[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

The Preparation of 5,5-Dimethylcyclopentadiene

C. F. WILCOX, JR., AND M. MESIROV

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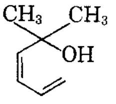
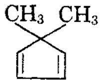
The preparation and identification of 5,5-dimethylcyclopentadiene is reported. The cyclodehydration of 2-methyl-3,5-hexadiene-2-ol is shown not to yield 5,5-dimethylcyclopentadiene.

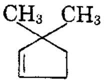
In 1939 Zonis reported that when 2-methyl-3,5-hexadiene-2-ol, I, was heated with 25% aqueous sulfuric acid for eight hours at 100° a hydrocarbon with a boiling point of 108–111° was isolated in 25% yield.[1] This hydrocarbon was assigned the structure 5,5-dimethylcyclopentadiene, II, on the basis



I



II



III

that (1) it had a molecular formula of C_7H_{10}, (2) it absorbed two equivalents of hydrogen, and (3) its molecular refractivity, 32.85, was consistent with the value of 31.40 calculated for a cyclic C_7 diene.[2] This evidence is inadequate to exclude the numerous isomeric cyclopentadiene and cyclohexadiene structures which might easily have arisen during the long exposure to hot acid. Furthermore, the reported boiling point seemed anomalous for II. As shown in Fig. 1, the boiling points of cyclopentane, cyclopentene, and cyclopentadiene decrease smoothly.[3] Similarly, the boiling points of methylcyclopentane and 3,3-dimethylcyclopentane appear to follow the same trend except for the expected elevations due to increased molecular weight. Extrapolation of the dimethyl line yields a predicted boiling point for II of 74°, *a value 35° lower than reported.*

These considerations and our interest in cyclic dienes[4] made it desirable to prepare an authentic sample of 5,5-dimethylcyclopentadiene by an independent route. A key compound in the proposed route was the known 3,3-dimethylcyclopentene, III. This compound was not prepared by one of the published sequences[5] but rather by the route shown in Fig. 2. Starting from the commercially available 2-methylcyclohexanol, the olefin, III, was prepared in 11% over-all yield. The physical properties of our III agreed closely with those reported previously.[5]

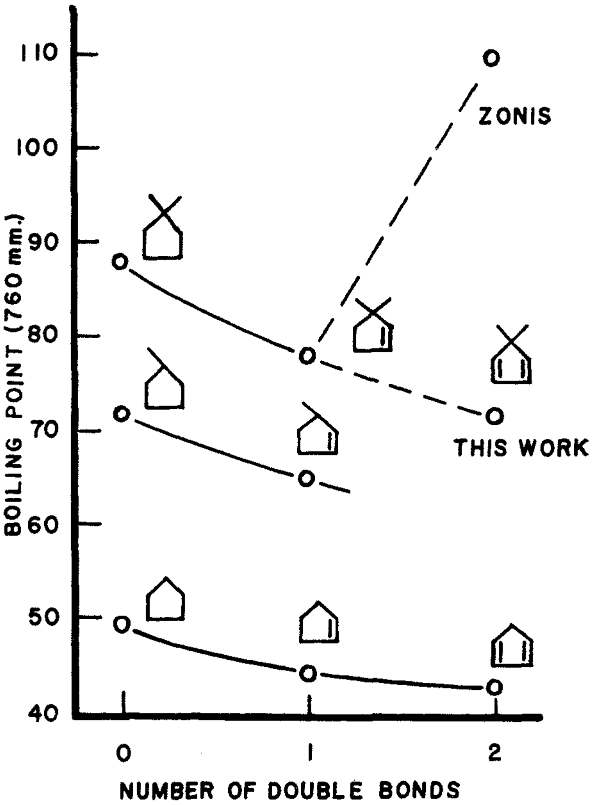


Fig. 1. The variation of boiling point of various methyl substituted cyclopentanes as a function of the number of double bonds contained in the ring

The planned scheme to convert III into II was to brominate III with *N*-bromosuccinimide and then split out a molecule of hydrogen bromide with base. Trial experiments had shown that 3-bromocyclohexene gave a 55% yield of 1,3-cyclohexadiene when heated in a 5:4 mixture of quinoline and chlorobenzene at 95° for forty-five minutes. When this reaction was applied to III by first treating it with *N*-bromosuccinimide in chlorobenzene, then adding quinoline, and heating further, the only low boiling material obtained was a 10% recovery of III.

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(1) S. Zonis, *Zhur. Obscheĭ Khim.*, **9**, 2191 (1939).

(2) This value is not corrected for the conjugation or *cis* nature of the double bonds. The exaltation for a cyclic conjugated diene is uncertain. K. Fajans, *Physical Methods of Organic Chemistry*, Vol. 1, A. Weissberger, ed., Interscience Publishers, Inc., New York, 1945, pp. 672–683.

(3) American Petroleum Institute Research Project 44 at the National Bureau of Standards. Selected Values of Properties of Hydrocarbons. Tables No. 6a and 18a. The boiling point given for 3,3-dimethylcyclopentene, III, appears to be in error. This value does not agree with that given by the references cited[5] nor with our own determination. It is perhaps significant that all of the physical properties given for III are identical with those given for 4,4-dimethylcyclopentene. The original value was used in preparing Fig. 1.

(4) Unpublished results of Mrs. R. Craig on spiro[4.4]-1,3-nonadiene.

(5) N. Kishner, *J. Russ. Phys. Chem. Soc.*, **40**, 994 (1908); G. Chavanne and G. Chivrdoglu, *Bull. soc. chim. Belg.*, **51**, 11 (1942).

TABLE I

PRODUCTS FROM THE CYCLODEHYDRATION OF 2-METHYL-3,5-HEXADIENE-2-OL

Fraction	B.P.	%	n_D^{25}	M_D	% Composition by Gas Chromatography[b]				
					A	B	C	D	E
1	64–100	6.7	1.4140	23.5	10	54	36		
2	101–104.5	8.8	1.4555	33.4		25	75		
3	104.5–107	11.1	1.4660	34.4		3	96	1	
4	107–110	7.5	1.4598	32.5			77	1	22
Zonis	108–111	25	1.4580[a]	32.9			?		
I	71.3		1.4240	31.4					

[a] This value is estimated from the n_D^{20} 1.4600 actually reported by Zonis. [b] Peak C is actually two peaks; these could not be resolved completely with helium carrier gas on dinonyl phthalate at either 104° or 76°.

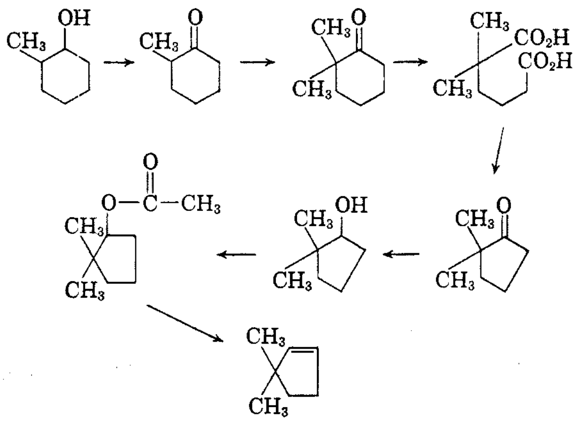

Fig. 2. Preparation of 3,3-dimethylcyclopentene

This one-step bromination-dehydrobromination was abandoned and 3,3-dimethyl-5-bromocyclopentene was prepared and isolated in 33–40% yield by use of *N*-bromosuccinimide in the lower boiling solvent, carbon tetrachloride. This easily decomposed bromide was freed of carbon tetrachloride and other gross impurities by cautious vacuum distillation at temperatures below 40°. The purified bromide was immediately heated with quinoline in such a manner that the diene distilled out of the reaction flask as it was formed. The hydrocarbon thus obtained (60%–80% yield) was shown to be 5,5-dimethylcyclopentadiene, II, by the following chain of evidence: (1) the isolated hydrocarbon was at least 99% pure as measured by vapor phase chromatography, (2) the presence of a *cis*-diene was indicated by an ultraviolet maximum at 250 mμ (log ε 3.45) which was very similar to that of spiro [4.4]-1,3-nonadiene,[4] λ_{max} (ethanol) 254 mμ, log ε 3.44, (3) it formed Diels-Alder adducts of the expected composition with maleic anhydride and *N*-phenylmaleimide, (4) the NMR showed only two types of hydrogen in a ratio of 3:2 with an unresolved vinyl peak similar to that of spiro [4.4]-1,3-nonadiene,[4] (5) under conditions where cyclopentadiene (Enjay, 95%) liberated 93% of the theoretical amount of ammonia from sodamide in dry tetrahydrofuran, this hydrocarbon liberated at most only 1%, (6) the hydrocarbon could be reduced with hydrogen to 1,1-dimethylcyclopentane, which was identical in every way with that obtained from the known 3,3-dimethylcyclopentene, III.

With an authentic sample of 5,5-dimethylcyclopentadiene, II, now available for comparison, the dehydration of I was repeated according to the recipe of Zonis[1] to see if it would provide a shorter route to II. The steam-distillable organic products thus obtained were redistilled and separated into four arbitrary fractions. The composition of these fractions as indicated by gas chromatography and their physical properties are given in Table I. The properties reported by Zonis as well as those of 5,5-dimethylcyclopentadiene are also given for reference. From these data it is difficult to be certain of the structure of the original Zonis product except that it was not 5,5-dimethylcyclopentadiene. The low boiling fraction 1 was shown to be free of 5,5-dimethylcyclopentadiene by the total absence of infrared bands at 10.55, 10.62, and 13.40 μ, which were present as medium to strong peaks in the authentic sample. Fraction 1 also failed to yield a maleic anhydride or *N*-phenylmaleimide derivative.

EXPERIMENTAL[6]

2-Methylcyclohexanone. This compound was prepared from 2-methylcyclohexanol according to the chromic acid oxidation procedure of Ouderkirk and Meinwald[7] in 83% yield; b.p. 160–162° (745 mm.), n_D^{52} 1.4508.

2,2-Dimethylcyclohexanone. The 2-methylcyclohexanone was methylated and isolated by the procedure of King, *et al.*[8] in 52% yield; b.p. 100–102° (100 mm.), n_D^{24} 1.4451; reported, b.p. 170–171° (765 mm.), $n_D^{18.5}$ 1.4492.

2,2-Dimethyladipic acid. The oxidation of 2,2-dimethylcyclohexanone was carried out by the method of Meerwein and Unkel,[9] except that only 4 ml. of concd. nitric acid was used for each gram of ketone. The recrystallized acid was obtained in 45% yield, m.p. 85–86°; reported, m.p. 86–87°.

2,2-Dimethylcyclopentanone. In a 500-ml. distilling flask was placed an intimate mixture of 6 g. of barium hydroxide and 120 g. of 2,2-dimethyladipic acid and a thermometer was inserted in the flask so that the bulb was 4 cm. from the bottom. The flask was heated gradually in a silicone oil bath to 280° and the heating was continued until only a dry residue remained (about 90 min.). The organic distillate

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[6] Analyses performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[7] J. Ouderkirk, Ph.D. dissertation, Cornell University, 1957.

[8] F. E. King, T. J. King, and J. G. Topliss, *J. Chem. Soc.*, 919 (1957).

[9] H. Meerwein and W. Unkel, *Ann.*, **376**, 152 (1910).

was separated from the aqueous phase and the aqueous layer was saturated with sodium chloride and extracted once with ether. After the combined organic materials had been dried over potassium carbonate, the ether was stripped off through a short column. On distillation the residue gave 57 g. (74%) of 2,2-dimethylcyclopentanone, b.p. 140–143° (745 mm.), $n_D^{22.5}$ 1.4312; reported,[10] b.p. 143–144° (corr., $n_D^{19.5}$ 1.4322.

The 2,4-dinitrophenylhydrazone of the ketone melted at 144° (sharp); reported,[11] 141–141.5°.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: C, 53.42; H, 5.52; N, 19.17. Found: C, 53.43; H, 5.54; N, 18.68.

2,2-Dimethylcyclopentanol. The 2,2-dimethylcyclopentanone (32 g.) was reduced with a mixture of 11.1 g. of lithium aluminum hydride and 600 ml. of ether. The excess hydride was decomposed with 44 ml. of water and after the organic layer had been decanted, the salts were washed well with ether and the washings added to the organic layer. The ether solution was dried and the solvent distilled through a short column. The residue was distilled to yield 31 g. (95%) of alcohol; b.p. 151–152° (744 mm.), n_D^{20} 1.4532, reported,[12] b.p. 100° (110 mm.).

The p-nitrobenzoate of the alcohol melted at 90° (sharp).

Anal. Calcd. for $C_{14}H_{17}NO_4$: C, 63.85; H, 6.51; N, 5.32. Found: C, 63.93; H, 6.56; N, 5.49.

2,2-Dimethylcyclopentyl acetate. Ketene was bubbled into a solution of 16.1 g. of 2,2-dimethylcyclopentanol and 0.04 g. of *p*-toluenesulfonic acid in 45 ml. of ether. The complete conversion (about 3 hr.) was gauged by the disappearance of the hydroxyl peak (2.90 μ) in the infrared. After this time, the ether solution was extracted three times with 10% sodium carbonate solution and then dried over anhydrous magnesium sulfate. After the ether had been removed, the residue was vacuum distilled to yield 21 g. (95%) of the acetate; b.p. 84–86° (40 mm.) and 169–173° (744 mm.) $n_D^{24.6}$ 1.4303.

Anal. Calcd. for $C_9H_{16}O_2$: C, 69.19; H, 10.33. Found: C, 68.41, 70.07; H, 10.23, 10.44.

A sample of the acetate was hydrolyzed by refluxing it in 25% aqueous sodium hydroxide for 20 hr. The *p*-nitrobenzoate of the resulting alcohol melted at the same temperature as the previous sample and a mixed melting point showed no depression.

3,3-Dimethylcyclopentene. A Pyrex tube (37 cm. × 1.5 cm.) was packed with carborundum chips and heated to 525° in a jacket furnace. From a Hirschberg funnel equipped with a nitrogen inlet tube, 19.2 g. of the acetate was dropped onto the hot column at the rate of 0.25 g./min. The hot vapors issuing from the bottom of the column were collected in a Dry Ice trap and then neutralized first with a 30 ml. wash of 10% sodium carbonate solution and finally with solid sodium carbonate. After the organic material had been dried over anhydrous potassium carbonate, it was distilled and the material boiling from 76 to 86° collected. This fraction was redistilled to given an 88% yield of 3,3-dimethylcyclopentene which gas chromatography indicated to be at least 99% pure; b.p. 77.5–78.3° (760 mm.), n_D^{23} 1.4161, reported,[4] b.p. 77.6–78°, 78–78.5° (754 mm.), n_D^{20} 1.4190.

One gram of the olefin was dissolved in 10 ml. of diglyme and the solution hydrogenated over a prereduced platinum oxide catalyst in a Parr bomb under 30 pounds of hydrogen until there was no further uptake (0.95 equiv.). The catalyst was removed and the 1,1-dimethylcyclopentane was distilled from the solvent through a 12-cm. glass helices packed column. Only the low boiling fraction was collected to give about a 50% yield; b.p. 88.5° (capillary tube), n_D^{21} 1.4128, reported,[2] b.p. 87–88°, n_D^{20} 1.4136.

Attempted preparation of 5,5-dimethylcyclopentadiene. A solution of 5 g. of 3,3-dimethylcyclopentene and 9.7 g. of *N*-bromosuccinimide in 20 ml. of chlorobenzene was heated for 90 min. at 75–85° and then for an additional 45 min. at 95°. The reaction flask was cooled in an ice bath and the succinimide filtered. To the filtrate was added 25 ml. of quinoline and this solution was then heated to 220° and kept at this temperature until no more volatile material distilled (about 40 min.).

The only low boiling material thus obtained was 0.5 g. of starting olefin.

Under identical dehydrobromination conditions, 3-bromocyclohexene gave a 55% yield of 1,3-cyclohexadiene.

3,3-Dimethyl-5-bromocyclopentene. A solution of 9.3 g. of *N*-bromosuccinimide and 5 g. of 3,3-dimethylcyclopentene in 36 ml. of carbon tetrachloride was refluxed for 4 hr. After the reaction mixture had been cooled and the precipitated succinimide removed, the solvent was removed under vacuum (with a nitrogen bubbler) at 40°. The pressure was lowered and the 3,3-dimethyl-5-bromocyclopentene distilled at temperatures below 40° quickly to give a 33% yield of a slightly yellow liquid. This material was then redistilled; b.p. 39.5–40° (8.2 mm.) n_D^{27} 1.4877, d_4^{27} 1.27 g./ml., M_D (calcd. for $C_7H_{11}Br$, 1 F) 39.6, M_D (obs.) 39.8.

5,5-Dimethylcyclopentadiene. The dehydrobromination of the bromide above was carried out in a flask equipped with a cold finger filled with ethanol. In this flask was placed 4.8 g. of the bromide and 15 g. of quinoline and the solution was heated to 150° and maintained at this temperature until no more material distilled (about 15 min.). The temperature was then raised to 220° and kept there for 30 min. The product was distilled on a vacuum line at 10 mm. pressure to give a 60% yield of pure hydrocarbon, b.p. 71.3° (760 mm.), n_D^{25} 1.4240, d_4^{25} 0.7660 g./ml., λ_{max} 250 mμ (ethanol), ϵ 2,900, λ_{min} 221 mμ, ϵ 85. A gas phase infrared spectrum showed medium to strong bands at 3.27, 3.36, 3.51, 6.07, 6.80, 7.31, 7.35, 8.84, 9.25, 10.55, 10.62, 12.57, and 13.40 μ. A vapor phase chromatogram indicated that this sample of diene was at least 99% pure. The NMR spectrum (40 mc.) of the pure liquid showed two peaks in the ratio of 2.9 to 2.0 at +3.95 p.p.m. and −0.93 p.p.m. relative to methylene chloride as an internal standard. All attempts to resolve the pairs of vinyl hydrogens failed.

A sample of the diene was reduced under the same conditions used for the reduction of 3,3-dimethylcyclopentene. The hydrocarbon was identical with that obtained previously and its infrared spectrum was essentially identical with that reported in the A.P.I. tables.[3]

One fifth of a milliliter of the diene liberated less than 0.1 ml. of ammonia gas when injected into a mixture of sodamide in dry tetrahydrofuran. This corresponds to less than 0.25 mole % active hydrogen. Under these same conditions freshly cracked cyclopentadiene (95%-Enjay) liberated 93% of the theoretical amount based on the sample being pure diene.

The *N*-phenylmaleimide adduct, *7,7-dimethyl-N-phenylbicyclo[2.2.1]-5-heptene-2,3 dicarboximide,* melted at 174–175°.

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.51; H, 6.28; N, 5.05.

A maleic anhydride adduct, *7,7-dimethyl-bicyclo[2.2.1]-5-heptene-2,3-dicarboxylic anhydride,* melted at 91–92°.

Anal. Calcd. for $C_{11}H_{12}O_2$: C, 68.73; H, 6.30. Found: C, 68.57; H, 6.45.

2-Methyl-5-hexen-3-yn-2-ol. This compound was prepared by the method of Croxall and Van Hook[13] except that commercial sodamide was used instead of preparing it directly in liquid ammonia. The alcohol was obtained in 58% yield, b.p. 56–60° (13 mm.), n_D^{27} 1.4752.

2-Methyl-3,5-pentadien-2-ol. This compound was prepared

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(10) A. Haller and R. Cornubert, *Compt. rend.*, **179**, 315 (1924); see also: M. Blanc, *Bull. soc. chim.*, [4] **3**, 780 (1908) and P. Bartlett and A. Bavley, *J. Am. Chem. Soc.*, **60**, 2416 (1936) and reference 11.

(11) P. Seifert and H. Schinz, *Helv. Chim. Acta.*, **34**, 728 (1951).

(12) A. Eschenmoser and A. Frey, *Helv. Chim. Acta*, **35**, 1660 (1952).

(13) W. Croxall and J. Van Hook, *J. Am. Chem. Soc.*, **76**, 1700 (1954).

by the selective hydrogenation over Lindlar's catalyst of the triple bond of 2-methyl-5-hexen-3-yn-2-ol. The alcohol was obtained in 83% yield, b.p. 47–52° (8 mm.), n_D^{21} 1.4560; reported: 78–80° (12 mm.), n_D^{20} 1.4566.

Cyclization of 2-methyl-3,5-pentadien-2-ol. The cyclization was carried out according to the method of Zonis.[1] In a 1-l. flask was heated for 10 hr. at 100° a solution of 2-methyl-3,5-hexadiene-2-ol and 120 ml. of 25% sulfuric acid. The reaction mixture was then distilled until only a clear aqueous phase was collected. The distillate was neutralized with 10% sodium carbonate solution and the organic material separated and dried over potassium carbonate. This product was then distilled and separated into four fractions shown in Table I. This table also lists the gas chromatographic analysis and physical properties of these fractions. Fractions 1 and 3 did not show active hydrogen by the sodamide method nor did they yield maleic anhydride or *N*-phenylmaleimide derivatives.

ITHACA, N. Y.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, NORTHWESTERN UNIVERSITY]

peri-Substituted Naphthalenes. IV. The Tetrahydro-8-isopropyl-1-naphthoic Acids[1]

ROBERT L. LETSINGER AND WILLIAM J. VULLO[2]

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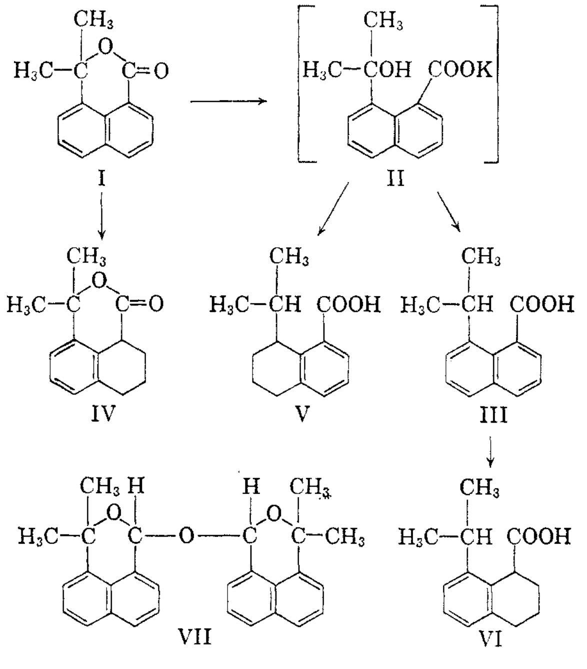
3,3-Dimethyl-1,8-naphthalide may be reduced by appropriate use of nickel-aluminum alloy and sodium metal to give tetrahydro-3,3-dimethyl-1,8-naphthalide (IV), 8-isopropyl-1-naphthoic acid (III), 5,6,7,8-tetrahydro-8-isopropyl-1-naphthoic acid (V), or 1,2,3,4-tetrahydro-8-isopropyl-1-naphthoic acid (VI). A nickel-aluminum alloy reduction was also employed in a simplified synthesis of 2-isobutylbenzoic acid. Tetrahydro acid V isomerized readily in sulfuric acid or liquid hydrogen fluoride to a neutral aldol-type product. Neither 5,6,7,8-tetrahydro-1-naphthoic acid nor 2-isobutylbenzoic acid underwent a transformation of this type under comparable conditions. The unusual lability of compound V is ascribed to the particular geometrical relationship existing between the carboxyl group and the alkyl side chain in compound V.



It has been shown that 8-isopropyl-1-naphthoic acid (III) yields an aldal (VII) when treated with sulfuric acid or hydrogen fluoride.[1] This reaction involves a hydrogen transfer from the isopropyl group to the neighboring carbonyl group. The present paper concerns the preparation and acid treatment of three related compounds—5,6,7,8-tetrahydro-8-isopropyl-1-naphthoic acid (V), 1,2,3,4-tetrahydro-8-isopropyl-1-naphthoic acid (VI), and 2-isobutylbenzoic acid (IX)—in which the relative positions of the carboxyl and isopropyl groups are similar to that in 8-isopropyl-1-naphthoic acid.

Synthesis and structure. Acids V and VI, as well as acid III and lactone IV, could be obtained by appropriate reduction of 3,3-dimethyl-1,8-naphthalide (I). The direct action of a coarse, granular grade of Raney nickel-aluminum alloy[3] on an alkaline ethanol-water solution of lactone I afforded (10%) the tetrahydrolactone (IV). This lactone was also formed, and in somewhat better yield (31%) when an ethanol solution of I was treated with sodium. By saponifying compound I with potassium hydroxide in triethylene glycol prior to addition of the alloy the course of the reaction could be altered. In this case reduction with the granular grade of alloy yielded isopropylnaphthoic acid III[1] (16–29%) and a small amount of V. When the saponification product was similarly treated with the more active, finely powdered nickel-aluminum alloy[4] in place of the granular alloy, tetrahydro acid V was the principal product (48%). Tetrahydro acid VI was prepared (57%) by reduction of acid III with sodium and boiling amyl alcohol. The isomeric tetrahydroisopropylnaphthoic acids melted at the same temperature; however, the mixture

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(1) For the previous paper in this series see R. L. Letsinger, W. J. Vullo, and A. S. Hussey, *J. Am. Chem. Soc.*, **81**, 1965 (1959).

(2) Standard Oil Company of Indiana Fellow, 1957–1958. Sinclair Oil Company Harvey Fellow, 1956–1957.

(3) Procured from the Gilman Paint and Varnish Co., Chattanooga, Tenn.

(4) Procured from the Raney Catalyst Co., Chattanooga, Tenn.