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"Trans"-2,2,6-Trimethylcyclohexanecarboxylic Acid: a Second Solid Naphthenic Acid from California Petroleum[1]

BY BILLIE SHIVE,[2] JOE HORECZY, GEORGE WASH AND H. L. LOCHTE

There have been isolated and definitely identified from petroleum six naphthenic acids: 3,3,4-trimethylcyclopentaneacetic,[3] cyclopentanecarboxylic,[4] cyclopentaneacetic,[4] 3-methylcyclopentaneacetic,[4] *dl*-1,2,2-trimethylcyclopentanecarboxylic[5] and solid 4-methylcyclohexanecarboxylic[6] acids. Since this manuscript was prepared, however, Buchman and Sargent have been able to show that von Braun's acid is not 3,3,4-trimethylcyclopentaneacetic acid.

Results reported in this paper were obtained in a continuation of the petroleum acid research on a complex mixture of acids obtained from the sodium carbonate washing of Signal Hill, California, straight run gasoline.[5,7]

Since Hancock was able to isolate camphonanic acid from the higher boiling acids through the fact that it is not esterified by treatment with methanol and dry hydrochloric acid, it seemed possible that other unesterifiable acids might be present in the acids containing eight to ten carbon atoms. Accordingly various fractions of acids boiling in the C_8 to C_{10} range were carefully fractionated and then each fraction was separately heated for twenty-four hours with methanol and dry hydrogen chloride. These operations yielded a total of 800 g. of unesterified acids. By subjecting 22 liters of still higher boiling stored material to the same treatment another 2030 g. of unesterified material was obtained.

Careful fractionation of these acids yielded 400 cc. of esters that had been dissolved in the acids, 700 cc. of liquid acids and 940 g. of acids that solidified in the receiver or in the condenser. Fractional liberation of these solid acids from their sodium salts yielded 280 g. of camphonanic acid, 500 g. of another solid acid melting 70–80°, and 100 g. of liquid acids. Purification raised the melting point of the new acid to 83°, which is close to that of an acid isolated from Iranian petroleum by Kennedy.[8] A mixture of this acid and the $C_{10}H_{18}O_2$ acid obtained by Shive, Roberts and Bailey[9] by degradation of their $C_{16}H_{25}N$ California petroleum base showed no melting point depression. Similar operations on all remaining material of the proper boiling range yielded an additional 1300 g. of acid melting above 80°, so that the total yield of the new acid from 70 liters of crude acids is 1800 g. Since the ester could not be prepared by direct esterification the acid was converted to the chloride boiling at 218.5°, from which a number of derivatives were prepared.

Since the acid could not be esterified, we were not surprised to find that the ester was equally unreactive. Refluxing for thirty-six hours with a 20% solution of potassium hydroxide in 85% alcohol yielded only a trace of acid when the solution was diluted with water and the aqueous layer was acidified. An attempt to form the amide by heating the ester with concentrated ammonium hydroxide at 125° in a sealed tube for twenty-four hours failed. While ethyl *n*-caproate was quantitatively hydrogenated at 250° in the presence of copper chromite catalyst under 4000 pounds of hydrogen, the methyl ester of the new acid was not affected under the same conditions with the same catalyst.

While these and other properties of the acid seemed to indicate that it could only be a tertiary acid, synthesis of most probable acids of the correct molecular weight threw doubt on the tertiary acid hypothesis. Two methods of distin-

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[1] From theses submitted by Billie Shive, Joe Horeczy and George Wash in partial fulfillment of requirements for the Doctor of Philosophy degree, June, 1941.

[2] Research Assistant, University Research Institute, Project No. 28.

[3] (a) von Braun, Mannes, and Reuter, *Ber.*, **66**, 1499 (1933); (b) Buchman and Sargent, private communication.

[4] Nenitzescu, Isacescu and Volrap, *ibid.*, **71**, 2056 (1938).

[5] Hancock and Lochte, THIS JOURNAL, **61**, 2448 (1939).

[6] Schutze, Shive and Lochte, *Ind. Eng. Chem., Anal. Ed.*, **12**, 262 (1940).

[7] The crude acids were donated by the Macmillan Petroleum Corporation of Long Beach, California.

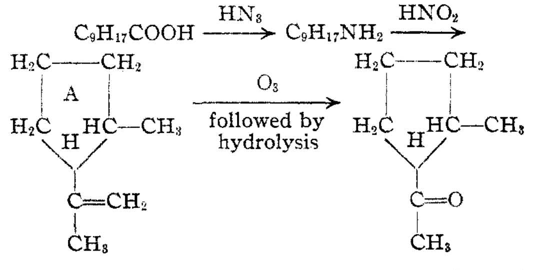
[8] Kennedy, *Nature*, **144**, 832 (1939). A sample of the Iranian acid furnished through the kindness of Dr. Kennedy has just been compared with our California acid. Melting and mixed melting points of acids and anilides agree, thus showing that Kennedy's acid is identical with the California acid.

[9] Roberts and Bailey, Paper presented before the Meeting of the Petroleum Division, American Chemical Society, April, 1939, "Structural Study of a $C_{16}H_{25}N$ Base from California Petroleum." Shive and Bailey, Papers presented before the Meeting of the Petroleum Division, American Chemical Society, April, 1940, "The Use of Ozonization in Structural Proof of Petroleum Bases." "The Structure of a $C_{16}H_{25}N$ Base from California Petroleum and Proof of its Structural Correlation with a Naphthenic Acid from California Petroleum."

guishing tertiary from secondary acids (the only possible types) have been described. Whitmore and Crooks[10] have tested and described a method which depends on the ratio of carbon monoxide to carbon dioxide evolved when an acid is heated with phosphorus pentoxide. When the new acid was tested by this method 52% of carbon monoxide and only a trace of carbon dioxide were evolved, thus indicating a tertiary acid. Whitmore and Crooks found that dineopentylacetic acid gave 30% carbon monoxide and trimethylacetic acid gave 55% carbon monoxide with other tertiary acids giving still larger amounts. The other method is von Braun's chlorine number test,[11] which is essentially a method of determining the number of alpha hydrogen atoms present. When the new acid was tested by this method one chlorine atom was introduced; so the two tests gave contradictory results. It thus seemed best to attempt to determine the structure of the acid through degradation and synthesis.

Degradation of the acid by the K. F. Schmidt method[20] to a $C_9H_{17}NH_2$ amine, treatment of the amine with nitrous acid to obtain a C_9H_{16} unsaturated naphthene, and ozonolysis of this hydrocarbon led to a known ketone, 2-methylcyclopentyl methyl ketone, which was identified as the semicarbazone.

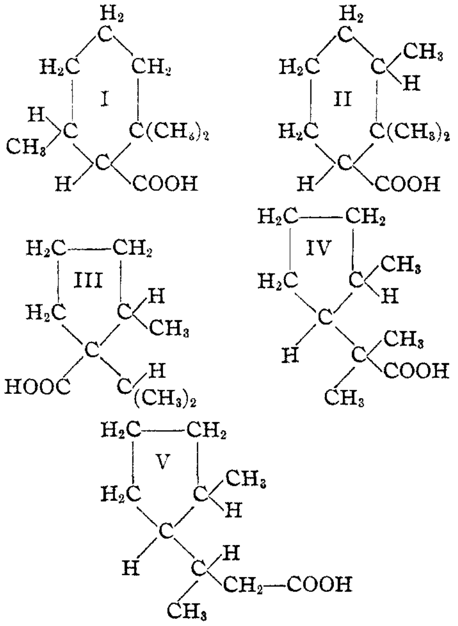
The following equations depict the steps involved in this series of reactions



Synthesis of the 2-methylcyclopentyl methyl ketone was accomplished by the action of acetyl chloride and aluminum chloride on cyclohexane, according to the method of Zelinsky and Tarassowa[12] and of Nenitzescu and Cantuniari.[13]

As the first and the last reactions employed in the degradation of the naphthenic acid to the ketone do not lead to rearranged products, only the treatment of the $C_9H_{17}NH_2$ amine with nitrous acid would be expected to lead to "abnormal" products. Whitmore[14] has proposed a general electronic concept as a common basis for interpreting intramolecular rearrangements: If a nonionic attachment between an atom such as carbon or nitrogen and a strongly electronegative atom or group is broken during a reaction, the electronegative group takes with it a complete octet of electrons, and the atom sharing the electron pair with the electronegative group thus retains only a sextet of electrons. Migration of an electron pair from an adjacent atom may result from this deficiency, thus giving rise to rearranged products.

If the acid is assumed to be of cyclopentyl or cyclohexyl structure, isolation of 2-methylcyclopentyl methyl ketone as a degradation product limits the possibilities to the following structures, assuming Whitmore's mechanism for probable rearrangements holds on treatment of the amine with nitrous acid:



The theoretical rearrangements that may take place to form 1-isopropenyl-2-methylcyclopentane when the amines corresponding to 2,2,6-trimethyl- and 2,2,3-trimethylcyclohexanecarboxylic acids (structures I and II, respectively) are treated with nitrous acid are identical. Action of nitrous acid on 2,2,6-trimethylcyclohexylamine could produce this hydrocarbon according to the following proposed mechanism: (1) decomposition of the diazonium compound leaves carbon 1

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[10] Whitmore and Crooks, THIS JOURNAL, **60**, 2078 (1938).

[11] Von Braun, Jostes and Münch, *Ann.*, **453**, 113 (1927); von Braun, *ibid.*, **490**, 108 (1931).

[12] Zelinsky and Tarassowa, *ibid.*, **508**, 115 (1934).

[13] Nenitzescu and Cantuniari, *ibid.*, **510**, 269 (1934).

[14] Whitmore, THIS JOURNAL, **54**, 3274 (1932).

with a sextet of electrons; (2) the electron pair between carbon 2 and 3 shifts to carbon 1 with carbon 3; (3) loss of a proton of one of the methyls attached to carbon 2 then produces 1-isopropenyl-2-methylcyclopentane.

The mechanism involved in the action of nitrous acid upon the amine corresponding to 1-isopropyl-2-methylcyclopentanecarboxylic acid (III) is similar, except the second step involves the migration of an electron pair with the hydrogen atom from the adjacent carbon atom of the isopropyl group. Subsequent loss of a proton results in the formation of the desired hydrocarbon. No rearrangement mechanism is necessary for α,α,2-trimethylcyclopentaneacetic acid (IV) and β,2-dimethylcyclopentanepropionic acid (V). Though not conforming to this mechanism, 1-isopropylcyclohexanecarboxylic acid and 1,2,2-trimethylcyclohexanecarboxylic acid were considered as remote possibilities.

In view of the behavior of the acid and of its ester and its amide the most probable structures were considered to be those with a carboxyl tied to a tertiary carbon, and these, of the possible structures listed, were first studied.

Synthesis of the two tertiary acids,[15] 1-isopropyl-2-methylcyclopentanecarboxylic (III) and α,α,2-trimethylcyclopentylacetic acid (IV) gave acids and derivatives with melting points much lower than those of the new petroleum acid. Since two geometrical isomers of each should exist, it was thought at first that the wrong form might have been synthesized by the procedures employed. However, elimination of the substituted acetic acid was evident upon examination of the hydrocarbons produced by the pyrolysis of the phosphate of the $C_9H_{17}NH_2$ amine in an atmosphere of carbon dioxide,[16] as neither 1-isopropenyl-2-methylcyclopentane nor 1-isopropylidine-2-methylcyclopentane was isolated from the hydrocarbon mixture. The first should have yielded 2-methylcyclopentyl methyl ketone and the second acetone on ozonolysis, but neither of these compounds could be detected. The remote possibilities, 1-isopropylcyclohexanecarboxylic acid and 1,2,2-trimethylcyclohexanecarboxylic acid were eliminated by synthesis and comparison of constants.[15]

As the melting points of the synthesized form of 1-isopropyl-2-methylcyclopentanecarboxylic acid and its derivatives were much lower than those of the new petroleum acid (for example, the anilide of the synthetic acid melted 70° lower than that of the petroleum acid), it was considered unlikely that the difference in properties could be due to *cis–trans* isomerism.

Since the chlorine number test indicated a secondary acid and since von Braun showed that certain branched secondary acids may be very difficult to esterify,[17] 2,2,6-trimethylcyclohexanecarboxylic acid was prepared by the method of Wallach.[18] He obtained an acid melting at 82–83° on hydrogenating α-cyclogeranic acid with palladium as catalyst. In our synthesis, Adams catalyst was employed and a product melting at 74–75° was obtained instead of the acid reported by Wallach. A mixture of this acid and the petroleum acid melted at 50–55°. Hydrogenation with palladium on barium sulfate yielded a mixture melting at 40–44° which gave very little depression in a mixed melting point determination with the natural acid, indicating that possibly the mixture represented one near the eutectic of *cis* and *trans* forms of the acid. On the hypothesis that the acid melting at 74–75° was the lower melting (probably *cis*) modification, a sample of it was heated for twenty-four hours with an equal weight of glacial acetic acid and a few drops of concentrated hydrochloric acid at 180–190°. The resulting mixture on repeated recrystallization from petroleum ether melted at 82–83° and showed no depression when mixed with the natural acid. The anilides of the two acids also proved to be identical, thus *establishing the structure of the acid as 2,2,6-trimethylcyclohexanecarboxylic acid.* As the higher melting acid it is tentatively assigned the *trans* configuration.

Experimental

I. Isolation of a New $C_{10}H_{18}O_2$ Acid.—Hancock[5] and other workers in this Laboratory fractionated the original 70 liters of crude petroleum acids first through a 15-liter steel still and then through 4-ft. glass marble-packed columns. Fractions boiling in the range of C_8 to C_{10} acids (90–110° at 3 mm.) were refractionated to yield the fractions shown in Table I.

Similar treatment of various distillation residues obtained in earlier work with the lower boiling acids yielded finally a total of over 38 liters of acids with approximately the properties shown in Table I. Similar fractions from these fractionations were combined on the basis of atmospheric boiling point and index of refraction, and each frac-

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[15] Shive, Crouch and Lochte, THIS JOURNAL, **63**, 2979 (1941).

[16] Von Braun and Kurtz, *Ber.*, **67**, 227 (1934).

[17] Von Braun and Fischer, *ibid.*, **66**, 101 (1933); von Braun and Kurtz, *ibid.*, **70**, 1224 (1937).

[18] Wallach, *Ann.*, **418**, 57 (1919).

TABLE I

Fraction number	Volume, cc.	B. p., °C., 3 mm.	n^{20}D
1	275	93–100	1.4349
2	2265	100–103	1.4374
3	1865	103–104	1.4384
4	8650	104–108	1.4390
5	1725	108–109	1.4398
6	1005	109–110	1.4405
7	665	110–111	1.4415
8	585	111–112	1.4426
9	175	.....	1.4437
10	1300	.....	1.4450
11	1250	113–114	1.4480

tion was then separately refluxed for twenty-four hours with 1.5 volumes of absolute methanol containing 2% by weight of dry hydrochloric acid. The reaction mixture was then diluted with water and the ester and aqueous layers separated. The ester layer was washed with 500-cc. portions of 0.7 *N* sodium carbonate solution and finally with 500 cc. of cold 0.1 *N* sodium hydroxide. Each washing was effected by stirring the mixture for at least two hours. The water layer and alkali washing were combined, 40 g. of sodium hydroxide was added, and the mixture was evaporated to one-tenth the original volume before liberating the acids. These recovered acids were again subjected to the esterification procedure just described. The first treatment yielded 39,438 cc. of esters and 4006 cc. of unchanged acids from 38,670 cc. of acids. The second treatment of the 4006 cc. yielded 2230 cc. of esters and 2030 cc. of unchanged acids. A third treatment, again for twenty-four hours, yielded another 400 cc. of esters and left 1600 cc. of acids. They were fractionated at 8 mm. through a 6 ft. Berl saddle-packed column to obtain material which on chilling with ice–salt mixture partially solidified to yield 940 g. of solid acids. These were converted to a solution of their sodium salts, which was then cooled and treated with carbon dioxide. Solid acids were filtered off as liberated, and the remaining acids were finally fractionally liberated by dilute hydrochloric acid. This procedure yielded 280 g. of Hancock's *dl*-camphonanic acid,[6] 500 g. of solid acid melting at 70–80° and 100 cc. of liquid acids. Recrystallization of the new acid from petroleum ether raised its melting point to 83°, from which it could not be raised by recrystallization from acetone, dilute alcohol, or by fractional precipitation of its silver salts.[19] The melting point of a mixture of this acid with the $C_{10}H_{18}O_2$ acid obtained by Roberts and Bailey[9] by degradation of the $C_{16}H_{25}N$ base from California petroleum showed no depression.

Since most of the new acid was obtained from the higher boiling fractions of acids of Table I, all remaining acids boiling just above these acids were treated in the same manner and another 1300 g. of the new acid was obtained.

II. Structure of the $C_{10}H_{81}O_2$ Acid

Reaction Rate

Reactivity of the Methyl Ester.—The following series of experiments indicate the extreme unreactivity of the methyl ester:

(1) Under 4000 lb. pressure at 250° for two hours in the presence of copper–chromium oxide, hydrogen converted ethyl *n*-caproate quantitatively to *n*-hexyl alcohol. The methyl ester did not react with hydrogen during six hours under these conditions in the presence of the same catalyst.

(2) The methyl ester was boiled for thirty-six hours with a 20% solution of potassium hydroxide in 85% ethanol. The mixture was diluted with water and the layers separated. Acidification of the aqueous layer yielded only a trace of the acid.

(3) Ammonolysis of the methyl ester by concentrated ammonium hydroxide at 125° in a sealed tube for twenty-four hours produced none of the corresponding amide.

Attempted Application of the Whitmore Method of Distinguishing between Primary, Secondary and Tertiary Aliphatic Acids.—Into a three-neck, 200-cc., round-bottom flask provided with a gas inlet, a reflux condenser and dropping funnel, was placed 12 g. of phosphorus pentoxide. The apparatus used is described by Whitmore and Crooks.[10] The flask was heated to 110°, the system swept out with nitrogen gas, and the condenser connected to a gas-collecting graduated cylinder. The gas collected was analyzed by an Orsat apparatus. The acid (2,2,6-trimethylcyclohexanecarboxylic) was added according to directions given by Whitmore and Crooks. The results of the experiments performed are tabulated below, together with typical results on primary, secondary and tertiary aliphatic acids as obtained by the earlier workers.

TABLE II

Acid used	Gas evolved, % of theoretical CO	CO_2
2,2,6-Trimethylcyclohexanecarboxylic	52	0.15
1,2,2-Trimethylcyclopentanecarboxylic	90	0.05
Cyclohexanecarboxylic	19	1.00
Aliphatic acids:[10]		
n-Butyric	1.1	5.5
Stearic	0.0	13
Isobutyric	8.8	1.7
Di-*n*-propylacetic	27.5	0.6
Dineopentylacetic	30	0.5
Trimethylacetic	55	0.2
Methyl-*t*-butylneopentylacetic	90	0.2

Von Braun Chlorine Number Test.—To 5 g. of the ethylamide derivative of the $C_8H_{18}O_2$ acid was added 10.5 g. of phosphorus pentachloride dissolved in 12 cc. of anhydrous benzene and the mixture was refluxed for thirty minutes. The resulting mixture was distilled under 15 mm. pressure and the product boiling at 128–132° was collected (5 cc.). This product was fractionated under 8 mm. pressure through a micro-column and there was obtained 4 cc. of product boiling at 96°.

Anal. Calcd. for $C_{12}H_{21}NCl_2$: Cl, 28.30. Found: Cl, 32.1.

The high percentage of chlorine was undoubtedly due to the presence of phosphorus pentachloride or some of its hydrolysis products. The dichloro compound was hydrolyzed by boiling with water for one hour. Upon cooling, the hydrolysis mixture yielded a solid which was recrystallized from petroleum ether to obtain long needles melting at 84°; yield, 50% of theoretical.

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(19) Schutze, Shive and Lochte, *Ind. Eng. Chem., Anal. Ed.* **12**, 264 (1940).

Anal. Calcd. for $C_{12}H_{22}ONCl$: Cl, 15.3. Found: Cl, 15.38.

$$\text{Chlorine number} = \frac{x}{100 - x}\,\frac{M}{35.457} \times 100$$

where $x = 15.38$ and M is 231.75. The chlorine number of the ethylamide derivative is 120, as calculated by this formula, thus indicating that this acid is secondary.

Attempts to hydrolyze the chlorinated ethylamide derivative into the chloro acid produced a mixture of unsaturated compounds from which no acid could be separated.

Action of Hydrazoic Acid on the $C_{10}H_{18}O_2$ Acid.—According to the modified K. F. Schmidt method described by Oesterlin,[20] 100 g. of the acid was converted into the amine by the action of hydrazoic acid. This method gave a 90% yield of the $C_9H_{17}NH_2$ amine characterized by Roberts and Bailey.[9]

The **picrate** prepared in the manner described by these authors melted after recrystallization from dilute alcohol at 226–227°, and a mixed melting point of this picrate and a sample of the picrate from their base showed no depression.

The **acetyl derivative** of the amine was prepared by treating an anhydrous ether solution of the amine with acetyl chloride. After two recrystallizations from dilute alcohol and two from petroleum ether, respectively, the product appeared as very small needles, m. p. 133–134°.

Anal. Calcd. for $C_{11}H_{21}ON$: N, 7.64. Found: N, 7.60.

Exhaustive Methylation of the $C_9H_{17}NH_2$ Amine.—The N,N-dimethyl derivative of the $C_9H_{17}NH_2$ amine was prepared by heating a mixture of 10 g. of amine, 18 g. of formalin and 10 g. of formic acid in a sealed tube for twelve hours at 120°. Upon diluting the mixture with water, adding dilute sodium hydroxide until basic, extracting with ether, drying with solid potassium hydroxide and fractionating, the methylated amine with the following physical properties was obtained: b. p. 204–205° at 746 mm., d^{20}_4 0.8543, n^{20}_D 1.4604.

The **picrate** prepared for the purpose of analysis by adding aqueous picric acid to a sulfur dioxide solution of the base appeared as medium-sized needles, m. p. 262–263°, when it was recrystallized from dilute alcohol.

Anal. Calcd. for $C_{17}H_{26}O_7N_4$: N, 14.06. Found: N, 13.92.

The methylated amine was heated in a sealed tube for twelve hours at 100° with a slight excess of methyl iodide in a double volume of ethyl alcohol. The resulting quaternary ammonium iodide was recrystallized from ethyl alcohol to obtain small plates, m. p. 272–273°; yield, 80% of theoretical.

The quaternary ammonium hydroxide was prepared by digesting this iodide with an aqueous suspension of freshly prepared silver oxide. Upon steam distillation of the quaternary base the product collected proved to be the original N,N-dimethyl derivative of the $C_9H_{17}NH_2$ amine, with none of the expected hydrocarbon.

Action of Nitrous Acid on the $C_9H_{17}NH_2$ Amine.—In an equal volume of glacial acetic acid diluted with enough water to dissolve the acetate, 35 g. of the $C_9H_{17}NH_2$ amine was treated at 0° with an equivalent of sodium nitrite which was added over a period of thirty minutes, and the mixture then was allowed to stand two hours. By subjecting the mixture to steam distillation, 26 g. of neutral material was obtained which was extracted with dilute hydrochloric acid to remove any unreacted amine, dried over sodium, and fractionated at atmospheric pressure through a 3-foot rotary column to obtain 10 g. of a C_9H_{16} unsaturated hydrocarbon, b. p. 140° (750 mm.), d^{20}_4 0.7998, n^{20}_D 1.4452.

Anal. Calcd. for C_9H_{16}: C, 87.01; H, 12.90. Found: C, 86.78; H, 13.20.

Five grams of unchanged amine was recovered from the reaction mixture. The higher-boiling fractions consisted of a mixture of alcohol and unsaturated hydrocarbons as characterized by the following physical properties: b. p. 140–195° (750 mm.), d^{20}_4 0.7998–0.8180, n^{20}_4 1.4452–1.4482. Attempts to prepare the acetyl, benzoyl and 3,5-dinitrobenzoyl derivatives of the higher-boiling fractions were unsuccessful since in all cases dehydration of the alcohol occurred.

Ozonization of the C_9H_{16} Hydrocarbon.—A stream of ozonized oxygen was passed through a 20% solution of 10 g. of the C_9H_{16} hydrocarbon in carbon tetrachloride for twenty-four hours at 0°. The ozonide was hydrolyzed by the addition of 5% hydrogen peroxide followed by refluxing for one hour. The resulting mixture was extracted with 10% sodium hydroxide, and the solvent removed from the carbon tetrachloride layer. The neutral residue which gave a positive iodoform test was dissolved in dilute alcohol, and following addition of an excess of semicarbazide hydrochloride and an equal weight of sodium acetate, standing and diluting with water, white flakes crystallized from the solution. After several recrystallizations from alcohol and one from benzene, the semicarbazone melted at 160–161°; yield, 4 g. of purified semicarbazone.

Anal. Calcd. for $C_9H_{17}ON_3$: N, 22.95. Found: N, 23.11.

This product was identified as 2-methylcyclopentyl methyl ketone which was synthesized from cyclohexane and acetyl chloride with the aid of aluminum chloride according to the methods described by Zelinsky and Tarassowa[12] and by Nenitzescu and Cantuniari.[13] A mixed melting point determination of the semicarbazone of this synthetic ketone and that obtained by degradation of the $C_{10}H_{18}O_2$ acid showed no depression.

Acidification of the alkaline extract produced only a small amount of acidic material, which probably was 2-methylcyclopentanecarboxylic acid arising from the oxidation of the 2-methylcyclopentyl methyl ketone by alkaline peroxide.

Amine Phosphate Method

Distillation of the $C_9H_{17}NH_2$ Amine Phosphate.—To 20 g. of the amine of the $C_{10}H_{18}O_2$ acid there was added 1.1 times the theoretical amount of phosphoric acid dissolved in 100 cc. of water according to the procedure of von Braun and Kurtz.[16] The excess water was evaporated under 15 mm. pressure at 100° and the dry phosphate was distilled. The distillate was washed with dilute hydrochloric acid to obtain 5 g. of unchanged amine. The remainder of the distillate consisted of unsaturated hydrocarbons which

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(20) Oesterlin, *Angew. Chem.*, **45**, 536 (1932).

were washed well with dilute sodium hydroxide solution, then with water, and finally dried over sodium.

Fractionation through a 15-plate rotary column yielded eight fractions with: boiling point 142.5 to 150.5 (754 mm.), $n^{20}D$ 1.4496 to 1.4560, and d^{20}_4 0.8056 to 0.8148.

Anal. on Fraction 2. Calcd. for C_9H_{16}: C, 87.01; H, 12.90. Found: C, 86.93; H, 13.02.

Ozonization of the C_9H_{16} Hydrocarbons.—Fractions 1–4 were dissolved in 30 cc. of petroleum ether and into this solution was passed a stream of ozonized oxygen at 0° for twenty-four hours. The ozonide was hydrolyzed by refluxing with water containing a few drops of 5% hydrogen peroxide. The hydrolysis mixture was extracted with dilute sodium hydroxide solution to obtain 3 g. of acidic material. After evaporation of the petroleum ether there was obtained 2 g. of non-acidic material which formed a di-semicarbazone melting at 206°. The absence of 2-methylcyclopentyl methyl ketone showed that 1-isopropenyl-2-methylcyclopentane was not present in the hydrocarbon mixture.

Another portion of hydrocarbons similar to those indicated in Table III was prepared. Ozonization was carried out as described above. Part of the ozonide was hydrolyzed in the presence of zinc dust. The hydrolysis product was distilled into an alcoholic solution of benzaldehyde. The benzaldehyde solution containing the first portions of the distillate was made basic with dilute sodium hydroxide and boiled for one minute. The test for the presence of acetone was negative. A di-carbonyl compound yielding the same di-semicarbazone mentioned above was isolated from the remainder of the hydrolysis products of the ozonide decomposed with zinc dust. The other portion of the ozonide was decomposed in the presence of a large excess of alkaline hydrogen peroxide. No non-acidic material was obtained, indicating that the dicarbonyl compound obtained above must be either a keto-aldehyde or a di-aldehyde; and in the presence of an excess of hydrogen peroxide is oxidized to either a keto-acid or a dicarboxylic acid.

The presence of a neutral carbonyl compound in the first hydrolysis mixture may be attributed to an insufficient amount of hydrogen peroxide.

Synthesis of the $C_{10}H_{18}O_2$ Acid

α-Cyclogeranic Acid.—Following the procedure of Bernhauer and Forster,[21] α-cyclogeranic acid, m. p. 106–107°, was prepared by oxidizing citral with silver oxide in an alkaline solution to obtain geranic acid and treating this product six hours with 95% formic acid.

"*cis*"-2,2,6-Trimethylcyclohexanecarboxylic Acid.—In glacial acetic acid, 15 g. of α-cyclogeranic acid rapidly consumed the calculated quantity of hydrogen at atmospheric pressure upon being shaken in the presence of Adams platinum catalyst. After removal of the catalyst, the product was precipitated by addition of water and, upon filtering and drying, it melted at 60–62°. Recrystallization from petroleum ether gave the pure "*cis*" isomer in the form of colorless rhombic crystals, m. p. 74–75°; yield, 12 g.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.55; H, 10.80.

A mixture of this "*cis*" isomer and the $C_{10}H_{18}O_2$ acid isolated from petroleum melted at 50–55°.

Hydrogenation of α-cyclogeranic acid dissolved in glacial acetic acid in the presence of palladium upon barium sulfate produced a mixture of geometric isomers, melting at 39–43°, which on mixing with the $C_{10}H_{18}O_2$ acid isolated from petroleum depressed to 38–45°, indicating that palladium hydrogenation resulted in the formation of a mixture approaching the composition at the eutectic point of the two geometric isomers.

"*trans*"-2,2,6-Trimethylcyclohexanecarboxylic Acid.—To obtain the "*trans*" isomer, 5 g. of "*cis*"-2,2,6-trimethylcyclohexanecarboxylic acid was heated in a sealed tube with 2.5 g. of glacial acetic acid and 5 drops of concentrated hydrochloric acid at 180–190° for twenty-four hours. Addition of water precipitated an oil which readily crystallized upon agitating the liquid. After drying, these crystals melted at 67–69°. Recrystallization from petroleum ether yielded colorless microscopic needles, m. p. 82–83°, yield, 3 g.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.42; H, 10.67.

A mixed melting point determination upon this acid and the $C_{10}H_{18}O_2$ acid from petroleum showed no depression.

"*trans*"-2,2,6-Trimethylcyclohexanecarboxanilide.—The acid chloride of the "*trans*" isomer was prepared by adding a small excess of thionyl chloride to 2 g. of the "*trans*" acid; after standing several hours, removal of excess thionyl chloride was effected by heating in a partial vacuum. To the resulting acid chloride in 5 cc. of anhydrous ether, two equivalents of aniline were added, and after standing several hours, the excess aniline was removed by extraction with dilute hydrochloric acid and then with water. Evaporation of the ether layer and recrystallization of the resulting anilide from benzene produced colorless microscopic needles, m. p. 191–192°; yield, 1.5 g.

Anal. Calcd. for $C_{15}H_{23}ON$: N, 5.71. Found: N, 5.82.

A mixture of this anilide and the same derivative obtained from the natural acid showed no depression in melting point, 191–192°.

Following the identical procedure employed in the preparation of the above anilide, the "*cis*" acid upon treatment with thionyl chloride and aniline gave a mixture of products from which only the "*trans*" anilide could be isolated. The crude mixture, m. p. 168–178°, upon recrystallizing once from benzene and twice from alcohol yielded the "*trans*" anilide, m. p. 191–192°, which showed no depression in melting point when mixed with the anilide prepared from the "*trans*" isomer. Therefore, isomerization to the "*trans*" form must have taken place on treatment of the "*cis*" isomer with thionyl chloride.

III. Derivatives

2,2,6-Trimethylcyclohexanecarboxylchloride.—To 100 g. of the acid was added 1.2 molecular equivalents of thionyl chloride. The reaction mixture was allowed to remain at room temperature for one hour, after which time it was refluxed for the same length of time. Distillation yielded a product with the following physical characteristics: b. p. 218.5° (747 mm.); d^{20}_4 1.0195; $n^{20}D$ 1.4703; yield, 106 g.

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[21] Bernhauer and Forster, *J. prakt. Chem.*, **147**, 199 (1936).

Methyl 2,2,6-Trimethylcyclohexanecarboxylate.—The methyl ester was prepared by the action of an excess of absolute methanol upon the acid chloride. When evolution of hydrogen chloride had ceased at room temperature, the mixture was refluxed for thirty minutes, after which it was cooled, transferred to a separatory funnel, washed well with sodium carbonate solution and water, dried over anhydrous sodium sulfate and fractionated under reduced pressure to yield a compound with the following physical characteristics: b. p. 210° (747 mm.); d^{20}_4 0.9421; $n^{20}\text{D}$ 1.4481; yield, 95% of theoretical.

Ethyl 2,2,6-Trimethylcyclohexanecarboxylate.—The ethyl ester was prepared by the procedure described for the methyl ester; b. p. 225° (747 mm.); $n^{20}\text{D}$ 1.4465; d^{20}_4 0.9285.

Phenyl 2,2,6-Trimethylcyclohexanecarboxylate.—The action of phenol upon the acid chloride resulted in the formation of the phenyl ester; b. p. 275° (750 mm.); $n^{20}\text{D}$ 1.5060; d^{20}_4 1.0142.

2,2,6-Trimethylcyclohexanecarboxamide.—Into 5 g. of the acid chloride dissolved in 50 cc. of dry ether was bubbled dry ammonia gas at 10°. Water was added to dissolve the ammonium chloride formed and the mixture was filtered. Recrystallization of the crude product once from petroleum ether yielded cubical crystals melting at 191°; yield, 80% of the theoretical. No amide could be formed by treating the acid chloride with concentrated ammonium hydroxide. A mixed melting point determination on this amide with the one obtained by Shive and Bailey[9] showed no depression.

2,2,6-Trimethylcyclohexanecarboxethylamide.—An excess of anhydrous ethylamine dissolved in benzene was added to 32 g. of the acid chloride. The mixture was allowed to stand overnight, washed well with dilute hydrochloric acid, then with dilute sodium carbonate solution and finally with water. The benzene layer was evaporated to dryness and the residue recrystallized from dilute ethanol. Two recrystallizations from petroleum ether-benzene mixture gave a product which appeared as needles melting at 126°; yield, 90% of the theoretical.

Anal. Calcd. for $C_{12}H_{23}ON$: N, 7.11. Found: N, 7.12.

2,2,6-Trimethylcyclohexanecarboxanilide.—The action of a benzene solution of aniline upon the acid chloride by a procedure analogous to the preparation of the ethylamide derivative produced a crude product which after recrystallization from petroleum ether-benzene mixture yielded long needles melting at 192°.

Anal. Calcd. for $C_{16}H_{23}ON$: N, 5.71. Found: N, 5.73.

2,2,6 - Trimethylcyclohexanecarboxy - *p* - toluidide.—The *p*-toluidide prepared from the acid chloride and *p*-toluidine yielded needles from petroleum ether and melted at 193°.

Anal. Calcd. for $C_{17}H_{25}ON$: N, 5.40. Found: N, 5.36.

2,2,6-Trimethylcyclohexanecarboxy-*p*-bromoanilide.—The *p*-bromoanilide was prepared in the same manner as the anilide. Recrystallization from a petroleum ether-benzene mixture yielded small needles melting at 216°.

2,2,6-Trimethylcyclohexanecarbonitrile.—To 47 g. of the amide was added 94 g. of phosphorus pentoxide and the mixture was subjected to distillation. The distillate was dissolved in benzene and washed with water, then with dilute sodium hydroxide and finally with water, after which it was dried over calcium chloride. The product was fractionated to give a liquid with the following physical constants: b. p. 221-2° (748 mm.); $n^{20}\text{D}$ 1.4550; d^{20}_4 0.8730; yield, 42 cc.

Anal. Calcd. for $C_{10}H_{17}N$: C, 79.40; H, 11.35. Found: C, 79.4; H, 11.47.

Summary

"*trans*" - 2,2,6 - Trimethylcyclohexanecarboxylic acid has been isolated and identified among the unesterifiable naphthenic acids in California petroleum. Derivatives have been prepared, its degradation products have been studied, and finally the acid was synthesized.

This secondary acid and its methyl ester and amide behave as highly hindered compounds.

The Whitmore method for distinguishing types of aliphatic acids fails when applied to this acid.

AUSTIN, TEXAS

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