

(prepared by direct alkylation), m.p. 60.5–61.7°, melted 59.5–60.5°.

1,3-Dibenzyl-2,3-dibromoindane.⁶ From 3 g. (10 mmole) of dibenzylindene there was obtained 1.4 g. (3.07 mmole, 30%) of 1,3-dibenzyl-1,2-dibromoindane, m.p. 99–100° (dec., heated at a rate of 1°/min.) (reported⁶ 103–104°).

3-Benzyl-1-benzylideneindene from 1,3-dibenzyl-2,3-dibromoindane.⁶ From 0.75 g. (1.64 mmole) of 1,3-dibenzyl-2,3-dibromoindane in 3 ml. of pyridine there was obtained 0.25 g. (0.85 mmole, 52%) of yellow 3-benzyl-1-benzylideneindene, m.p. 137.6–138.7°.

1-Benzylideneindane (III). Fourteen and one-half grams (0.125 mole) of indene was refluxed with a solution of 5.2 g. (0.040 mole) of sodium benzylate in 22.7 g. (0.21 mole) of benzyl alcohol (made by adding 0.92 g. of sodium to 27 g. of benzyl alcohol) in the presence of 1.0 g. of UOP nickel for 16 hr. Two volumes of benzene were added, the mixture filtered, washed with water, and dried over sodium sulfate. Distillation of the benzene solution gave a fraction b.p. 148–185° (1 mm.). Upon standing for one week crystals deposited. Three recrystallizations from acetone-water and then two from ethanol-water afforded 0.20 g. (0.00097 mole, 0.8%) of colorless product, m.p. 73.4–74.4°.

9-Dimethylaminoethylfluorene (IV). To 42 g. (0.252 mole) of fluorene and 2 g. of Raney nickel in 250 ml. of *p*-cymene was added a solution of 38.6 g. (0.348 mole) of sodium dimethylaminoethylate in 167 ml. of dimethylaminoethanol (made by adding 8.0 g. of sodium to 202 ml. of dimethylaminoethanol). A condenser and Dean-Stark trap were attached to the flask and the contents were heated at reflux for 16 hr. The cooled reaction mixture was extracted with 1:1 hydrochloric acid, the aqueous layer basified and then extracted with benzene. After washing the benzene layer with water and drying it, it was distilled and redistilled to give a purified fraction, b.p. 134–137° (2 mm.).

9-Diethylaminoethylfluorene (V). This alkylation reaction was carried out in the same manner, except that a Soxhlet extractor filled with barium oxide was used in place of the Dean-Stark trap to remove the water. The pure product was vacuum distilled and boiled at 167–169° (1 mm.).

The *methiodides* and the *picrates* of IV and of V were prepared according to standard procedures.¹² From 1.471 g. of IV, 2.251 g. of methiodide was obtained and from 0.975 g., 1.201 g. of picrate. From 1.207 g. of V, 0.966 g. of methiodide

was obtained and from 1.112 g., 1.315 g. of picrate. The methiodides were first recrystallized from acetone, then from water and finally from ethanol-ethyl acetate (1:8). The picrates were recrystallized twice from ethanol and once from methanol. The yields (see Table) are for the final products.

9-Ethoxyethylfluorene (VI). To 42 g. (0.252 mole) of fluorene in 200 ml. of *p*-cymene was added a solution of 39 g. (0.348 mole) of sodium ethoxyethylate in 160 ml. of ethoxyethanol (made by adding 8.0 g. of sodium to 194 ml. of ethoxy ethanol). A Soxhlet extractor filled with barium oxide and reflux condenser were attached and the contents were heated under reflux for 16 hr. After washing the cooled reaction mixture with water, dilute hydrochloric acid, and water again, the aqueous layer was extracted once with benzene. The combined organic layers were concentrated and vacuum distilled twice to give the product fraction, b.p. 145–150° (1 mm.).

Reaction of fluorene with methoxyethanol. The same procedure as that of the other ether alkylation was used except that on vacuum distillation a white solid crystallized from a yellow liquid. After crystallization from acetone, the white solid melted 112–113°. A mixture melting point with fluorene gave no depression. Only fluorene could be isolated in a pure state, the liquid always containing some fluorene. The yellow liquid did not have any other peaks on infrared analysis.

Spectra. Infrared spectra were obtained as liquid films and in potassium bromide pellets with a Perkin-Elmer Infrared Spectrophotometer, Model 21, using sodium chloride optics. Nuclear magnetic resonance spectra were recorded on a Varian Associates 40-Megacycle Nuclear Magnetic Resonance Spectrometer. Methylene chloride was the solvent and water the reference. Ultraviolet spectra were obtained on a Beckman DK-2 Ultraviolet Spectrophotometer using *iso*-octane as solvent.

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[CONTRIBUTION FROM THE MCPHERSON CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

A New Method for Introducing a Two Carbon Acid Side Chain into Ketones

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The alkali-catalyzed condensation of glyoxylic acid, or esters thereof, with α -tetralone (and other α -tetralones) to yield 1-keto-1,2,3,4-tetrahydro-2-naphthylideneacetic acid, III (and similar acids), is described. The reasons for assigning a trans structure to III are given. The reductions of III to 1,2,3,4-tetrahydro-2-naphthylacetic acid, V, and to the cyclopropanecarboxylic acid, VI, are described.

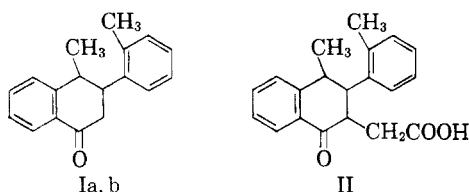
Several methods have found use in the conversion of compounds containing a cyclohexanone

moiety into compounds containing an acetic acid side chain adjacent to the carbonyl function. One method involves conversion of cyclohexanone to cyclohexanone glyoxalate; decarbonylation to 2-carbethoxycyclohexanone; alkylation to ethyl 2-keto-1-carbethoxy-1-cyclohexylacetate; hydrolysis;

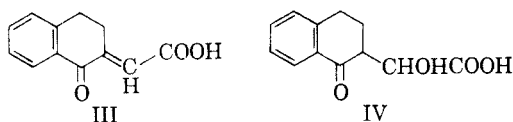
(1) This research was supported in part by a grant from the National Science Foundation and formed part of the Ph.D. thesis of W. C. Sagar, O.S.U., 1958, and C. C. Cochrane, O.S.U., 1951.

and decarboxylation to 2-keto-1-cyclohexylacetic acid.² Another method involves conversion of cyclohexanone to the enamine,³ followed by treatment with ethyl bromoacetate and subsequent hydrolysis to yield ethyl 2-ketocyclohexylacetate.⁴ Another method involves chlorination of cyclohexanone to α -chlorocyclohexanone, reaction of this with sodiomalonic ester, and subsequent hydrolysis and decarboxylation.⁵

In all of these methods, several steps are needed and the over-all yields are not good. In view of this fact and also because these methods might be difficult of accomplishment in certain projected synthetic work, we sought an alternate method of introducing a two carbon side chain acid group adjacent to a ketonic group. Specifically, we were interested in converting I to II⁶ or to an acid comparable to II in which the ketonic carbonyl had been reduced to a methylene group. However, since supplies of the isomeric ketones, I, were small, preliminary studies on a new method were carried out on α -tetralone.



The new method consists of the condensation of glyoxylic acid, or an ester thereof, with a ketone under alkaline conditions to yield an unsaturated ketoacid.⁷ When applied to α -tetralone, 55–60% yields of 1-oxo-1,2,3,4-tetrahydro-2-naphthylideneacetic acid, III, were obtained together with small yields of α -hydroxy-1-oxo-1,2,3,4-tetrahydronaphthylacetic acid, IV. Yields similar to those obtained with α -tetralone were obtained with 7-methyl- α -tetralone.



In preliminary experiments 2-ethylhexyl glyoxylate and *n*-butyl glyoxylate were used. However, in later work, aqueous alkaline solutions

(2) See F. A. Kuehl, R. P. Linstead, and B. A. Orkin, *J. Chem. Soc.*, 2213 (1950) for a review of this method. Also, R. Ghosh, *J. Indian Chem. Soc.*, 12, 601 (1935) and N. N. Chatterjee, *J. Indian Chem. Soc.*, 12, 591 (1935).

(3) Compare C. Mannich and H. Davidsen, *Ber.*, 69, 2106 (1936); F. W. Heyl and M. E. Herr, *J. Am. Chem. Soc.*, 75, 1918 (1953).

(4) G. Stork, R. Terrell, and J. Szmuszkowicz, *J. Am. Chem. Soc.*, 76, 2029 (1954).

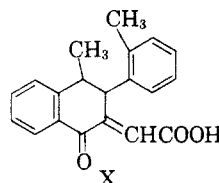
(5) W. Cocker and S. Hornsby, *J. Chem. Soc.*, 1157 (1947).

(6) The successful synthesis of II will be described in a forthcoming publication.

(7) The condensations of glyoxylic acid with malonic acid [O. Doebner, *Ber.*, 34, 53 (1901), and diethyl malonate, W. Traube, *Ber.*, 40, 4954 (1907)] have been described.

of glyoxylic acid, obtained by periodate oxidation of tartaric acid,⁸ were used directly.

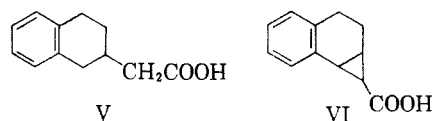
That this method may be very sensitive to steric effects is shown by the fact that the low melting isomer, Ib, m.p. 72–73°, underwent the condensation with 2-ethylhexyl glyoxylate to yield VII in 55% yield, whereas the high melting isomer, Ia, m.p. 150.6–151.8°, was recovered unchanged under comparable conditions.



The ketoacid III is written in the trans form since all attempts to prepare a cyclic pseudo ester yielded only normal ketoester. Were the *cis* structure at hand a cyclic ester should have been preparable as in the case of other *cis* α,β -unsaturated ketoacids.⁹

Clemmensen-Martin reduction¹⁰ of III afforded 1,2,3,4-tetrahydro-2-naphthylacetic acid,¹¹ V, in good yield. Similar reduction of an α,β -unsaturated ketone to a saturated hydrocarbon has been reported.¹²

Huang-Minlon reduction¹³ of III afforded the cyclopropanecarboxylic acid, VI, and the corresponding decarboxylated cyclopropane derivative in high yield. Similar conversions of α,β -unsaturated acids to cyclopropanecarboxylic acids are known.¹⁴ Heating of the methyl ester of VI with palladium-on-charcoal afforded no hydrogen under



conditions obtaining when the methyl ester of V readily yielded methyl 2-naphthaleneacetate.¹⁵

At about this point in our studies another route to the desired analogs of II was discovered¹⁶ and hence further developmental work on the glyoxylic method was terminated. The work is

(8) D. B. Sprinson and E. Chargaff, *J. Biol. Chem.*, 164, 433 (1946).

(9) R. E. Lutz, P. S. Bailey, C. Dien, and J. W. Rinker, *J. Am. Chem. Soc.*, 75, 5039 (1953).

(10) E. L. Martin, *J. Am. Chem. Soc.*, 58, 1438 (1936).

(11) See W. G. Dauben and R. Teranishi, *J. Org. Chem.*, 16, 550 (1951).

(12) H. Burton and C. W. Shoppee, *J. Chem. Soc.*, 567 (1939).

(13) Huang-Minlon, *J. Am. Chem. Soc.*, 68, 2487 (1946).

(14) See E. Vogel, *Fortschr. chem. Forsch.*, 3, 437 (1955) for references.

(15) M. S. Newman and H. V. Zahm, *J. Am. Chem. Soc.*, 65, 1097 (1943).

(16) The successful synthesis 1',9-dimethyl-1,2-benzanthracene [see J. Cason and D. D. Phillips, *J. Org. Chem.*, 17, 298 (1952)] in our laboratory will be reported soon.

being reported in a somewhat incomplete state because of its possible application to other synthetic problems.

EXPERIMENTAL¹⁷

Di-2-ethylhexyl tartrate. A mixture of 75 g. of tartaric acid, 160 g. of 2-ethylhexanol, and 160 ml. of benzene was saturated with dry hydrogen chloride and refluxed into a column topped with a phase-separating head until no more aqueous phase was formed (31 hr.). After extraction of the acid with alkali distillation afforded 164 g. (88%) of di-2-ethylhexyl tartrate, b.p. 187–201° at 0.07–0.3 mm. A middle cut, b.p. 222° at 2 mm, n_D^{20} 1.454 was taken for analysis.¹⁸

Anal. calcd. for $C_{20}H_{38}O_6$: C, 64.1; H, 10.2. Found^{18g}: C, 64.4, 64.2; H, 10.3, 10.5.

2-Ethylhexyl glyoxylate. To a cooled (15°) well stirred solution of 31.2 g. of di-2-ethylhexyl tartrate in 1 l. of alcohol was added a solution of 18 g. of sodium periodate in 340 ml. of *N* sulfuric acid. The temperature rose to 23°. After 5 min. the ice bath was removed and stirring was continued for 3 hr. The ester was extracted with ether and finally distilled to yield 19.2 g. (62%) of 2-ethylhexyl glyoxylate, b.p. 74–92° at 1 mm, n_D^{20} 1.451. This material afforded pure ester, b.p. 70–71° at 1 mm., n_D^{20} 1.442, with little loss on redistillation. About 25% of di-2-ethylhexyl tartrate was recoverable by distillation of the higher boiling fractions.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.5; H, 9.8. Found^{18c}: C, 64.5, 64.4; H, 9.8, 10.0.

The *2,4-dinitrophenylhydrazone* melted at 96–108° after recrystallization from alcohol.

Anal. Calcd. for $C_{18}H_{22}O_6N_4$: C, 52.5; H, 6.1; N, 15.3. Found^{18c}: C, 52.8; H, 6.2; N, 15.3.

1-Oxo-1,2,3,4-tetrahydro-2-naphthylideneacetic acid, III. To a cooled suspension of 4.28 g. of sodium periodate partly dissolved in 0.4 ml. of concd. sulfuric acid and 24 ml. of water was added 3 g. of tartaric acid in 6 ml. of water. After 5 min. the ice bath was removed and the mixture was shaken mechanically for 25 min. at room temperature. In order 2.92 g. of freshly distilled α -tetralone, 3 g. of sodium hydroxide in 54 ml. of water, and 50 ml. of alcohol were added. After 14 hr. at room temperature the mixture was heated to 60° for 10 min., cooled, diluted with water, and extracted with ether. Acidification of the alkaline layer yielded 2.67 g. (67%) of light yellow acid, III, m.p. 184–185° (dec.). Recrystallization from alcohol afforded pure III, m.p. 184.5–185.5° (dec.), with little loss. Infrared bands at 5.87(s); 5.95(s), and 6.1(m) μ .

Anal. Calcd. for $C_{12}H_{10}O_3$: C, 71.3; H, 5.0. Found^{18c}: C, 70.9, 71.2; H, 4.7, 4.7.

From the original aqueous filtrate after III had crystallized was isolated 0.15 g. (3%) of α -hydroxy- α -(1-oxo-1,2,3,4-tetrahydro-2-naphthyl)acetic acid, IV, m.p. 183.0–184.2° (dec.), by ether extraction and crystallization from methanol.

Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.4; H, 5.5. Found^{18c}: C, 65.6, 65.7; H, 5.6, 5.7.

When a solution of 2.92 g. of freshly distilled α -tetralone, 7.44 g. of 2-ethylhexyl glyoxylate, 100 ml. of 4% aqueous sodium hydroxide, and 75 ml. of alcohol was allowed to stand at room temperature for 19 hr. and heated just to reflux for 10 min., there was isolated by a procedure similar to that described above a 64% yield of III, m.p. 181–183°, and a 4% yield of IV. Thus, since the yield is not quite as good as that starting from tartaric acid described above, the

use of esters of glyoxylic acid seems contraindicated. A similar result was obtained with di-*n*-butyl glyoxylate.¹⁹

7-Methyl-1-oxo-1,2,3,4-tetrahydro-2-naphthylideneacetic acid. A solution of 1.60 g. of 7-methyl- α -tetralone, 3.72 g. of 2-ethylhexyl glyoxylate, 50 ml. of 4% aqueous sodium hydroxide, and 60 ml. of alcohol was left for 50 hr. at 23–27°, after which it was diluted with water and extracted with ether. Acidification of the aqueous portion afforded a tan acid, m.p. 160–173° (dec.). Recrystallization from methanol yielded purified acid, m.p. 177–178° (dec.) in 58% yield. The analytical sample, m.p. 180.4–181.4° (dec.), crystallized in pale yellow needles.

Anal. Calcd. for $C_{13}H_{12}O_3$: C, 72.0; H, 5.6. Found^{18c}: C, 72.1, 72.0; H, 5.9, 5.9.

β -Phenyl- α -o-tolylbutyronitrile, VII. In the best of several runs a solution of 131 g. of *o*-tolylacetonitrile²⁰ in 200 ml. of dry toluene was rapidly added to a stirred suspension of 48 g. of sodium amide under nitrogen in toluene. The solution darkened and ammonia was evolved copiously. After heating to reflux for 1 hr. the solution was cooled, diluted with 200 ml. of dry ether, and cooled to –70°. With rapid stirring 200 g. of α -bromoethylbenzene²¹ was added. After 1 hr. the cooling bath was removed and the reaction was completed by refluxing for 1 hr. There was obtained 209 g. (89%) of crude product, b.p. 151–166° at 0.8 mm. After purification by washing with 50% sulfuric acid²² there was obtained 189 g. (80%) of VII, b.p. 168° at 1.5 mm.

Anal. Calcd. for $C_{17}H_{17}N$: C, 86.8; H, 7.3. Found^{18c}: C, 86.5; H, 7.2.

β -Phenyl- α -o-tolylbutyric acid, VIII a,b. On hydrolysis of 164 g. of VII by refluxing for 72 hr. in aqueous acetic acid containing sulfuric acid, there was obtained 173 g. (97%) of brown solid, m.p. 129–135°. Recrystallization from methanol afforded 19 g. of the higher melting racemate, VIIIA, m.p. 171.8–172.8° corr.

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.3; H, 7.1. Found^{18c}: C, 80.5; H, 7.2.

The lower melting isomer was not obtained pure by crystallization but the mixture of isomers could be used for the next step.

γ -Phenyl- β -o-tolylvaleric acid, IXa,b. In the best of many experiments the crude acid chloride, prepared from 25.4 g. of a mixture of VIIIA and VIIIB by means of purified thionyl chloride, in 50 ml. of benzene was added dropwise to a rapidly stirred ice cold ethereal solution of diazomethane, prepared from 35 g. of nitrosomethyl urea, in 500 ml. of ether. After standing for 1 hr. during which the mixture was allowed to come to room temperature the solvent was removed under vacuum and the yellow oily residue was dissolved in 200 ml. of absolute methanol. Treatment with three portions of silver benzoate-triethylamine reagent²³ for 20 min. yielded 22.5 g. of methyl ester, b.p. 146–156° at 1.2 mm. Alkaline hydrolysis yielded 20.2 g. (76%) of a mixture of crystalline acids, IXa and IXb, which could be hand sorted into colorless plates, m.p. 78–98°, of IXa and colorless needles, m.p. 113–120°, of IXb. Recrystallization of each afforded pure IXa, m.p. 100.0–101.5°, and IXb, m.p. 125.2–126.4°. It is assumed that the higher melting isomer is IXb as it was present in much the larger amount and the low melting acid, VIIIB, from the previous step was present in the larger amount.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.6; H, 7.5. Found^{18c}: (for IXa) C, 80.5; H, 7.4 (for IXb) C, 80.8; H, 7.4.

(19) F. J. Wolf and J. Weijlard, *Org. Syntheses*, **35**, 18 (1955).

(20) M. S. Newman, *J. Am. Chem. Soc.*, **62**, 2295 (1940).

(21) Prepared by addition of hydrogen bromide to styrene as described by F. Ashworth and C. N. Burkhardt, *J. Chem. Soc.*, 1791 (1928).

(22) J. R. Johnson, *Org. Syntheses*, **16**, 89 (1936).

(23) M. S. Newman and P. F. Beal, *J. Am. Chem. Soc.*, **72**, 5163 (1950).

(17) All melting points are uncorrected unless otherwise indicated.

(18) All microanalyses marked g by the Galbraith Laboratory, Knoxville, Tenn., marked c by Clark Microanalytical Laboratory, Urbana, Ill., marked k by Mrs. E. Klotz, Ohio State University.

4-Methyl-3-o-tolyl-1-tetralone, Ia, b. A mixture of 43 g. of phosphorus pentachloride and 40.0 g. of IXa,²⁴ m.p. 100–101°, in 280 ml. of benzene was allowed to react for 30 min. The mixture was then cooled in an ice bath and treated with 89 g. of stannic chloride. After 1 hr. in the cold and another at room temperature, ice and hydrochloric acid were added. After the usual work-up 33.4 g. (90%) of colorless ketone, Ia, m.p. 148.4–150.4°, was obtained. The analytical sample, m.p. 149.0–151.0°, obtained by recrystallization from alcohol, did not depress the melting point of the ketone, Ia, prepared by cyclizing the low melting, 100°, isomer, IXa, prepared as described above. In a similar way, IXb, m.p. 125–126°, was cyclized to Ib, m.p. 72.6–73.4°, in 89% yield. Thus the high melting acid, IXb, gives the low melting ketone, Ib, on cyclization.

Anal. Calcd. for C₁₈H₁₈O: C, 86.4; H, 7.3 Found: (for 73° isomer)* C, 86.6; H, 7.2. (for 151° isomer)° C, 86.6; H, 7.0.

4-Methyl-1-oxo-3-o-tolyl-1,2,3,4-tetrahydro-2-naphthylideneacetic acid, X. To a well stirred solution of 1.06 g. of Ib and 1.57 g. of 2-ethylhexylglyoxylate in 40 ml. of alcohol was added dropwise over 50 min. 20 ml. of 4% aqueous sodium hydroxide. After 1 hr. at room temperature and 0.5 hr. at 40–60° the cooled solution was diluted with water and extracted with ether. Acidification of the aqueous solution yielded 0.88 g. of pale yellow acid, m.p. 187–189° (dec.), while 0.29 g. (27%) of starting ketone was recovered from the ether extracts. Recrystallization of the acid from ethanol yielded 0.70 g. (55%) of X, m.p. 200.7–202.0° (dec.) (Anal. sample, m.p. 202.3–203.2° corr.). Infrared absorption: 5.90(s), 5.95(s), 6.08(m).

Anal. Calcd. for C₂₀H₁₈O₃: C, 78.4; H, 5.9. Found: C, 77.9, 77.8; H, 6.0, 6.1.

Esterification studies on III. Esterification of III by refluxing with methanol and sulfuric acid for 3 hr. yielded the methyl ester in 95% yield as yellow crystals, m.p. 102.0–103.5°. The analytical sample melted at 103.8–104.7° corr., and had infrared absorption bands at 5.79(s), 5.93(s), and 6.08(m) μ (compare bands of III).

Anal. Calcd. for C₁₃H₁₂O₃: C, 72.2; H, 5.6 Found: C, 72.2, 72.2; H, 5.6, 5.6.

Esterification of III with one equivalent of ethereal diazomethane²⁵ yielded the same methyl ester described above, as determined by mixed melting point and infrared absorption.

Esterification by adding the crude acid chloride of III, prepared with phosphorus pentachloride in benzene, and having infrared absorption bands at 5.65(m) and 5.94(s) μ, to methanol containing dissolved urea²⁶ yielded the same

methyl ester as described above as determined by mixed melting point and infrared absorption.

1,2,3,4-Tetrahydro-2-naphthaleneacetic acid, V. A rapidly stirred mixture of 10.0 g. of III, 67 g. of freshly amalgamated zinc, 80 ml. of concd. hydrochloric acid, 23 ml. of water, and 100 ml. of toluene was held at reflux for 24 hr.²⁷ There was isolated 7.58 g. (81%) of colorless acid, V, m.p. 83.5–86.0°, by usual methods (including decolorization with carbon). A pure sample, m.p. 88.3–88.8°, agreeing in melting point with that reported,¹¹ was analyzed.

Anal. Calcd. for C₁₂H₁₄O₂: C, 75.8; H, 7.4. Found: C, 75.7, 75.7; H, 7.6, 7.6.

The methyl ester of V, m.p. 43.2–43.5°, was prepared with diazomethane.

Anal. Calcd. for C₁₃H₁₆O₂: C, 76.4; H, 7.9. Found: C, 76.8, 76.6; H, 8.1, 8.1.

On heating 0.5 g. of the above methyl ester over 0.03 g. of 20% palladium-on-charcoal at 215–308° during 30 min., there was obtained, after hydrolysis, 2-naphthaleneacetic acid,¹⁵ m.p. and mixed m.p., 140.7–141.7°, absorption, 5.84 μ(s).

1a,2,3,7b-Tetrahydro-1-cyclopropa(a)naphthalene-carboxylic acid, VI, and 1a,2,3,7b-tetrahydrocyclopropa(a)naphthalene, VIII. A solution of 4.04 g. of III, 3 g. of sodium hydroxide, 3 ml. of 98% hydrazine, and 45 ml. of diethyleneglycol was heated at reflux for 1 hr. The temperature was then brought to 200° by allowing the water to distill and the solution was refluxed for 3 hr. The crude acid fraction, (2.27 g. m.p. 147–158°) was esterified with diazomethane in methanol to yield 1.92 g. (79% of a faintly yellow oil, b.p. 130–135° at 2 mm. n_D²⁰ 1.561. Redistillation afforded an analytical sample of the methyl ester of VI, b.p. 130° at 2 mm, n_D²⁰ 1.560, infrared absorption at 5.92(s) and 9.92(w),²⁸ very weak at 9.83 μ.

Anal. Calcd. for C₁₃H₁₄O₂: C, 77.2; H, 7.0. Found: C, 77.1, 77.2; H, 7.1, 7.2.

From another similar run, a sample of pure acid, VI, m.p. 164.0–164.4° corr., infrared absorption, 5.92(s), 9.83 (very weak) μ was obtained.

Anal. Calcd. for C₁₂H₁₂O₂: C, 76.6; H, 6.4. Found: C, 76.4, 76.3; H, 6.5, 6.5.

From the neutral portion of the reduction mixture was isolated 0.76 g. (26%) of VIII. The analytical sample boiled near 60° at 2 mm, n_D²⁰ 1.5688, infrared absorption, 9.81(m).²⁸

Anal. Calcd. for C₁₁H₁₂: C, 91.6; H, 8.4. Found: C, 91.9, 91.7; H, 8.6, 8.6.

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(24) The sample of XIa used in this preparation was prepared by a different method (see ref. 6).

(25) Prepared according to F. Arndt, *Org. Syntheses*, 15, 4 (1935), and standardized according to L. F. Fieser, *Experiments in Organic Chemistry*, 3rd ed., D. C. Heath and Co., Boston, Mass., 1955, p. 313.

(26) Compare M. S. Newman, and K. G. Ihrman, *J. Org. Chem.*, 23, 3652 (1958).

(27) Procedure developed by C. S. Sherman, Cooper Union, and described in L. F. Fieser *et al.*, *J. Am. Chem. Soc.*, 70, 3203 (1948).

(28) Note comments on cyclopropyl absorption, C. F. H. Allen, T. V. Davis, W. J. Humphlett, and D. W. Stewart, *J. Org. Chem.*, 22, 1291 (1957), concerning absence of the 9.8 μ band in carbonyl containing compounds.