[CONTRIBUTION NO. 240 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Normal and Abnormal Alkylation of 2-Methylcyclopentyl Methyl Ketone

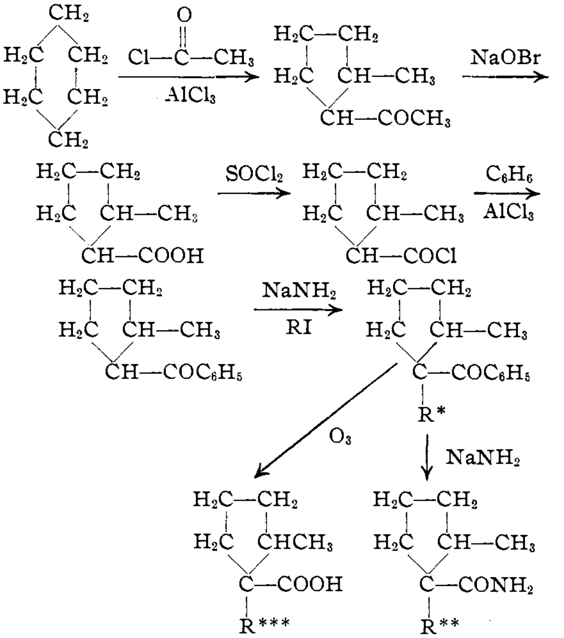
BY GEORGE WASH,[1] BILLIE SHIVE[2] AND H. L. LOCHTE

During the course of research upon tertiary naphthenic acids in this Laboratory, the most important method of synthesis of these acids has been alkylation of either ketones or ketoesters. Since alkylation of methyl cyclopentyl ketones introduces the alkyl into the methyl instead of cyclopentyl group, the use of cyclopentyl phenyl ketones is indicated even though it is difficult to remove the phenyl group after the desired alkylation has been secured. As only methylation of substituted cyclopentyl phenyl ketones has been reported, the effect of size of the group in this type of alkylation seemed worthy of investigation.

The general method for alkylation of ketones with sodium amide and an alkyl halide was developed by Haller and Bauer[3] who reported that the larger the alkylating group the more difficult the alkylation and the lower the yields. These workers[4] also investigated the action of sodium amide on ketones containing no hydrogen in the alpha position, benzophenone (from which benzamide was obtained) being the first such ketone studied.

Applying the work of Haller and Bauer to alicyclic compounds, Bouveault and Levalois[5] effected a partial synthesis of fencholic acid, 1-methyl-3-isopropylcyclopentanecarboxylic acid, through alkylation of 3-isopropylcyclopentyl phenyl ketone (derived from camphenilone) by means of sodium amide and methyl iodide; they cleaved the alkylated molecule with sodium amide to obtain the amide of fencholic acid. Similarly Shive, Horeczy, and Lochte[6] synthesized 1,2,3,3-tetramethylcyclopentanecarboxylic acid from 2,3,3-trimethylcyclopentyl phenyl ketone which was obtained from dihydroisolauronoyl chloride. These last investigators found that, in addition to sodium amide cleavage of the ketone, the phenyl group could be removed in small yields by ozonolysis to give the acid directly.

In this investigation 2-methylcyclopentyl phenyl ketone was treated with an equimolecular quantity of sodium amide in various inert solvents to form the sodium derivative which in turn was treated with the alkyl iodide. The following series of equations represent the synthesis of 2-methylcyclopentyl phenyl ketone (according to the method of Nenitzescu, *et al.*[7]) and its subsequent alkylation and cleavage to form the tertiary acid or amide where R^* represents methyl, ethyl, propyl, and isopropyl, R^{**} represents methyl and ethyl, and R^{***} represents propyl and isopropyl groups.



With benzene as the solvent, alkylation of 2-methylcyclopentyl phenyl ketone proceeded in accordance with the results of Haller and Bauer,[3] who reported that increasing the size of the group slowed down the reaction and lowered the yield. The same difficulties were encountered in cleaving the alkylated ketone with sodium amide: the ketones alkylated with the smaller groups gave good yields of the expected amide and those containing larger groups gave poor yields. In the case of the isopropyl- and *n*-propyl-alkylated ketones, cleaving with sodium amide produced a mixture from

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[1] From the thesis submitted by George Wash in partial fulfillment of requirements for the Doctor of Philosophy Degree, June, 1941.

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[3] Haller and Bauer, *Compt. rend.*, **148**, 70 (1909); **152**, 551 (1911).

[4] Haller and Bauer, *ibid.*, **147**, 842 (1908).

[5] Bouveault and Levalois, *Bull. soc. chim.*, (4) **7**, 968 (1910).

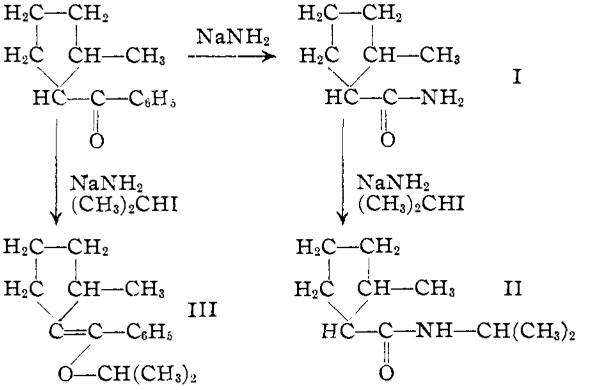
[6] Shive, Horeczy and Lochte, THIS JOURNAL, **62**, 2744 (1940).

[7] Nenitzescu and Ionescu, *Ann.*, **491**, 189 (1931).

which no crystalline amide could be obtained. Hence, even though yields were poor, ozonolysis of the benzene ring was employed to obtain the desired acid.

When xylene was used as a solvent in the alkylation, a series of peculiar reactions occurred to form a group of unexpected compounds. In the case of alkylation with isopropyl iodide, 2-methylcyclopentanecarboxamide (I), N-isopropyl-2-methylcyclopentanecarboxamide (II), and 2-methylcyclopentylidene-(phenyl)-methyl isopropyl ether (III) were formed. No 1-isopropyl-2-methylcyclopentyl phenyl ketone was formed.

This series of reactions may be depicted as follows



This is the first case reported in which a ketone containing an alpha hydrogen has been cleaved by sodium amide. The 2-methylcyclopentylidene-(phenyl)-methyl isopropyl ether was identified by ozonolysis to obtain 2-methylcyclopentanone and isopropyl benzoate, the latter being hydrolyzed and the parts identified.

Similar results were obtained in the case of alkylation with both ethyl and *n*-propyl iodide in xylene; however, when toluene was used as a solvent, both normal alkylation and abnormal alkylation occurred. As the alkylations were carried out at the boiling point of the solvent, it seems likely that the change in the course of the reaction was a temperature rather than a solvent effect. The higher temperature in this case favored the abnormal reaction while lower temperatures produced the normal alkylation product. Such a large change in course of reaction was not expected from the small difference in temperature.

While textbooks usually state that either C-alkylation or O-alkylation may occur in any given case depending on conditions, direct O-alkylation rarely has been reported. Claisen[8] studied O-alkyl compounds and methods of synthesis and found that they are not rearranged to C-alkyl compounds (except in case of allyl ethers), while the corresponding change in case of O-acyl compounds proceeds readily. In conformity with his findings, we find that our O-alkyl compounds are stable. Attempts to change the abnormal to the normal products by refluxing with potassium hydroxide and attempts to change the normal to abnormal products by very slow fractionation through the 3-foot rotary column failed. The study of this reaction and of the behavior of these ethers is being continued.

Experimental

I. Normal Alkylation of 2-Methylcyclopentyl Phenyl Ketone

2-Methylcyclopentyl Phenyl Ketone.—Three hundred grams of 2-methylcyclopentyl methyl ketone was prepared from 4.2 l. of cyclohexane and 630 g. of acetyl chloride in presence of anhydrous aluminum chloride according to the methods described by Zelinsky and Tarassowa[9] and by Nenitzescu and Canturiari.[10] This 300 g. of ketone was converted to 224 g. of 2-methylcyclopentanecarboxylic acid by treatment with sodium hypobromite as described by Nenitzescu,[7] and the acid was converted to 224 g. of the acid chloride by the thionyl chloride method. The acid chloride was mixed with 190 cc. of anhydrous benzene and added slowly to a mixture of 237 g. of anhydrous aluminum chloride and 620 cc. of anhydrous benzene in a flask equipped with a reflux condenser and a dropping funnel. After addition of the acid chloride, the reaction mixture was refluxed over a water-bath for one hour.

The contents of the flask were dissolved in dilute hydrochloric acid containing ice and were extracted with ether. The ether layer was washed with a dilute sodium carbonate solution to remove any remaining acid chloride or acid. After drying over anhydrous sodium sulfate, the ketone was fractionated *in vacuo* to yield 210 g. of product with the following physical properties: b. p. 281° at 760 mm.; $n^{20}{}_{\rm D}$ 1.5350; $d^{20}{}_4$ 1.0179. Nenitzescu, *et al.*,[11] reported the following physical properties for this ketone: b. p. 160-162° at 36 mm.; $n^{18}{}_{\rm D}$ 1.5380; $d^{18}{}_4$ 1.0255.

1-Isopropyl-2-methylcyclopentyl Phenyl Ketone.—To a flask equipped with a mercury-sealed stirrer, a reflux condenser with a calcium chloride tube at the end and a dropping funnel with a long stem was added 7 g. of sodium amide in 100 cc. of anhydrous benzene. Thirty grams of 2-methylcyclopentyl phenyl ketone was added (with stirring) through the dropping funnel, the mixture was heated on an oil-bath to such temperature that the evolution of ammonia was not too vigorous and then the reaction mixture was refluxed for six hours, at which time the evolution of ammonia had ceased. After the mixture had

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[8] Claisen, *Ber.*, **26**, 2729 (1893); **29**, 1005 (1896); **29**, 2931 (1896); **31**, 1021 (1898); **33**, 3778 (1900); **45**, 3157 (1912).

[9] Zelinsky and Tarassowa, *Ann.*, **508**, 115 (1933).

[10] Nenitzescu and Canturiari, *ibid.*, **510**, 269 (1934).

[11] Nenitzescu and Ionescu, *ibid.*, **491**, 209 (1931).

TABLE I

C-ALKYLATED 2-METHYLCYCLOPENTYL PHENYL KETONES

Alkyl	Reflux required, hr.	Yield, %	B. p., °C., 760 mm.	$n^{20}D$	d^{20}_4	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
CH_3[a]	6	49	288	1.5368	1.0247	83.12	83.04	8.97	9.05
C_2H_5[b]	18	56	304	1.5350	1.0184	83.28	83.17	9.32	9.45
n-C_3H_7[c]	36	27	312	1.5290	1.0016	83.43	83.39	9.63	9.69
i-C_3H_7	90	26	315	1.5360	1.0178	83.43	83.40	9.63	9.64

[a] Oxime, m. p. 161–162°. *Anal.* Calcd.: N, 6.42. Found: N, 6.48. [b] Oxime, m. p. 115–116°. *Anal.* Calcd.: N, 6.06. Found: N, 6.09. [c] Oxime and semicarbazone could not be prepared.

cooled to room temperature, 100% excess of isopropyl iodide was added with continuous stirring, and refluxing was again begun. After about two hours the precipitation of sodium iodide was apparent and the mixture was allowed to reflux for ninety hours before final treatment with water and dilute sodium carbonate. After drying the ketone was rectified *in vacuo* through a three-foot (1 meter) rotary column to give a colorless, slightly viscous liquid. The other normal alkylations were carried out in similar manner with variations in reflux time as shown in Table I.

1,2-Dimethylcyclopentanecarboxamide.—Refluxing 6 g. of 1,2-dimethylcyclopentyl phenyl ketone with an equivalent of sodium amide and a few drops of benzene over a five-hour period gave on standing overnight with 5 cc. each of water and petroleum ether the amide of the acid. Repeated recrystallization of the amide from benzene–petroleum ether gave small white plates melting at 98.5–99.5°; yield, 0.5 g.

Anal. Calcd. for $C_8H_{15}ON$: C, 68.04; H, 10.64; N, 9.93. Found: C, 68.22; H, 10.79; N, 9.94.

1-Ethyl-2-methylcyclopentanecarboxamide.—Four grams of 1-ethyl-2-methylcyclopentyl phenyl ketone on treatment with sodium amide in xylene, as described above, and subsequent recrystallization of the amide from petroleum ether resulted in white fluffy needles melting at 84.5–85.5°; yield, 0.5 g.

Anal. Calcd. for $C_9H_{17}ON$: C, 69.63; H, 11.04; N, 9.02. Found: C, 69.80; H, 11.06; N, 9.02.

1-Isopropyl-2-methylcyclopentanecarboxanilide.—Attempts to prepare the amide from 1-isopropyl-2-methylcyclopentyl phenyl ketone with sodium amide did not give a crystalline amide; therefore, direct ozonization of the ketone was employed.

A stream of ozonized oxygen was passed into a 20% solution of 4 g. of 1-isopropyl-2-methylcyclopentyl phenyl ketone in petroleum ether for thirty-six hours at 0°. The ozonide was decomposed with water and refluxed with alkaline peroxide to oxidize any keto acid formed. The basic water layer was acidified, and the acid steam-distilled and extracted with ether. The ether was distilled, leaving about 0.5 g. of liquid acid. The chloride of this acid was prepared by the thionyl chloride method and to the acid chloride in ether solution was added two equivalents of aniline. After standing for one hour, the reaction mixture was poured into water and the anilide recrystallized from ethyl alcohol to give short white needles melting at 115–116°. A mixed melting point determination with the anilide of the acid prepared by Shive, Crouch and Lochte[12] showed no depression.

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

1-*n*-Propyl-2-methylcyclopentanecarboxanilide.—Three-tenths gram of the liquid acid was prepared by ozonization of 6 g. of 1-*n*-propyl-2-methylcyclopentyl phenyl ketone as described above. This small amount of acid naturally did not permit purification and determination of physical properties, so the acid was converted to the acid chloride and in turn to the anilide as described above. Repeated recrystallization from ethyl alcohol gave short white needles melting at 141–142°.

Anal. Calcd. for $C_{16}H_{23}ON$: N, 5.71. Found: N, 5.83.

2-Methylcyclopentanecarboxanilide.—This anilide was prepared because it was thought that perhaps 2-methylcyclopentanecarboxylic acid resulted from ozonization of 2-methylcyclopentyl phenyl ketone in an attempt to prepare 1-isopropyl-2-methylcyclopentanecarboxylic acid as described above. Addition of aniline to the acid chloride in ether resulted in an instantaneous reaction. Water was added and the anilide was filtered and recrystallized repeatedly from benzene–petroleum ether to give gray needle clusters melting at 107–108°.

Anal. Calcd. for $C_{13}H_{17}ON$: N, 6.89. Found: N, 6.93.

II. Abnormal Alkylation of 2-Methylcyclopentyl Phenyl Ketone

Alkylation of 2-Methylcyclopentyl Phenyl Ketone in Xylene.—To a flask equipped with a mercury-sealed stirrer, a reflux condenser with a calcium chloride tube at the end and a dropping funnel with a long stem was added 5.5 g. of freshly-prepared sodium amide in 150 cc. of anhydrous xylene. Xylene was used as a solvent in an attempt to improve the yields of the normal alkylated ketones. A few drops of 2-methylcyclopentyl phenyl ketone was added to the sodium amide–xylene mixture with stirring and the contents heated to 110°, at which point evolution of ammonia began. The temperature was gradually raised to 135° as the remainder of the 25 g. of ketone, diluted with 25 cc. of xylene, was added at such rate that evolution of ammonia was not too vigorous. Formation of the sodium derivative was evident as indicated by the abundant gray flocculent precipitate. After addition of all of the ketone over a period of two hours, the temperature of the bath was raised to 140° and the mixture refluxed and stirred for three hours to allow for completion of the reaction and evolution of all ammonia; however, it appeared that the reaction was essentially complete as the last amount of the ketone was added.

After the mixture had cooled to near room temperature,

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(12) Shive, Crouch and Lochte, THIS JOURNAL, **63**, 2979 (1941).

100% excess of isopropyl iodide was added, and the mixture refluxed for twelve hours. Sodium iodide formation was evident after about thirty minutes of refluxing. The contents of the flask were treated with water and dilute sodium carbonate solution, dried and rectified *in vacuo* through a three-foot rotary column into fractions of 2.25 cc. each. A solid appeared in fractions 1–4.

Similar results were obtained in an attempt to alkylate 2-methylcyclopentyl phenyl ketone in xylene with *n*-propyl and ethyl iodide, respectively, wherein a solid was more abundant in the ethyl alkylation with solid appearing in practically every fraction. A solid appeared in fraction 1 of the *n*-propyl alkylation product.

Identification of 2-Methylcyclopentanecarboxamide (I).—Separation of the solid in fraction 1 of the isopropyl alkylation and its subsequent recrystallization from benzene–petroleum ether gave needles melting at 152–153°. The compound was suspected of being 2-methylcyclopentanecarboxamide, melting point 154°, and a mixed melting point determination with an authentic sample of the amide showed no depression from 154°.

The amide was also separated and identified in the ethyl and *n*-propyl alkylation products, its separation from the other solids being accomplished because of its very slight solubility in petroleum ether; yield in each of the three cases was about 100 mg.

Identification of N-Isopropyl-2-methylcyclopentanecarboxamide (II).—The solid was separated from all fractions in which it occurred in the isopropyl alkylation products and repeated recrystallization from petroleum ether gave long, white, fluffy needles melting at 87–88°. The compound was suspected of being N-isopropyl-2-methylcyclopentanecarboxamide (II), and this derivative was prepared by treating the acid chloride of 2-methylcyclopentanecarboxylic acid with isopropylamine. Upon repeated recrystallization from petroleum ether, the product melted at 87–88°, and a mixed melting point determination of the two compounds showed no depression. Twenty-five grams of 2-methylcyclopentyl phenyl ketone gave 1.7 g. of this amide.

Anal. Calcd. for $C_{10}H_{19}ON$: N, 8.31. Found: N, 8.27.

Identification of N-Ethyl-2-methylcyclopentanecarboxamide.—The solid in the ethyl alkylation products upon repeated recrystallization from petroleum ether gave glistening white needles melting at 86–87°. The yield was 3.2 g. from 25 g. of 2-methylcyclopentyl phenyl ketone. The compound was suspected of being N-ethyl-2-methylcyclopentanecarboxamide, and this derivative was prepared from the acid chloride and ethylamine as described above. Recrystallization from petroleum ether gave white needles melting at 86–87° and a mixed melting point determination showed no depression.

Anal. Calcd. for $C_9H_{17}ON$: N, 9.02. Found: N, 8.96.

Preparation of N-*n*-Propyl-2-methylcyclopentanecarboxamide.—This amide was prepared from the acid chloride and *n*-propylamine as described above. It proved to be a low-melting solid which could not be recrystallized and consequently could not be separated from the liquid alkylation products.

Identification of 2-Methylcyclopentylidene-(phenyl)-methyl Isopropyl Ether (III).—The liquid portion of the alkylation products of 2-methylcyclopentyl phenyl ketone with isopropyl iodide boiled at about 274° at 760 mm. as compared to a boiling point of 281° for 2-methylcyclopentyl phenyl ketone and a boiling point of 315° for 1-isopropyl-2-methylcyclopentyl phenyl ketone. Furthermore, the liquid gave positive unsaturation tests and was, therefore, suspected of being the enol ether of 1-isopropyl-2-methylcyclopentyl phenyl ketone. Since it could not be purified by any methods attempted, the impure compound was investigated.

If the unsaturated compound had the ether structure (III), ozonolysis should yield 2-methylcyclopentanone and isopropyl benzoate. The isopropyl benzoate in turn can be saponified to yield finally isopropyl alcohol and benzoic acid.

A stream of ozonized oxygen was passed into a 20% solution of 4 g. of the unsaturated isopropyl compound in petroleum ether for eight hours at 0°. The ozonide was decomposed by refluxing with water in the presence of zinc dust and the product was washed with dilute sodium hydroxide solution which on acidification gave no acid.

The petroleum ether was removed and the residue subjected to steam distillation. To about 0.3 cc. of the oily layer in the distillate was added 0.3 g. of semicarbazide hydrochloride and 0.5 g. of sodium acetate dissolved in 3 cc. of water, and enough alcohol to form one liquid phase. The mixture was heated for one-half hour and after standing in a refrigerator overnight the semicarbazone had separated as a solid. Repeated recrystallization from petroleum ether–benzene gave small plates melting at 174–175°. Since the melting point could be lowered or raised over a range of about four degrees by recrystallization from petroleum ether–benzene followed by dilute alcohol or vice versa, and since the compound is reported in the literature[13] as melting from 171 to 184° when recrystallized from alcohol, the semicarbazone of 2-methylcyclopentanone synthesized from the ethyl ester of 1-methyl-2-ketocyclopentanecarboxylic acid was prepared and recrystallized. This semicarbazone also behaved as did the one above. A final recrystallization of each semicarbazone from benzene resulted in a melting point of 174–175° for each semicarbazone and a mixture of the two. This melting point corresponds to that reported by Best and Thorpe, Kötz and Schaeffer, and Wallach.[13] 2-Methylcyclopentanone was thus definitely identified as a product of ozonolysis.

After the steam distillation of 2-methylcyclopentanone, the remaining material was refluxed three hours with aqueous potassium hydroxide to hydrolyze isopropyl benzoate if present. The isopropyl alcohol formed was fractionated from the mixture and was identified by a procedure described by Mulliken[14] in which the alcohol was oxidized to acetone and the resulting acetone vapors were condensed with benzaldehyde to give dibenzylidene-acetone. Upon recrystallization from alcohol this product gave pale yellow plates melting at 111–112°. A portion of known iso-

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(13) Bouveault, *Bull. soc. chim.*, (3) **21**, 1022 (1898); Wallach, *Ann.*, **331**, 322 (1904); Best and Thorpe, *J. Chem. Soc. London*, **95**, 704 (1909); Nametkin, *J. Russ. Phys.-Chem. Ges.*, **47**, 1609, through *Chem. Zentr.*, **87**, 1702 (1912); Kötz and Schaeffer, *J. prakt. Chem.*, (2) **88**, 626 (1913); Wallach, *Ann.*, **414**, 317 (1917).

(14) S. P. Mulliken, "Identification of Pure Organic Compounds," first edition, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1905, p. 170.

propyl alcohol was similarly converted to dibenzylideneacetone, and a mixture of the two derivatives melted at 111–112°.

The basic water layer on acidification yielded an acid which on sublimation melted at 122° and with an authentic sample of benzoic acid showed no depression in melting point. This completed the identification since all three of the ozonolysis products were identified.

Identification of 2-Methylcyclopentylidene-(phenyl)-methyl *n*-Propyl Ether.—This compound was ozonized and the products isolated in the same manner as above to obtain the semicarbazone of 2-methylcyclopentanone and benzoic acid. Because of difficulty in separation, no attempt was made to identify *n*-propyl alcohol.

Identification of 2-Methylcyclopentylidene-(phenyl)-methyl Ethyl Ether.—This compound was also ozonized and 2-methylcyclopentanone and benzoic acid were again identified as above. No attempt was made to identify ethyl alcohol.

Summary

Alkylation of 2-methylcyclopentyl phenyl ketone with sodium amide and alkyl iodides in boiling dry benzene leads to the normal C-alkyl products.

Alkylation of the same ketone with the same reagents in boiling dry xylene leads to O-alkyl products, while alkylation at the temperature of boiling toluene leads to a mixture of C- and O-alkylation products.

In the presence of boiling xylene sodium amide partially cleaves the phenyl ketone to produce the amide of 2-methylcyclopentanecarboxylic acid which is then alkylated to produce the corresponding alkyl amide.

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The Synthesis and Characterization of Some Tertiary Naphthenic Acids

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In connection with the study of the structure of the $C_{10}H_{18}O_2$ acid isolated from straight-run California petroleum by Shive, Horeczy, Wash and Lochte[2] and apparently from Iranian petroleum by Kennedy[3] and obtained by Roberts and Bailey[4] through degradation of a $C_{16}H_{25}N$ naphthenic base which was also isolated from California petroleum, synthesis of several structural isomers which would yield the degradation product obtained by Shive, Horeczy, Wash and Lochte[2] was undertaken.

The chemical behavior of the acid and its methyl ester and the corresponding amide indicated a tertiary acid, and the degradation product obtained by Shive, Horeczy, Wash and Lochte[2] apparently limited the acid to five probable structures, of which only two (1-isopropyl-2-methylcyclopentanecarboxylic acid and α,α,2-trimethylcyclopentaneacetic acid) were tertiary. Hence, synthesis of these two acids (as well as 1,2,2-trimethylcyclohexanecarboxylic and 1-isopropylcyclohexanecarboxylic acid, both of which were remote possibilities) was undertaken.

1,2,2-Trimethylcyclohexanecarboxylic Acid.—Although first investigated by Kachler and Spitzer,[5] the action of fuming nitric acid upon an optically active dibromocamphor was extensively studied by Forster,[6] who prepared without knowledge of its structure the corresponding optically active camphorenic acid (V) according to the equations shown.

The work of Lapworth[7] and of Lapworth and Lenton[8] was devoted to the proof of structure of camphorenic acid as well as of the intermediate compounds. Thus, the action of fuming nitric acid upon dibromocamphor produced dibromocampholide (III), which was reduced by zinc and ammonium hydroxide to bromocamphorenic acid (IV) which in turn was reduced to camphorenic acid (V) by sodium amalgam.

In this investigation, the procedure of Forster[6] was repeated employing *dl*-camphor to give optically inactive intermediates in the preparation of racemic camphorenic acid; hence, the melting points of these optically inactive compounds varied several degrees from the optically active forms reported by Forster.[6] Reduction of the *dl*-camphorenic acid to *dl*-1,2,2-trimethylcyclohexanecarboxylic acid was accomplished by hydrogenation

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

[2] Shive, Horeczy, Wash and Lochte, in process of publication.

[3] Kennedy, *Nature*, **144**, 832 (1939).

[4] Roberts and Bailey, paper presented before the Meeting of the Petroleum Division, American Chemical Society, Baltimore, Md., April, 1939, "Structural Study of a $C_{16}H_{25}N$ Base from California Petroleum."

[5] Kachler and Spitzer, *Monatsh.*, **4**, 554 (1883).

[6] Forster, *J. Chem. Soc.*, **69**, 36 (1896).

[7] Lapworth, *ibid.*, **75**, 1137 (1899).

[8] Lapworth and Lenton, *ibid.*, **81**, 20 (1902).