of decahydro-1-naphthoic acid. Long and Burger<sup>4</sup> report 112–115° and Price and co-workers<sup>9</sup> report 115–117° for a similar mixture. Ungnade and Morriss<sup>9</sup> report a value of 124–125° for a single pure isomer.

*Anal.* Calcd. for  $C_{11}H_{18}O_2$ : C, 72.39; H, 9.95. Found: C, 72.66; H, 9.97.

An 8.0-g. sample of methyl 6-acetoxydecahydro-1-naphthoate was saponified with aqueous sodium hydroxide, the solution made just acid to litmus with concentrated hydrochloric acid and upon standing at room temperature a small amount of dark solid separated. This was removed by filtration and the filtrate then allowed to stand 24 hours at 0°. A crystalline precipitate formed (0.88 g., 14.1% based upon ester), m.p. 142–151°, which after several recrystallizations from 10% ethanol yielded 6-hydroxydecahydro-1-naphthoic acid, m.p. 151–154.5°.

*Anal.* Calcd. for  $C_{11}H_{18}O_3$ : C, 66.64; H, 9.15. Found: C, 66.66; H, 9.09.

The further acidification of the filtrate from the above fractional acidification gave 0.10 g. of solid acid, m.p. 175–210°, indicating the existence of isomers of the perhydro acid melting above 200°. Ungnade and Morriss<sup>9</sup> report two isomers melting at 220.5–221.5° and 219–220°.

**Perhydrogenation of 6-Hydroxy-2-naphthoic Acid (a)**  
*In Alkaline Solution.*—The procedure followed was essentially the same as that employed in the tetrahydrogenation experiment except that the temperature was raised to 150°. About 12 hours was required for the perhydrogenation of 14.0 g. (0.074 mole) of 6-hydroxy-2-naphthoic acid. Acidification of the filtrate produced an oil which did not solidify on standing in the cold. The aqueous phase<sup>21</sup> was decanted and the residual sirup triturated with cold ether. The resulting white solid was filtered and recrystallized from acetone–hexane; yield 2.28 g. (15%), m.p. 196.3–197.3°.<sup>22</sup>

*Anal.* Calcd. for  $C_{11}H_{18}O_3$ : C, 66.64; H, 9.15. Found: C, 66.83; H, 9.17.

From the ether filtrate there was obtained 8.18 g. of a yellow, viscous liquid.

The combined liquid acids from the hydrogenation of 72.5 g. of starting acid were esterified by refluxing with ethanol and concentrated sulfuric acid, then acetylated by heating with acetic anhydride and sodium acetate and finally distilled through a column. The lower boiling fraction consisted of ethyl decahydro-2-naphthoate, 11.2 g. (13.9% from 6-hydroxy-2-naphthoic acid), b.p. 115–116° (3 mm.),  $n_D^{25}$  1.4768,  $d_4^{25}$  0.999.

*Anal.* Calcd. for  $C_{13}H_{22}O_2$ : C, 74.24; H, 10.55; mol. wt., 210.3. Found: C, 74.23; H, 10.37; sapon. equiv., 209–212.

The oily acid obtained on saponification of this ester gave an amide melting 168–173.3°.

The higher boiling fraction gave 19.8 g. (19%) of ethyl 6-acetoxydecahydro-2-naphthoate, b.p. 151–155° (3 mm.),  $n_D^{25}$  1.4763,  $d_4^{25}$  1.102. Saponification yielded a liquid acid.

*Anal.* Calcd. for  $C_{13}H_{20}O_4$ : C, 67.14; H, 9.02; mol. wt., 268.3. Found: C, 67.33; H, 8.93; sapon. equiv., 133, 135.

(b) *In Acidic Solution.*—In a perhydrogenation attempt in ethanol solution acidified with acetic acid, a temperature of 200° was required for reduction beyond the tetrahydro stage. The hydrogen uptake was slow and after 41 hours

(21) The hydroxydecahydro acids are somewhat soluble in water and the aqueous phase often was found to contain up to 10% of the hydrogenated material.

(22) From several hydrogenations, however, a sharp melting solid was not obtained.

amounted to about seven mole equivalents. After saponification of the reaction mixture from 15.0 g. of 6-hydroxy-2-naphthoic acid, there was obtained 6.5 g. of an oily acid (from which could be isolated 1.35 g. of solid perhydro acid, m.p. 178–196°) and 6.1 g. of a non-saponifiable neutral liquid. This latter fraction was acetylated and distilled. A fraction boiling 100–103° (2 mm.), 2 g., is considered to be 6-acetoxydecahydro-2-methylnaphthalene.

*Anal.* Calcd. for  $C_{13}H_{20}O_2$ : C, 74.24; H, 10.55. Found: C, 73.39; H, 9.86.

**Decahydro-2-naphthoic Acid from Solid 6-Hydroxydecahydro-2-naphthoic Acid.**—A solution of 2.0 g. (0.01 mole) of 6-hydroxydecahydro-2-naphthoic acid (m.p. 194.1–196.1°) in 5 g. of acetic acid saturated with hydrogen bromide was warmed on a steam-bath for 6 hours. The solution was then poured into water and the insoluble oil dissolved in ether. The ether was evaporated, the residual oil dissolved in a solution of 0.46 g. (0.02 mole) of sodium in 50 cc. of methanol and the solution hydrogenated<sup>11</sup> over Raney nickel (5 cc.) at low pressure. The catalyst was filtered and the filtrate diluted with 200 cc. of water and then acidified. The oil which separated solidified on standing overnight in the cold and yielded 1.38 g. (75%) of decahydro-2-naphthoic acid as a waxy white solid, m.p. 45–75°. This solid (590 mg.) was recrystallized from a few cc. of hexane and deposited 131 mg. as the first crop, m.p. 76.1–79.4°. From the mother liquor was obtained an additional 270 mg. of a crystalline solid, m.p. 71.3–78.8°. Further processing of the mother liquor afforded only a liquid acid.

The amide was prepared directly from the crude acid (0.5 g.) and was purified by recrystallization from dilute ethanol. The white flakes melt 169.2–174.5°; yield 0.32 g. (64.4%).

*Anal.* Calcd. for  $C_{11}H_{19}ON$ : C, 72.88; H, 10.57. Found: C, 73.16; H, 10.42.

**6-Acetoxydecahydro-2-naphthoic Acid.**—A mixture of 0.30 g. of 6-hydroxydecahydro-2-naphthoic acid (m.p. 194.1–196.1°), 5 cc. of acetic anhydride and 0.1 g. of freshly fused sodium acetate was heated on a steam-bath for 1 hour. The solution was cooled, stirred into ice-water and allowed to stand 1 hour. The crystalline 6-acetoxydecahydro-2-naphthoic acid was filtered and recrystallized from benzene-hexane; yield 0.32 g. (88%), m.p. 137.9–140.2°.

*Anal.* Calcd. for  $C_{13}H_{20}O_4$ : C, 64.98; H, 8.39. Found: C, 65.23; H, 8.31.

**Low Pressure Hydrogenation of 6-Hydroxy-5,6,7,8-tetrahydro-2-naphthoic Acid.**—A mixture of 1.0 g. (5 mmoles) of 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid in 25 cc. of glacial acetic acid and 0.20 g. of platinum oxide was hydrogenated at low pressure for 8 hours. The oil remaining after removal of the solvent was treated with ether and the resulting white crystals were filtered, yield 0.53 g. Four recrystallizations from acetone-hexane gave 0.26 g. (25.2%), m.p. 196.4–196.9°; a mixed melting point with solid 6-hydroxydecahydro-2-naphthoic acid obtained from the one-step perhydrogenation of 6-hydroxy-2-naphthoic acid showed no depression. There was obtained 0.41 g. of oil on evaporation of the ether from the filtrate.

**High Pressure Hydrogenation of 6-Hydroxy-1,2,3,4-tetrahydro and 6-Hydroxy-5,6,7,8-tetrahydro-2-naphthoic Acid.**—A solution of 1.0 g. of the tetrahydro acid was hydrogenated over Raney nickel in a manner similar to that described for the perhydrogenation of 6-hydroxy-2-naphthoic acid. The 5,6,7,8-tetrahydro acid gave 0.20 g. (19.4%) of solid 6-hydroxydecahydro-2-naphthoic acid, m.p. 196.8–197.2°, and 0.5 g. of liquid acids. The 1,2,3,4-tetrahydro isomer yielded 0.12 g. (11.6%) of the hydroxyperhydro acid, m.p. 196.8–198.8°, and 0.84 g. of sirupy acids.

**Hydrogenation and Ethyl 6-Hydroxy-2-naphthoate.**—A solution of 3.0 g. (0.014 mole) of ethyl 6-hydroxy-2-naphthoate in 8 cc. of absolute ethanol was hydrogenated over 0.3 g. of copper chromite catalyst under an initial pressure of 2460 p.s.i. at 20°. The hydrogenation was conducted at 200° for 8 hours after which time the pressure remained constant and the pressure drop indicated an uptake of four mole equivalents of hydrogen. An ethereal solution of the reaction mixture was extracted with 5% sodium hydroxide. The phenolic ester gave an oily acid which was not further investigated.

Removal of the ether from the neutral fraction left 1.90 g. of a liquid which was separated into a saponifiable and a non-saponifiable fraction by refluxing overnight with 10% alcoholic potassium hydroxide. There was obtained 0.55 g. of acidic material which was purified by recrystallization from acetone-hexane; yield 0.30 g. (11.3%) of white needles, m.p. 173–177°, mixed melting point with 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid, 174–179°.

*Anal.* Calcd. for  $C_{11}H_{14}O_3$ : C, 68.73; H, 6.29. Found: H, 68.64; H, 6.38.

The neutral fraction amounted to 0.9 g. (40%) of an oil which solidified on standing in the cold. Purification was accomplished by sublimation, m.p. 54–57° and mixed melting point with 6-hydroxy-5,6,7,8-tetrahydro-2-methylnaphthalene, m.p. 54.9–59.2°.

*Anal.* Calcd. for  $C_{11}H_{14}O$ : C, 81.44; H, 8.70. Found: C, 81.46; H, 8.67.

The *p*-phenylbenzoate ester was prepared by heating a solution of the solid (0.3 g.) with 0.45 g. of *p*-phenylbenzoyl chloride in 10 cc. of dry pyridine. After recrystallization from ethanol, the derivative melts 107.4–110.5° and on admixture with the *p*-phenylbenzoate of authentic 6-hydroxy-5,6,7,8-tetrahydro-2-methylnaphthalene, m.p. 108.5–111.2°.

*Anal.* Calcd. for  $C_{21}H_{22}O_2$ : C, 84.18; H, 6.48. Found: C, 84.23; H, 6.57.

**6-Hydroxy-5,6,7,8-tetrahydro-2-naphthylcarbinol.**—The procedure of Nystrom and Brown<sup>28</sup> for the reduction of ether-insoluble acids was followed. From 2.0 g. (0.01 mole) of 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid and 0.95 g. (0.025 mole) of lithium aluminum hydride there was obtained 0.75 g. (40%) of crude 6-hydroxy-5,6,7,8-tetrahydro-2-naphthylcarbinol (m.p. 124–126°) and 0.7 g. of starting acid. An analytical sample was prepared by sublimation, m.p. 126.5–127.5°.

*Anal.* Calcd. for  $C_{11}H_{14}O_2$ : C, 74.11; H, 7.92. Found: C, 74.17; H, 7.90.

**6-Hydroxy-5,6,7,8-tetrahydro-2-methylnaphthalene.**—A solution of 0.295 g. (1.7 mmoles) of 6-hydroxy-5,6,7,8-tetrahydro-2-naphthylcarbinol in 10 cc. of absolute methanol was hydrogenated over 0.5 g. of 5% palladium-on-charcoal at atmospheric pressure. After 2 hours the reduction had ceased and the theoretical amount of hydrogen (46 cc.) had been absorbed. The catalyst was filtered and the solvent removed under reduced pressure leaving 0.23 g. (85%) of sirupy 6-hydroxy-5,6,7,8-tetrahydro-2-methylnaphthalene.

The crude product was converted directly to the *p*-phenylbenzoate by heating the above material and 0.40 g. of *p*-phenylbenzoyl chloride in 5 cc. of dry pyridine. The crude derivative was recrystallized from 95% ethanol; yield 0.34 g. (70%), m.p. 109.2–111.8°.

*Anal.* Calcd. for  $C_{21}H_{22}O_2$ : C, 84.18; H, 6.84. Found: C, 84.14; H, 6.68.

Saponification of the ester (0.22 g.) gave 0.10 g. of liquid 6-hydroxy-5,6,7,8-tetrahydro-2-methylnaphthalene which solidified to a waxy white solid, m.p. 60.2–61.4° (after sublimation).

*Anal.* Calcd. for  $C_{11}H_{14}O$ : C, 81.44; H, 8.70. Found: C, 81.82; H, 8.76.

**Hydrogenation of 6-Hydroxy-2-naphthoic Acid.** (a) *With Platinum Oxide at Low Pressure in Acidic Solution.*—A solution of 3.0 g. (0.016 mole) of 6-hydroxy-2-naphthoic acid in 150 cc. of glacial acetic acid was hydrogenated over 1.0 g. of platinum oxide at forty-five p.s.i. The hydrogenation was stopped after three hours when the pressure drop corresponded to an uptake of two mole equivalents of hydrogen. The liquid acids remaining after removal of the solvent were esterified and separated by extraction with 5% sodium hydroxide. The crude acid obtained upon saponification of the phenolic ester (0.95 g.) was dissolved in 5 cc. of 1 N NaOH, and to the resulting solution three portions (1, 2 and 3 cc.) of 1 N HCl was added. The precipitated acid was filtered after each addition. Fractions one and two were combined (0.40 g.) and crystallized once from acetic acid and once from water. The material melts 244–247° and does not depress the melting point of 6-hydroxy-

(23) R. P. Nystrom and W. G. Brown, *THIS JOURNAL*, **69**, 2548 (1947).

2-naphthoic acid. The third fraction yielded no pure substance.

The acid recovered by saponification of the non-phenolic ester (1.45 g.) melts 110–133°. For purification, 1.1 g. of this crude acid was refluxed with 35 cc. of ligroin (b.p. 90–120°) and the insoluble material filtered (0.24 g., m.p. 148–230°, not further investigated). The filtrate was concentrated to 20 cc. and allowed to stand overnight. There was obtained 0.52 g. of a white solid which after repeated crystallization from ligroin gave 0.25 g. (8.9%) of white needles, m.p. 144–150°. Although a sharp melting sample could not be obtained, analysis showed it to be practically pure, 5,6,7,8-tetrahydro-2-naphthoic acid.

*Anal.* Calcd. for  $C_{11}H_{12}O_2$ : C, 74.98; H, 6.83. Found: C, 75.15; H, 6.76.

(b) *With Platinum Oxide at High Pressure in Acidic Solution.*<sup>14</sup>—A solution of 2.0 g. (0.01 mole) of 6-hydroxy-2-naphthoic acid in 20 cc. of ethanol and 20 cc. of acetic acid was hydrogenated over 0.1 g. of platinum oxide in a glass liner at room temperature and 1970 p.s.i. for 12 hours. The pressure drop corresponded to a hydrogen uptake of approximately two mole equivalents. The hydrogenated acids were separated as before. The phenolic ester yielded 0.9 g. of acid which after recrystallization from acetic acid melts 239–240° and does not depress the melting point of the starting acid. From the non-phenolic fraction there was obtained 0.52 g. of acid which yielded 0.25 g. (13.4%) of white needles from ligroin (b.p. 90–120°), m.p. 150.7–153.0° and a mixed melting point with 5,6,7,8-tetrahydro-2-naphthoic acid showed no depression.

(c) *With Platinum Oxide at Low Pressure in Alkaline Solution.*<sup>7</sup>—A solution of 2.0 g. (0.01 mole) of 6-hydroxy-2-naphthoic acid in 50 cc. of absolute ethanol and 5 drops of 10% aqueous sodium hydroxide was hydrogenated over 0.2 g. of platinum oxide. Although the hydrogen absorption, which corresponded to about one mole equivalent, ceased after 12 hours, the shaking was continued for an additional 34 hours. The reaction mixture was separated as before. The alkali soluble ester yielded 0.8 g. of starting acid which after recrystallization from dilute acetic acid melts 245.0–246.8°. The non-phenolic ester yielded 0.8 g. of an acid which was further purified by refluxing with ligroin (b.p. 90–120°). The insoluble fraction was filtered and is probably 6-hydroxy-5,6,7,8-tetrahydro-2-naphthoic acid; yield 0.1 g. (4.9%), m.p. 173.6–177.0°. The filtrate was allowed to cool and the crystals of crude 5,6,7,8-tetrahydro-2-naphthoic acid were filtered and recrystallized several times from ligroin to yield 0.32 g. (17.1%), m.p. 146–151°.

**Hydrogenation of 6-Methoxy-2-naphthoic Acid.** (a) *With Raney Nickel in Alkaline Solution.*—6-Methoxy-2-naphthoic acid (2.0 g., 0.01 mole) was added to a solution of 0.52 g. (5 mmoles) of sodium carbonate in 50 cc. of water and 3 cc. of 10% sodium hydroxide was added. The solid did not dissolve but the sodium salt is quite soluble in boiling water. This mixture was hydrogenated over Raney nickel (5 cc.) at 100° under an initial pressure of 2500 p.s.i. After 1 hour and 15 minutes the hydrogenation had ceased and the pressure drop corresponded to a hydrogen uptake of about three mole equivalents. The catalyst was filtered and the filtrate acidified. The crude acid thus obtained (1.53 g.) was recrystallized four times from ligroin (b.p. 90–120°) and yielded 0.39 g. (22%) of white needles, m.p. 149.9–152.9°. The acid showed no depression in melting point upon admixture with 5,6,7,8-tetrahydro-2-naphthoic acid.

(b) *With Raney Nickel in Acidic Solution.*—A solution of 5.0 g. (0.025 mole) of 6-methoxy-2-naphthoic acid in 50 cc. of absolute ethanol and 1 cc. of acetic acid was hydrogenated over Raney nickel (8 cc.) in a glass liner. The hydrogenation was conducted at 200° for 12 hours with an initial pressure of 2500 p.s.i. at 25°. The catalyst was filtered and the solvent removed under reduced pressure. Saponification of the residual sirup yielded 4.05 g. of acid. On recrystallization from dilute ethanol, 1.0 g. gave 0.37 g. of a white solid, m.p. 139–148°. This material was heated with ligroin and the insoluble material was filtered and recrystallized from dilute ethanol; yield 0.20 g. (16%), m.p. 148.6–150.4°. No depression in melting point was noticed upon admixture with 6-methoxy-1,2,3,4-tetrahydro-2-naphthoic acid.

**Sodium-Alcohol Reduction of 6-Hydroxy-2-naphthoic Acid.**<sup>13</sup>—Sodium (4.25 g., 0.185 mole), cut into small pieces,

was added to a boiling solution of 1.65 g. (9 mmoles) of 6-hydroxy-2-naphthoic acid dissolved in 55 cc. of boiling amyl alcohol over a period of 20 minutes. After the sodium had reacted, the reaction mixture was extracted with two 50-cc. portions of water. The combined aqueous extracts were extracted twice with ether and then acidified after the dissolved ether had been removed by boiling. The precipitated acid was collected, dried and then redissolved in aqueous sodium carbonate. Norit was added and the filtered solution acidified; the precipitate amounted to 0.8 g., m.p. 140–207°. The acidic aqueous filtrate was extracted with ether and the ether extracted with a small volume of aqueous sodium bicarbonate. Acidification of the carbonate extract gave an oil which soon solidified; yield after recrystallization from toluene, 0.42 g. (25%), m.p. 144.2–144.8°. This acid did not depress the melting point of 6-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid prepared by hydrogenation.

*cis-Decalin* from *cis-2-Decalol*.—A solution of 20 g. (0.13 mole) of *cis-2-decalol* (m.p. 103°) in 75 cc. of acetic acid saturated with hydrogen bromide was refluxed for 2 hours. The two phase reaction mixture was poured into 150 cc. of water and extracted with three 50-cc. portions of ether. The combined ethereal extracts were washed with aqueous sodium carbonate and dried over anhydrous magnesium sulfate. The ether was evaporated and the crude 2-bromodecalin was dissolved in a solution of 5.98 g. of sodium in 135 cc. of absolute ethanol. Raney nickel (10 cc.) was added and the mixture was shaken with hydrogen in the low pressure hydrogenator for 90 minutes. After filtration of the catalyst, the reaction mixture was poured into 300 cc. of water and extracted with three 120-cc. portions of ether. The combined ethereal extracts were added to 160 cc. of benzene and the solution, after drying over calcium chloride, was distilled through a 30-plate column. After removal of the solvents, only one fraction (10.1 g., 61.5%) was obtained, b.p. 192.2–193.8° (759 mm.),  $n_D^{20}$  1.4823,  $d_4^{25}$  0.896. These properties are in good agreement with the reported properties of *cis-decalin*,<sup>24</sup> b.p. 194.6° (760 mm.),  $n_D^{20}$  1.4811,  $d_4^{25}$  0.896. The properties of *trans-decalin* are b.p. 185.5° (760 mm.),  $n_D^{20}$  1.4697,  $d_4^{25}$  0.870.

**Hydrogenation of 1-Naphthoic Acid** (a) *With Raney Nickel in Alkaline Solution.*—A solution of 15.0 g. (0.087 mole) of 1-naphthoic acid and 5.43 g. (0.044 mole) of sodium carbonate monohydrate in 72 ml. of water was hydrogenated at 75° over Raney nickel catalyst (6 ml.) at an initial pressure of 2500 p.s.i. at 20°. The hydrogenation ceased after 2 hours at which time an uptake amounting to two mole equivalents of hydrogen had occurred. After cooling and filtering, the solution was fractionally acidified with dilute (1:1) hydrochloric acid by adding the acid to the hot solution until a faint turbidity was produced, then raising the temperature until a clear solution was obtained and finally allowing the temperature to fall slowly. A total of sixteen fractions was obtained in this manner and they could be divided into two groups. The first seven fractions melt between 120–149° and were combined, m.p. 120–140°, weight 5.27 g. Recrystallization from 125 ml. of 50% ethanol gave 4.65 g. (27.8%) of 5,6,7,8-tetrahydro-1-naphthoic acid, m.p. 148.0–149.5°. The amide melts 183–184.5°. Adkins and Burgoyne<sup>17</sup> report values of 148–150° for the acid and 185° for the amide.

The last nine fractions melt between 70–83° and were combined to give 7.48 g. (44.6%) of crude 1,2,3,4-tetrahydro-1-naphthoic acid. Recrystallization from an ethyl acetate-petroleum ether mixture (1:1) gave white crystals melting 81–84°. Bamberger and Bordt<sup>25</sup> report 85° and Newman and O'Leary<sup>26</sup> report 81°.

(b) *With Raney Nickel in Acidic Solution.*—A solution of 5.0 g. (0.029 mole) of 1-naphthoic acid in 26 cc. of absolute ethanol was hydrogenated as described above. The alcoholic solution was evaporated to dryness and the solid residue dissolved in 50 ml. of water containing one equivalent of sodium carbonate. The solution was fractionally acidified as before. The first seven fractions melt between 125–149° and were combined to give 2.93 g. (57%) of crude 5,6,7,8-tetrahydro-1-naphthoic acid. Two recrystalliza-

(24) W. F. Seyer and R. D. Walker, *THIS JOURNAL*, **60**, 2125 (1938); W. F. Seyer and C. H. Davenport, *ibid.*, **63**, 2425 (1941).

(25) E. Bamberger and F. Bordt, *Ber.*, **22**, 625 (1889).

(26) M. S. Newman and T. J. O'Leary, *THIS JOURNAL*, **63**, 258 (1946).

tions from 50% ethanol gave 2.27 g. (45%) of acid melting 145–149°. This product was identical with that obtained in the hydrogenation in alkaline solution.

The last three fractions from the fractional acidification were combined to give 0.86 g. (16.8%) of crude 1,2,3,4-tetrahydro-1-naphthoic acid, m.p. 68–75°.

(c) *With Platinum in Acetic Acid.*—A suspension of 25 g. (0.145 mole) of 1-naphthoic acid and 1.0 g. of platinum oxide in 200 ml. of acetic acid was hydrogenated at room temperature and a pressure of three atmospheres. During the

hydrogenation, some solid precipitated. The reaction mixture was warmed and filtered and upon cooling, 9.2 g. (34.8%) of 5,6,7,8-tetrahydro-1-naphthoic acid, m.p. 146–150°, precipitated. Concentration of the filtrate to 100 ml. yielded an additional 7.3 g. (27.7%) of material melting 146–150°. After removal of all of the acetic acid and fractional crystallization from 50% ethanol, 2.3 g. (9.5%) of the 1,2,3,4-tetrahydro isomer, m.p. 65–75°, was obtained.

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## Ketene Acetals. XXIII. Dealcoholation of Orthoesters with Aluminum *t*-Butoxide

BY S. M. McELVAIN AND WILLIAM R. DAVIE

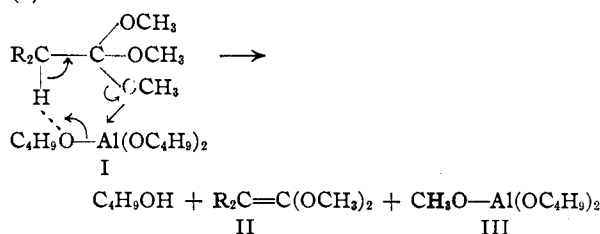
Aluminum *t*-butoxide is shown to be an efficient reagent for the dealcoholation of orthoesters to the corresponding ketene acetals. It is particularly valuable for the dealcoholation of the low-boiling orthoesters, e.g., methyl orthoisobutyrate, which distil unchanged from aluminum methoxide and ethoxide. The superiority of aluminum *t*-butoxide over its lower homologs in this reaction is attributed to a greater coordinative capacity resulting from a simpler molecular structure. The properties of two new ketene acetals, dimethylketene diethylacetal and ethoxyketene diethylacetal, are reported.

In paper XXI of this series the facile and practically quantitative dealcoholation of methyl orthophenylacetate to the corresponding ketene acetal with the aprotic acid, aluminum methoxide, was reported.<sup>1</sup> The higher boiling point and the greater reactivity of the  $\alpha$ -hydrogen of this orthoester made it possible to effect this dealcoholation by heating the reactants together at 210°. However, the lower boiling and less reactive aliphatic orthoesters, methyl orthopropionate and methyl orthoisobutyrate, simply distilled unchanged from the alkoxide under such conditions. Only partial dealcoholations (8–16%) of these aliphatic orthoesters were effected by passing their vapors through a column of aluminum methoxide heated to 240–290°.

In extending the study of these dealcoholations to the homologous aluminum alkoxides, it has been found that aluminum *t*-butoxide is a particularly effective agent for the dealcoholation of orthoesters to the corresponding ketene acetals. The temperatures of dealcoholation and the yields of the ketene acetals from some representative orthoesters are listed in Table I. In general these dealcoholations occur at much lower temperatures than those previously observed<sup>1</sup> with aluminum methoxide and for this reason each of them may be carried out by

heating a mixture of the orthoester and the aluminum *t*-butoxide.

A noteworthy feature of these dealcoholations is that pure *t*-butyl alcohol distils from the reaction of methyl and ethyl orthoesters with aluminum *t*-butoxide. This fact supports the earlier suggestion<sup>1</sup> that the alkoxide functions by coordination with the orthoester followed by the concerted elimination of the reaction products from the complex (I):



With the more reactive methyl orthophenylacetate all of the *t*-butyl groups of aluminum *t*-butoxide may be eliminated as *t*-butyl alcohol, i.e., one mole of the alkoxide converts three moles of the orthoester to the ketene acetal. With the lower-boiling aliphatic orthoesters, it was found necessary to use a molecular equivalent of the alkoxide to prevent distillation of the orthoester and to obtain maximum yields of the ketene acetals.

When either aluminum ethoxide or isopropoxide was used for the dealcoholation of methyl orthophenylacetate, a mixture of methyl and ethyl (or isopropyl) alcohols and non-homogeneous ketene acetals were obtained. These products are doubtless the result of the addition of the more reactive ethyl (or isopropyl) alcohol to the initially formed ketene acetal followed by dealcoholation of the resulting mixed orthoester. While aluminum ethoxide dealcoholates ethyl orthophenylacetate successfully, it is as ineffective with the lower-boiling aliphatic orthoesters, such as ethyl orthoacetate and ethyl orthopropionate, as the methoxide is with the corresponding methyl orthoesters.

It is apparent from Table I that a wide variety of orthoesters may be dealcoholated to the corresponding ketene acetals in good yields with alu-

TABLE I

DEALCOHOLATIONS OF ORTHOESTERS WITH ALUMINUM *t*-BUTOXIDE

Orthoester	Mole ratio alkoxide: ester	Reaction temp., °C.	Yield of <i>t</i> -C <sub>4</sub> H <sub>9</sub> -OH, %	Yield of ketene acetal, %
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(OCH <sub>3</sub> ) <sub>3</sub>	1:3	165–180	77	85 <sup>a</sup>
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> C(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1:3	160–180	82	85 <sup>a</sup>
CH <sub>3</sub> C(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1:1	180–185	70	65
CH <sub>3</sub> CH <sub>2</sub> C(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1:1	180–185	86	83
(CH <sub>3</sub> ) <sub>2</sub> CHC(OCH <sub>3</sub> ) <sub>3</sub>	1:1	185–190	63	54
(CH <sub>3</sub> ) <sub>2</sub> CHC(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1:1	185–190	82	62
C <sub>2</sub> H <sub>5</sub> OCH <sub>2</sub> C(OC <sub>2</sub> H <sub>5</sub> ) <sub>3</sub>	1:1	175–180 <sup>b</sup>	80	61

<sup>a</sup> This product was contaminated with some of the alkoxide that sublimed during the distillation of the ketene acetal. <sup>b</sup> This dealcoholation was carried out under diminished pressure (see experimental).