ir (CCl_4) 1790 cm^{-1}. *Anal.* Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.85; H, 8.75.

trans-**3,4-Dimethyl-γ-butyrolactone** (*trans*-**4b**) had bp 101–103° (12 mm); $n^{25}D$ 1.4350 [lit.[8] bp 86–86.5° (5 mm), $n^{22}D$ 1.4333]; ir (CCl_4) 1785 cm^{-1}. *Anal.* Calcd for $C_6H_{10}O_2$: C, 63.13; H, 8.83. Found: C, 62.93; H, 8.72.

3,4,4-Trimethyl-γ-butyrolactone (**4c**) had bp 97° (15 mm); $n^{20}D$ 1.4373 [lit. bp 216–217° (744 mm),[9] 219° (760 mm),[2f] $n^{17}D$ 1.4402]; ir (CCl_4) 1780 cm^{-1}. *Anal.* Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.32; H, 9.48.

cis-**3-Methyl-4-ethyl-γ-butyrolactone** (*cis*-**4d**) had bp 102–105° (11.5 mm); $n^{25}D$ 1.4375; ir (CCl_4) 1780 cm^{-1}; nmr (CCl_4) τ 8.96 (t, 3), 8.86 (d, 3), 6.13 (m, 1), 7.3–8.6 (m, 3); mass spectrum M^+ 128. *Anal.* Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.31; H, 9.58.

trans-**3-Methyl-4-ethyl-γ-butyrolactone** (*trans*-**4d**) had bp 102–105° (11.5 mm); $n^{25}D$ 1.4403; ir (CCl_4) 1775 cm^{-1}; nmr (CCl_4) τ 8.97 (t, 3), 9.00 (d, 3), 5.8 (m, 1), 7.3–8.7 (m, 3). *Anal.* Calcd for $C_7H_{12}O_2$: C, 65.59; H, 9.44. Found: C, 65.35; H, 9.52.

trans- **and** *cis*-**3,4-Dimethyl-4-ethyl-γ-butyrolactone** (**4e**) had bp 110–112° (15 mm); $n^{25}D$ 1.4435; ir (CCl_4) 1760–1780 cm^{-1} (broad); nmr (CCl_4) τ 8.65 [s, 3, $-OC(CH_3)$ of cis isomer], 8.78 [s, 3, $-OC(CH_3)$ of trans isomer], 8.99 (t, 3), 8.91 (d, 3), 7.66 (m, 2), 8.45 (q, 2), 7.3–8.1 (m, 1). *Anal.* Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.40; H, 9.99.

3-Methyl-4,4-diethyl-γ-butyrolactone (**4f**) had bp 80–84° (2 mm); $n^{20}D$ 1.4512; ir (CCl_4) 1770 cm^{-1}; mass spectrum M^+ 156. *Anal.* Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 68.92; H, 10.41.

trans- **and** *cis*-**3-Methyl-4-phenyl-γ-butyrolactone** (**4g**) had bp 128–130° (2.5 mm); $n^{25}D$ 1.5290; ir (CCl_4) 1788 cm^{-1}; nmr (CCl_4) τ 9.35 [d, 3, J = 7 Hz, $-CH(CH_3)$ of cis isomer], 8.85 [d, 3, J = 6 Hz, $-CH(CH_3)$ of trans isomer], 7.58 (m, 2), 7.1–8.2 (m, 1), 5.17 [d, 1, J = 8 Hz, $-CH(C_6H_5)O$ of trans isomer], 6.51 [d, 1, J = 6 Hz, $-CH(C_6H_5)O$ of cis isomer], 2.8 (s, 5); mass spectrum M^+ 176. *Anal.* Calcd for $C_{11}H_{12}O_2$: C, 74.97; H, 6.86. Found: C, 75.12; H, 6.86.

3-Methyl-γ-butyrolactone (**4a**).—The infrared spectrum of the condensed crude product revealed $\nu_{C=O}$ of γ-butyrolactone at 1780 cm^{-1}, although it could not be isolated because the quantity was so small [lit.[10] 1780 cm^{-1} ($\nu_{C=O}$ of **4a**)].

Diethyl 2-ethyl-3-methyl glutarate (**5**) had bp 105–107° (2 mm); $n^{25}D$ 1.4302; ir (CCl_4) 1735 cm^{-1}; nmr (CCl_4) τ 8.75 (t, 6), 9.07 (t, 3), 9.07 (d, 3), 5.93 (q, 4), 7.9 (m, 6); mass spectrum M^+ 230. *Anal.* Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.83; H, 9.53.

Diethyl 3,4-dimethyladipate (**6**) had bp 103–105° (2 mm), $n^{25}D$ 1.4353 [lit.[11] bp 103° (1.5 mm), $n^{25}D$ 1.4324]. *Anal.* Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.88; H, 9.47.

Registry No.—**1a**, 10544-63-5; *cis*-**4b**, 10150-95-5; *trans*-**4b**, 10150-96-6; **4c**, 2981-96-6; *cis*-**4d**, 34405-50-0; *trans*-**4d**, 34405-51-1; *cis*-**4e**, 34405-52-2; *trans*-**4e**, 34405-53-3; **4f**, 34405-54-4; *cis*-**4g**, 26620-41-7; *trans*-**4g**, 26704-17-6; **5**, 34405-57-7; **6**, 10348-54-6; **7**, 6776-19-8; **8**, 1617-18-1.

(9) J. W. Huffman and J. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965).
(10) *French Patent* 1,319,239 (1963); *Chem. Abstr.*, **59**, 8600*d* (1963).
(11) M. R. Ort and M. M. Baizer, *J. Org. Chem.*, **31**, 1646 (1966).

Reductive Synthesis of α,α-Dimethylphenethylamine

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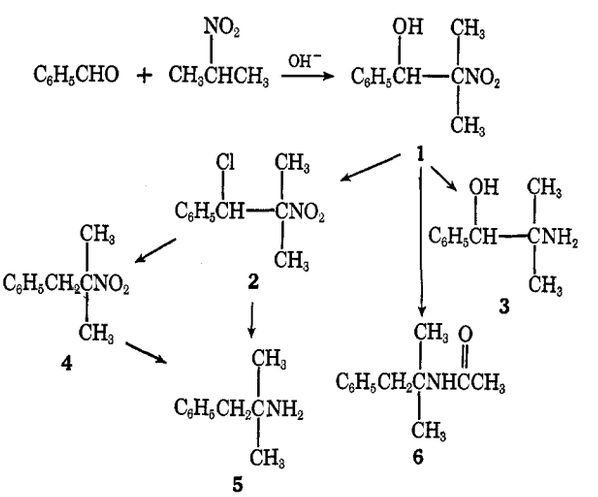
Received October 14, 1971

The pharmacological properties of the derivatives of α,α-dimethylphenethylamine (phenthermine) (**5**) have created considerable interest in the large-scale preparation of these compounds. The usual synthesis involves a Ritter reaction[1,2] between hydrogen cyanide and α,α-dimethylphenethyl alcohol or β,β-dimethylstyrene, to form the *N*-formyl derivative of **5**, and the hydrolysis of this intermediate. This reaction sequence is admirably suited for small-scale work, but, due to the hazards inherent in the use of hydrogen cyanide and in carrying out the Grignard reactions which lead to the alcohol or the styrene, it is not ideal for large-scale preparations. In view of these objections, a synthesis on the basis of a catalytic reduction, similar to those used for the derivatives of the less substituted phenethylamine[3] and α-methylphenethylamine (amphetamine),[4] would appear to be desirable.

The basic starting material for our work was α-(1-methyl-1-nitroethyl)benzyl alcohol (**1**), which can be prepared easily by the condensation of 2-nitropropane and benzaldehyde.[5] Palladium was used in all cases as hydrogenation catalyst, due to its well documented inactivity toward aromatic rings and its high effectiveness for the hydrogenolysis of benzyl groups and the reduction of aliphatic nitro groups.[6a] The variation of other reaction parameters resulted in rather selective reductions (Scheme I), which prompts us to report these in the present communication.

SCHEME I



The hydrogenation of the nitro alcohol **1** in ethanolic acetic acid over 10% palladium on charcoal yielded only the amino alcohol **3**,[7] as had already been reported by Zenitz, *et al.*[5] This is not an abnormal result, since the stabilization of a benzylic alcohol by a vicinal amino group is a well-known fact,[6b] which had already led Rosenmund and Kung[4] to the development of the tech-

(1) (a) J. J. Ritter and J. Kalish, *J. Amer. Chem. Soc.*, **70**, 4048 (1948); (b) J. J. Ritter and J. Kalish, *Org. Syn.*, **44**, 44 (1964).
(2) For a recent review of the Ritter reaction see L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 213 (1969).
(3) (a) K. Kindler, E. Brandt, and E. Gehlhaar, *Justus Liebigs Ann. Chem.*, **511**, 209 (1934); (b) J. Daley, L. Horner, and E. Withropp, *J. Amer. Chem. Soc.*, **83**, 4787 (1961); (c) D. P. Wagner, A. I. Rachlin, and S. Teitel, *Syn. Commun.*, **1**, 47 (1971).
(4) K. W. Rosenmund and E. Kung, *Ber.*, **75**, 1850 (1942).
(5) B. L. Zenitz, E. B. Macks, and M. L. Moore, *J. Amer. Chem. Soc.*, **70**, 955 (1948).
(6) (a) P. N. Rylander, "Catalytic Hydrogenation Over Platinum Metals," Academic Press, New York, N. Y., 1967, p 320; (b) 152.
(7) The nature of all the products, except **4**,[9] can be deduced unequivocally from the elemental analysis data and the nmr and ir spectra given in the Experimental Section.

nique by which nitro alcohols are reduced to amphetamines in a mixture of acetic and sulfuric acid. However, even these conditions were not satisfactory for the reduction of **1**, since up to 50° only 3 of the required 4 equiv of hydrogen were absorbed. Only at 75° was the last equivalent of hydrogen taken up, but at that temperature the product had undergone a secondary reaction, resulting in the formation of the *N*-acetyl derivative **6** of the expected amine **5**.

The lack of success in the direct reduction of **1** to **5** led us to attempt the reduction of the chloro nitro compound **2** which, aside from being prepared easily and quantitatively from **1**, should also have been much more reactive toward benzylic hydrogenolysis. The attempt to carry out the published reduction of **2** over palladium on calcium carbonate[8] failed to show any uptake of hydrogen. On the other hand, hydrogenation took place in ethanolic acetic acid over 10% palladium on charcoal, although the reaction stopped, after the hydrogenolysis of the benzylic chlorine had taken place, yielding the nitro compound **4**.[9] The cause for this stopping of the reaction was apparently a poisoning of the catalyst by the hydrogen chloride which had been generated, since we had also been unsuccessful in our attempts to reduce the nitro group of **1** in ethanolic acetic acid and over 10% palladium on charcoal, when 1 equiv of hydrogen chloride had been added to the reaction mixture. In agreement with this poisoning hypothesis, **4** was reduced to **5** when fresh catalyst was used, and **2** was reduced directly to **5** when at least 1 equiv of sodium acetate was present in the reaction mixture, *e.g.*, when the hydrogen chloride was instantaneously inactivated by formation of its sodium salt.

Experimental Section

Melting points were determined in capillaries and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 21 infrared spectrophotometer from methylene chloride solutions. Nmr spectra were recorded on a Varian Associates A-60 spectrometer with TMS as internal standard.

α-(1-Methyl-1-nitroethyl)benzyl Alcohol (1).—To a solution of 16.8 g (0.72 g-atom) of sodium in 1.3 l. of methanol was added 340.8 g (3.83 mol) of 2-nitropropane and 12.8 g (1.20 mol) of benzaldehyde, and the mixture was stirred for 24 hr at room temperature. On acidification with 720 ml of 1 *N* sulfuric acid the mixture was evaporated *in vacuo*, and the residue was taken up in 120 ml of water and extracted three times with 100 ml of ether. The combined ether extracts were washed with 10% aqueous sodium chloride, dried with anhydrous sodium sulfate, and evaporated *in vacuo*, and the residue was recrystallized in cyclohexane to yield 115 g (0.59 mol, 49%) of **1**: mp 67–68° (lit.[5] mp 64–66°); ir 1550 and 1350 cm^{-1} (NO_2); nmr ($CDCl_3$) 83.5 (s) and 91.5 (s) (CH_3), 313.0 (s, CH), 167.0 (s, OH), 438 cps (s, C_6H_5).

Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.17. Found: C, 61.65; H, 6.88; N, 7.06.

α-(1-Methyl-1-aminoethyl)benzyl Alcohol (3).—A mixture of 19.6 g (0.1 mol) of **1**, 250 ml of ethanol, 48 ml of glacial acetic acid, and 4 g of 10% palladium on charcoal[11] (50% water wet) was hydrogenated at 50° and 50 psi pressure until the hydrogen uptake ceased, resulting in the absorption of *ca.* 0.3 g-atom of hydrogen in 3 hr. After filtration, the solvent was distilled *in vacuo*, and the residue was taken up in 130 ml of 25% aqueous sodium hydroxide and extracted repeatedly with a total of 2.8 l. of ether. The ether solution was dried with anhydrous sodium sulfate and evaporated *in vacuo*, and the residue was recrystallized in ethyl acetate to yield 11.9 g (0.072 mol, 72%) of **3**: mp 96° (lit.[5] mp 99–101°); nmr ($CDCl_3$) 55.0 (s) and 65.5 (s) (CH_3), 258.5 (s, CH_3), 141.0 (OH and NH_2), 436.0 cps (s, C_6H_5).

Anal. Calcd for $C_{10}H_{15}NO$: C, 72.64; H, 9.13; N, 8.46. Found: C 72.43; H, 9.40; N, 8.35.

***N*-(α,α-Dimethylphenethyl)acetamide (6).**—A mixture of 9.8 g (0.05 mol) of **1**, 50 ml of glacial acetic acid, 3.4 ml of 95% sulfuric acid, and 2.0 g of palladium black catalyst[11] was hydrogenated at 50° and 50 psi until the hydrogen uptake ceased, resulting in the absorption of *ca.* 0.15 g-atom of hydrogen in 5.5 hr (no further absorption took place in the next 15 hr). On raising the temperature to 75° another *ca.* 0.05 g-atom of hydrogen was absorbed in 9 hr. After filtration, 5 g of sodium acetate was added to the solution, the acetic acid was distilled *in vacuo*, and the residue was taken up in 100 ml of aqueous 25% sodium hydroxide and extracted twice with 100 ml of ether. Drying the combined extracts with anhydrous sodium sulfate and distillation of the solvent *in vacuo* yielded 3.8 g (0.02 mol, 40%) of **6**: mp 89–90° (lit.[12] mp 91.5–92.5°); nmr ($CDCl_3$) 78.0 (s, CH_3), 111.5 (s, CH_3CO), 318 (NH), 182.0 (s, CH_2), 431.3 cps (C_6H_5).

Anal. Calcd for $C_{12}H_{17}NO$: C, 75.40; H, 8.96; N, 7.32. Found: C, 75.77; H, 9.11; N, 7.04.

α-(1-Methyl-1-nitroethyl)benzyl Chloride (2).—A mixture of 20 g (0.1 mol) of **1** and 100 g (0.84 mol) of thionyl chloride was boiled for 2 hr under reflux and evaporated *in vacuo*. The residue was taken up in 50 ml of methylene chloride, and the solution was washed with 75 ml of water, twice with 50 ml of 5% aqueous sodium bicarbonate (to pH 8), and 50 ml of water, dried with anhydrous sodium sulfate, and evaporated *in vacuo* to yield 21.2 g (0.1 mol, 100%) of **2**, which could be crystallized from isopropyl alcohol: mp 38–39°; ir 1549 and 1349 cm^{-1} (NO_2); nmr ($CDCl_3$) 88.0 (s) and 103.5 (s) (CH_3), 333 (s, CH), 440 cps (s, C_6H_5).

Anal. Calcd for $C_{10}H_{12}ClNO_2$: C, 56.17; H, 5.66; N, 6.56. Found: C, 55.98; H, 5.70; N, 6.59.

(2-Methyl-2-nitropropyl)benzene (4).—A mixture of 10.7 g (0.05 mol) of **2**, 125 ml of ethanol, 24 ml of glacial acetic acid, and 2.0 g of 10% palladium on charcoal (50% water wet)[11] was hydrogenated at 40–50° and 50 psi until the hydrogen uptake ceased, resulting in the absorption of *ca.* 0.1 g-atom of hydrogen in *ca.* 1 hr. After filtration, the solvent was distilled *in vacuo*, the residue was taken up in 20 ml of water and extracted twice with 100 ml ether, and the combined ether extracts were washed with aqueous sodium carbonate and with water, dried with anhydrous sodium sulfate, and evaporated *in vacuo* to yield 5.5 g (0.029 mol, 58%) of **4** as an oil: ir 1540 and 1350 cm^{-1} (NO_2); no band above 3100 cm^{-1}; nmr ($CDCl_3$) 93 (s, CH_3), 190 (s, CH_2), 432 cps (C_6H_5).

α,α-Dimethylphenethylamine (5). A.—A mixture of 5.0 g (0.027 mol) of **4**, 63 ml of ethanol, 12 ml of glacial acetic acid, and 1.0 g of 10% palladium on charcoal (50% water wet)[11] was hydrogenated at 40° and 50 psi until the hydrogen uptake ceased, resulting in the absorption of *ca.* 0.085 g-atom of hydrogen in *ca.* 3 hr. After filtration, the solvent was distilled *in vacuo*, and the residue was taken up in 30 ml of 25% aqueous sodium hydroxide and extracted three times with 300 ml of ether. The combined extracts were dried with anhydrous sodium sulfate and evaporated *in vacuo* to yield 4.1 g (0.027 mol, 100%) of **5** as an oil: hydrochloride mp 200° (lit.[8] mp 195–196°); ir identical with that of an authentic sample (Aldrich); nmr ($CDCl_3$) 66.0 (s, CH_3), 157.5 (s, CH_2), 75 (NH_2), 432 cps (s, C_6H_5).

Anal. Calcd for $C_{10}H_{16}ClN$ (hydrochloride): C, 64.60; H, 8.14; N, 7.56. Found: C, 63.58; H, 8.87; N, 7.27.

B.—A mixture of 10.7 g (0.05 mol) of **2**, 125 ml of ethanol, 24 ml of glacial acetic acid, 4.6 g (0.055 mol) of sodium acetate, and 2.0 g of 10% palladium on charcoal (50% water wet)[11] was hydrogenated at 54° and 50 psi until the hydrogen uptake ceased, resulting in the absorption of *ca.* 0.2 mol of hydrogen (90% of this uptake in 11 hr, work-up was started after 3 days under hydrogen). With the same work-up just described, the yield was 2.9 g (0.02 mol, 39%) of **5**.

Registry No.—**1**, 33687-74-0; **2**, 34405-41-9; **3**,

(8) R. S. Shelton and M. G. Van Campen, U. S. Patent 2,408,345 (1942).

(9) Compound **4** was identified by nmr (a two-proton CH_2 signal and a single signal for the two enantiotopic methyl groups) and ir (typical NO_2 bands at 1540 and 1350 cm^{-1} [10] and no bands in the NH stretching region).

(10) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, Wiley, New York, N. Y., 1958, p 298.

(11) Engelhard Industries, Inc., Newark, N. J.

(12) K-H. Boltze and H. Mühlenbein, German Patent 1,144,713 (1960).

34405-42-0; **4**, 34405-43-1; **5**, 122-09-8; **5** HCl, 1197-21-3; **6**, 5531-33-9.

Acknowledgment.—We wish to acknowledge the support of Dr. J. B. Ziegler and helpful discussions with Mr. L. Dorfman, whose staff we thank for microanalyses and spectra.

The Conformation of 1,4-Dihydro-1-naphthoic Acid. II. The Nuclear Magnetic Resonance Spectrum of the Heptadeuterio Analog

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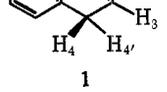
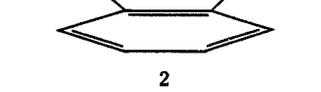
Received October 19, 1971

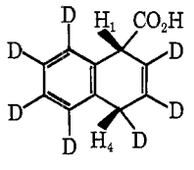
We previously reported[1] that the pmr spectrum of 1,4-dihydro-1-naphthoic acid (**1**) argued for a puckered conformation of the dihydro ring with the carboxylate group in the pseudoaxial position (see **2**) and that all nmr parameters of **1** could be determined from this study except the homoallylic coupling constants J_{14} and $J_{14'}$. We now wish to report the determination of these homoallylic parameters from the pmr spectrum of the heptadeuterio analog **3** and to present a more complete analysis of the conformation of **1**.



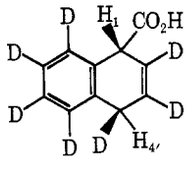
1



2



3a (cis)



3b (trans)

The heptadeuterio compound **3** was synthesized in a three-step sequence from perdeuterionaphthalene (see Experimental Section). The deuterium-decoupled pmr spectrum of **3** demonstrated an approximate 50:50 mixture of the *cis*- and *trans*-dihydro epimers (**3a** and **3b**) from the approximately equal areas corresponding to H_4 and $H_{4'}$. The H_4 and $H_{4'}$ signals were split into doublets, directly giving $J_{14} = J_{cis} = 3.84$ Hz and $J_{14'} = J_{trans} = 4.36$ Hz.[2] Since for the proposed conformation of **1** it is to be expected[3] that $J_{14} > J_{14'}$ these newly determined parameters are consistent with our previous contention that the carboxylate group was pseudoaxial.[1]

This completion of the determination of the pmr parameters for **1** allows a fuller analysis of the conformation of **1**. The similar values of J_{14} and $J_{14'}$ strongly suggest the dihydro ring is nearly flat.[4] Furthermore, a closer inspection of the previously determined parameters[1] of **1** also indicates the dihydro ring is not strongly puckered. First, if the dihydro ring of **1** were a true boat, the dihedral angle involving H_3 and $H_{4'}$ would be near 90° and $J_{34'}$ should be much less than the observed value of 2.44 Hz.[6] Second, the allylic coupling constants allow the calculation[5] that the dihedral angle involving H_2 and H_4 is much larger than 0°.[7] Third, the absolute value of $J_{44'}$[1] is suspiciously large for a highly puckered system,[8] and is much more consistent with a nearly planar ring. Thus, it appears that the conformation of **1** is a "flattened boat" in which the dihydro ring is only slightly puckered and that the pmr data for **1** lead to conclusions consistent with work for other 1,4-cyclohexadienes, in which it has been proposed that this system is planar or only slightly puckered.[9]

Experimental Section

Nmr spectra were recorded on a JEOL PS-100 spectrometer, using tetramethylsilane as the internal standard and deuteriochloroform as the solvent. Deuterium-decoupling was done with a JEOL deuterium radiofrequency oscillator JNM-RH-D, in conjunction with a JEOL heteronuclear decoupler JNM-SD-HC. Melting points were determined by a Thomas-Hoover melting point apparatus. All deuterated compounds were analyzed by pmr and were found to have a minimum isotopic purity of 98%.

Naphthalene-d_8 (minimum isotopic purity of 98%) was purchased from Diaprep, Inc., Atlanta, Ga.

1-Bromonaphthalene-d_7 was synthesized from naphthalene-d_8 in the fully developed bromination procedure[10] to give a 62% yield (9.78 g), bp 95–112° (0.5 mm) [lit.[10] bp 132–135° (12 mm), 1-bromonaphthalene].

1-Naphthoic acid-d_7 was synthesized from the bromo precursor by the usual Grignard procedure[11] to give an 88% yield (7.37 g), mp (H_2O) 155–159° (lit.[12] mp 159–160°, 1-naphthoic acid).

2,3,4,5,6,7,8-Heptadeuterio-1,4-dihydro-1-naphthoic acid (3) was prepared by the Birch reduction of the perdeuterionaphthoic precursor in the previous manner[1] to give a 73% yield (1.79 g), mp (hexane) 86–88° (lit.[13] mp 86°, **1**).

Registry No.—**1**, 5111-73-9; **3a**, 34405-19-1; **3b**, 34405-20-4.

Acknowledgment.—Acknowledgment is made to the Robert A. Welch Foundation (Grant No. B-325) and to North Texas State University for a Faculty Research Grant for support of this work. In addition, appreciation is extended to Dr. S. Sternhell and M. Barfield for stimulating discussions and suggestions for analysis of the data.

(1) J. L. Marshall and T. K. Folsom, *J. Org. Chem.*, **36**, 2011 (1971).

(2) The methine signal (H_1) was also split into a doublet with J_{obsd} = 4.1 Hz, but resolution was not sufficient to distinguish the two J values.

(3) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960); M. Barfield, *ibid.*, **48**, 4463 (1968).

(4) The Barfield INDO treatment[5] predicts that, for a flat dihydro ring, $J_{14'}/J_{14}$ = 1.12 and that this ratio increases with increased puckering to 3.3 for a true boat (S. Sternhell, private communication). The determined ratio is actually 1.14.

(5) M. Barfield, *J. Amer. Chem. Soc.*, **93**, 1066 (1971).

(6) K. L. Williamson and W. S. Johnson, *ibid.*, **83**, 4623 (1961); M. Karplus, *J. Chem. Phys.* **30**, 11 (1959); S. Sternhell, *Quart. Rev., Chem. Soc.*, **23**, 236 (1969); A. A. Bothner-By, S. Castellano, S. J. Ebersole, and H. Gunther, *J. Amer. Chem. Soc.*, **88**, 2466 (1966).

(7) It can be predicted[5] from the pmr data[1] of 1,4-dihydro-1-naphthoic acid that the dihedral angle involving H_2 and H_4 is ~52° and that involving H_2 and H_4 is ~68°.

(8) M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, **85**, 1899 (1963).

(9) H. Oberhammer and S. H. Bauer, *ibid*, **91**, 10 (1969); M. J. Bennett, J. T. Purdham, S. Takada, and S. Masamune, *ibid.*, **93**, 4063 (1971); R. J. Jandacek and S. H. Simonsen, *ibid*, **91**, 6663 (1969).

(10) H. T. Clarke and M. R. Brethen, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 1932, p 121.

(11) J. L. Marshall, K. C. Erickson, and T. K. Folsom, *J. Org. Chem.*, **35**, 2038 (1970).

(12) A. A. Morton, J. B. Davidson, T. R. P. Gibb, Jr., E. L. Little, E. F. Clarke, and A. G. Green, *J. Amer. Chem. Soc.*, **64**, 2250 (1942).

(13) K. Von Auwers and K. Moller, *J. Prakt. Chem.*, **109**, 144 (1925).