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.

Austin, Texas Received July 18, 1941

[Contribution No. 241 from the Chemical Laboratory of the University of Texas]

The Synthesis and Characterization of Some Tertiary Naphthenic Acids

By Billie Shive,[1] W. W. Crouch and H. L. Lochte

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).

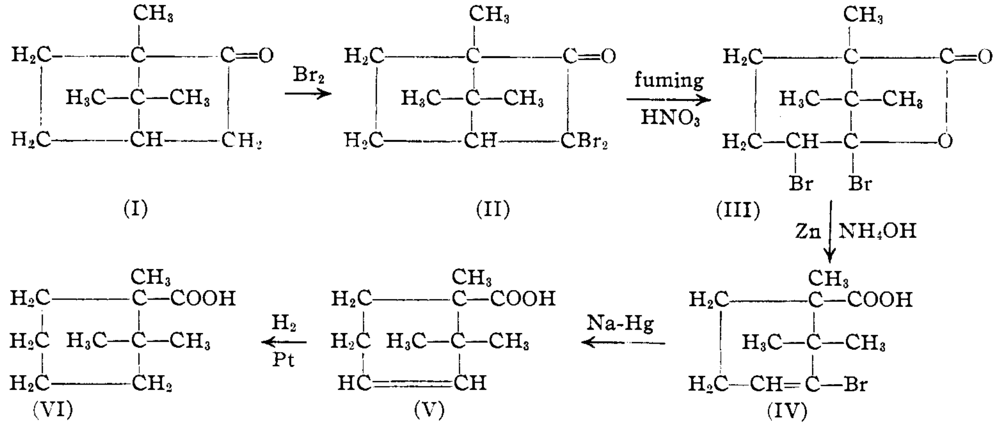
[4] Roberts and Bailey, paper presented before the Meeting of the Petroleum Division, American Chemical Society, Baltimore, Md., April, 1939, "Structural Study of a $C_{16}H_{25}N$ Base from California Petroleum."

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

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

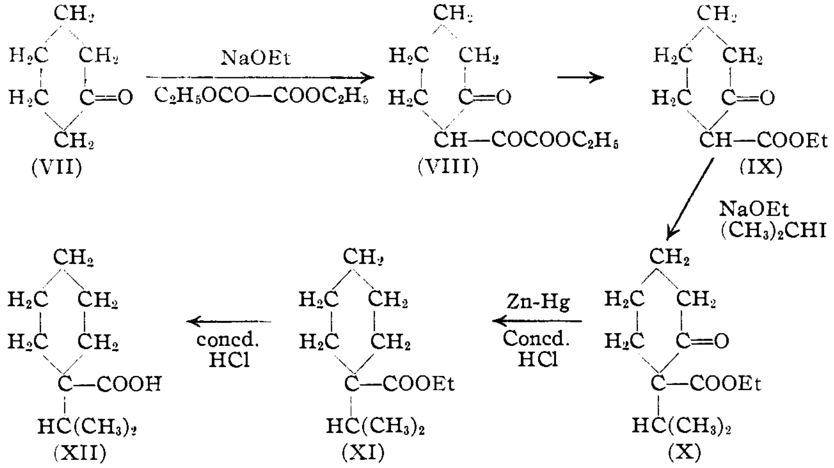
[7] Lapworth, *ibid.*, **75**, 1137 (1899).

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



in glacial acetic acid in the presence of Adams platinum catalyst.

1-Isopropylcyclohexanecarboxylic Acid.—Synthesis of 1-isopropylcyclohexanecarboxylic acid (XII) was accomplished according to the equations



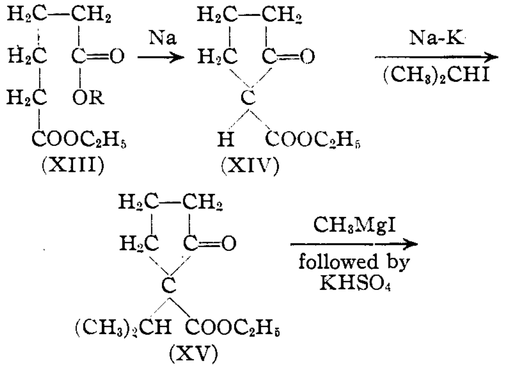
The preparation of 2-carboethoxy-2-isopropylcyclohexanone (X) was first accomplished by Kötz and Michels.[9] Following their procedure to that point, there remained only the reduction of the carbonyl group to obtain the desired product. This was accomplished by the Clemmensen method. The reduction product could not be separated from the keto ester, but on hydrolysis the 1-isopropylcyclohexanecarboxylic acid obtained was easily purified by recrystallization from dilute acetic acid.

This procedure represents a new general method of preparation of 1-alkylcycloalkanecarboxylic acids.

1-Isopropyl-2-methylcyclopentanecarboxylic Acid.—By treating 2-carboethoxy-2-isopropylcyclopentanone with methylmagnesium iodide, dehydrating the resulting hydroxyester, hydrogenating the unsaturated ester and hydrolyzing this saturated ester, 1-isopropyl-2-methylcyclopentanecarboxylic acid was synthesized as shown by the following equations.

The method employed in the preparation of 2-carboethoxy-2-isopropylcyclopentanone (XV) was identical with that of Kötz and Schuler,[10] while the 2-carboethoxycyclopentanone (XIV) was prepared according to the directions of Cornubert and Borrel.[11]

The addition of a methyl group to form 1-carboethoxy-1-isopropyl-2-methylcyclopentene-2 (XVI) was accomplished by heating a mixture of magnesium, methyl iodide and the ketoester in benzene or by treating the ketoester in ether with methylmagnesium iodide



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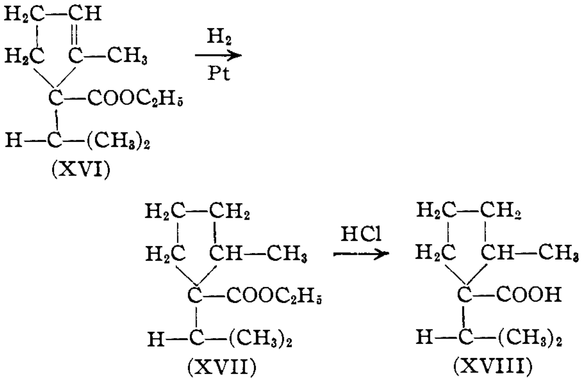
[9] Kötz and Michels, *Ann.*, **350**, 212 (1906).

[10] Kötz and Schuler, *ibid.*, **350**, 221 (1906).

[11] Cornubert and Borrel, *Bull. soc. chim.*, [4] **47**, 303 (1930).



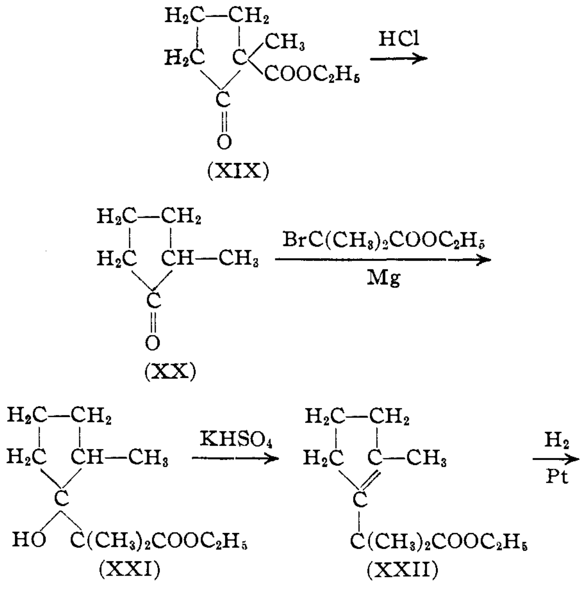
(XVI) (XVII) (XVIII)

or methyllithium. There was some difficulty, however, in the purification of the product as the hydroxyester and unsaturated ester apparently formed an azeotropic mixture; hence, complete dehydration of the hydroxy compound was necessary before fractionation.

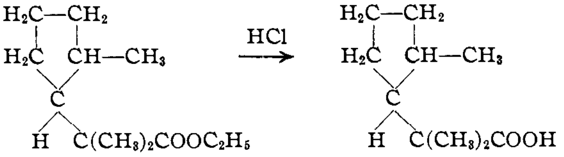
The unsaturated ester in glacial acetic acid rapidly consumed the calculated quantity of hydrogen upon shaking with hydrogen at atmospheric pressure in the presence of Adams catalyst. Hydrolysis of the saturated ester with concentrated hydrochloric acid at 140–150° gave 1-isopropyl-2-methylcyclopentanecarboxylic acid.

This series of reactions represents a general method for the synthesis of 1,2-dialkylcycloalkanecarboxylic acids.

α,α,2-Trimethylcyclopentaneacetic Acid.—Preparation of α,α,2-trimethylcyclopentaneacetic acid was accomplished as indicated by the equations



(XIX) (XX) (XXI) (XXII)



(XXIII) (XXIV)

Attempts to effect the first reaction resulted, in the first experiments, in condensation of two molecules of 2-methylcyclopentanone; however, by adding the ketone and bromo-ester in the same ether solution to the magnesium in a relatively large quantity of ether, the reaction proceeded smoothly to form ethyl 1-hydroxy-α,α,2-trimethylcyclopentaneacetate (XXI), which was dehydrated by heating with freshly fused potassium acid sulfate. Hydrogenation of ethyl α,α,2-trimethylcyclopentene-1-acetate (XXII) proceeded rapidly in acetic acid solution in the presence of Adams platinum catalyst and hydrolysis of the resulting saturated ester in a sealed tube with concentrated hydrochloric acid at 140–150° gave α,α,2-trimethylcyclopentaneacetic acid (XXIV).

Experimental

Synthesis of 1,2,2-Trimethylcyclohexanecarboxylic Acid

***dl*-α,α-Dibromocamphor.**—To 150 g. of *dl*-camphor in a flask equipped with a reflux condenser and a dropping funnel, two moles of bromine was added dropwise over a period of six hours. The reaction mixture was heated for an hour on a steam-cone to complete the reaction. After hydrogen bromide was no longer evolved, 50 cc. of water and enough glacial acetic acid to obtain a single phase were added and the resulting solution was heated for two hours on a steam-cone. After pouring this solution upon cracked ice, the precipitated *dl*-α,α-dibromocamphor was filtered and recrystallized four times from alcohol to obtain colorless crystals, m. p. 54–55°; yield, 220 g.

Anal. Calcd. for $C_{10}H_{14}OBr_2$: Br, 51.56. Found: Br, 51.76.

***dl*-Dibromocampholide.**—Into an open five-liter round-bottomed flask was placed 220 g. of *dl*-α,α-dibromocamphor which was then covered with 440 cc. of fuming nitric acid (sp. gr. 1.6). The mixture cooled itself at first and then became warm, at which point a vigorous reaction occurred with copious evolution of oxides of nitrogen. When the reaction was complete, the contents of the flask were poured upon cracked ice, and the heavy oily layer which separated was washed several times with cold water, agitated in boiling water for several minutes, separated, dried, dissolved in alcohol and set aside in an ice chest to crystallize. Recrystallization from alcohol gave long needle crystals, m. p. 138–139°; yield, 19 g.

Anal. Calcd. for $C_{10}H_{14}O_2Br_2$: Br, 49.03. Found: Br, 49.00.

***dl*-Bromocamphorenic Acid.**—To 25 g. of *dl*-dibromocampholide and 50 cc. of boiling alcohol, zinc dust and ammonium hydroxide were added successively in small quantities until a portion of the solution no longer became turbid when diluted with water. The liquid was decanted from the unreacted zinc, diluted with water and acidified. The precipitated acid was filtered and recrystallized from alcohol to give rhombic crystals, m. p. 180–181°; yield, 17 g.

Anal. Calcd. for $C_{10}H_{15}O_2Br$: Br, 32.35. Found: Br, 32.06.

dl-**Camphorenic Acid.**—Suspended in 70 cc. of boiling water, 17 g. of *dl*-bromocamphorenic acid was stirred vigorously during the addition of 170 g. of 5% sodium amalgam. When a drop of liquid became solid if placed on a watch glass and allowed to stand for a few seconds, the liquid was decanted from the mercury and allowed to cool. The crystalline sodium salt which separated was filtered through asbestos and then dissolved by addition of water. Acidification of the water layer precipitated the acid, which was again treated in the same manner with 17 g. of sodium amalgam. After this treatment, it was necessary to add a little sodium carbonate to successfully precipitate the sodium salt. Recrystallization of the acid from petroleum ether–benzene mixture gave small colorless needle crystals, m. p. 165–166°; yield, 8 g.

Anal. Calcd. for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.21; H, 9.76.

dl-**1,2,2-Trimethylcyclohexanecarboxylic Acid (Dihydrocamphorenic Acid).**—Absorbing 400 cc. of hydrogen in ten minutes, approximately 3 g. of *dl*-camphorenic acid in glacial acetic acid was hydrogenated at atmospheric pressure in the presence of Adams platinum catalyst. After removal of the catalyst the acid was precipitated by the addition of water, filtered off and recrystallized from dilute acetic acid to give colorless needle crystals, m. p. 179–180°; yield, 3 g.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.40; H, 10.87.

dl-**1,2,2-Trimethylcyclohexanecarboxamide.**—The acid chloride of *dl*-1,2,2-trimethylcyclohexanecarboxylic acid, prepared by treating 2 g. of the acid with an excess of thionyl chloride and removing the excess of this reagent under reduced pressure, was dissolved in 5 cc. of anhydrous ether and subjected to the action of anhydrous ammonia gas. After saturating the ether with ammonia, the mixture was stoppered tightly in a flask and allowed to stand several hours. The ether was removed on a steam-cone and aqueous ammonia was added. The precipitated amide was filtered off, and after removal of occluded ammonium chloride by recrystallization from dilute alcohol, recrystallization from petroleum ether–benzene mixture gave colorless microscopic needles, m. p. 164–165°; yield, 1.5 g.

Anal. Calcd. for $C_{10}H_{19}ON$: N, 8.28. Found: N, 8.40.

Synthesis of 1-Isopropylcyclohexanecarboxylic Acid

2-Carboethoxycyclohexanone.—According to the method of Kötz and Michels,[9] 2-carboethoxycyclohexanone was prepared by condensing cyclohexanone with ethyl oxalate in the presence of sodium ethylate and heating the resulting diketoester to split out carbon monoxide. After fractionation in vacuo, the following physical properties of the product were determined: b. p. 106° at 10 mm.; n^{20}_D 1.4792; d^{20}_4 1.0715.

2-Carboethoxy-2-isopropylcyclohexanone.—Following the procedure of Kötz and Michels,[9] 2-carboethoxycyclohexanone was alkylated in the presence of sodium alcoholate by the action of isopropyl iodide upon the sodium derivative of the ketoester. Fractionation *in vacuo* of the resulting 2-carboethoxy-2-isopropylcyclohexanone gave a liquid with the following physical properties: b. p. 122° at 10 mm.; n^{20}_D 1.4588; d^{20}_4 1.0206.

1-Isopropylcyclohexanecarboxylic Acid.—With 40 g. of amalgamated zinc, 15 g. of 2-carboethoxy-2-isopropylcyclohexanone and 80 cc. of hydrochloric acid (1:1) were heated to vigorous boiling in a flask attached to a reflux condenser by means of a ground joint. Boiling was continued for twelve hours and at the end of each hour 5 cc. of concentrated hydrochloric acid was added. After diluting the mixture with water, the oily material was extracted with ether. After washing the ether layer with dilute sodium carbonate and water, drying over sodium sulfate and removing the ether, the residual material was fractionated, 12 g. of the product distilling over at 92–95° at 10 mm. As the physical properties of the fractions (n^{20}_D 1.4579–1.4582; d^{20}_4 0.9513–0.9541) varied over a relatively large range and were high for the expected product, indicating a mixture of the original ketoester and the reduction product, the combined fractions were treated again, but results were only slightly improved. As the last traces of ketoester could not be removed easily by continued reduction nor by fractionation as apparently an azeotropic mixture was formed, 10 g. of the ester thus obtained was converted to the acid by heating in a sealed tube with 25 cc. of concentrated hydrochloric acid for twenty-four hours at 140–150°. After diluting with water, the mixture was extracted with ether, and the acid removed from the ether layer by extraction with dilute sodium hydroxide. Upon acidification of the alkaline layer, 1-isopropylcyclohexanecarboxylic acid was obtained, which upon recrystallization from dilute acetic acid gave colorless plates, m. p. 104–105°; yield, 7 g.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.31; H, 10.84.

1-Isopropylcyclohexanecarboxanilide.—The acid chloride of 1-isopropylcyclohexanecarboxylic acid, which was prepared by the action of a slight excess of thionyl chloride upon 2 g. of the acid followed by removal of the excess thionyl chloride by warming under a partial vacuum, was treated in 5 cc. of anhydrous ether with two equivalents of aniline. After standing several hours, the excess aniline was removed by extraction with dilute hydrochloric acid, and upon evaporation of the ether 1-isopropylcyclohexanecarboxanilide crystallized. After several recrystallizations from alcohol, colorless needles, m. p. 101–102°, were obtained; yield, 1.5 g.

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

Synthesis of 1-Isopropyl-2-methylcyclopentanecarboxylic Acid

2-Carboethoxy-2-isopropylcyclopentanone.—According to the procedure of Kötz and Schuler,[10] 2-carboethoxycyclopentanone, prepared from diethyl adipate by reaction with sodium in toluene as directed by Cornubert and Borrel,[11] was dropped slowly into xylene covering finely divided sodium–potassium alloy to form a mixture of sodium and potassium derivatives. To this mixture was added isopropyl iodide, forming 2-carboethoxy-2-isopropylcyclopentanone, which, after washing the xylene solution, was separated by fractionation giving a liquid with the following physical properties: b. p. 248–249° at 750 mm.; n^{20}_D 1.4525; d^{20}_4 1.0186. Kötz and Schuler[10] reported only the boiling point, 112° at 11 mm.

1-Carboethoxy-1-isopropyl-2-methylcyclopentene-2.—To 25 g. of 2-carboethoxy-2-isopropylcyclopentanone in 100 cc. of anhydrous ether an equal molecular quantity of methylmagnesium iodide dissolved in 100 cc. of anhydrous ether was added dropwise with vigorous stirring. Evolution of only a small quantity of heat was indicated by the slow rate of reflux during addition of the Grignard reagent. In order to complete the reaction, refluxing was continued for one hour following the addition of the Grignard reagent, and after standing several hours the mixture was poured into dilute sulfuric acid and ice. The ether layer was washed once with the dilute acid and several times with water and dried over sodium sulfate. Since heating at atmospheric pressure to 185° to remove the ether caused partial dehydration, the residue was refluxed for one hour at atmospheric pressure in the presence of an equal weight of freshly fused potassium acid sulfate and distilled under reduced pressure. The distillate, dissolved in an equal volume of ether, was washed with dilute sodium carbonate and several times with water and dried over sodium sulfate. Following removal of the ether, the residue was fractionated in a partial vacuum to obtain 1-carboethoxy-1-isopropyl-2-methylcyclopentene-2; b. p. 221–222° at 753 mm.; n^{20}_D 1.4566; d^{20}_4 0.9472; yield, 16 g.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.16; H, 10.32.

Refluxing 25 g. of 2-carboethoxy-2-isopropylcyclopentanone with equal molecular quantities of magnesium and methyl iodide in 150 cc. of anhydrous benzene and treatment of the reaction mixture in the same manner as described for the reaction mixture above gave a product identical with that above with only a slightly inferior yield, 14 g.

Replacing methylmagnesium iodide by methyl lithium caused other reactions which hampered purification of the resulting ester.

1-Carboethoxy-1-isopropyl-2-methylcyclopentane.—Hydrogenation in glacial acetic acid of 16 g. of 1-carboethoxy-1-isopropyl-2-methylcyclopentene-2 to the corresponding saturated ester was effected quantitatively at a rapid rate by means of hydrogen at atmospheric pressure in the presence of Adams catalyst. After removal of catalyst and solvent, fractionation *in vacuo* of the reduced product gave a liquid with the following physical properties: b. p. 225–226° at 745 mm.; n^{20}_D 1.4482; d^{20}_4 0.9356.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.51; H, 11.23.

1-Isopropyl-2-methylcyclopentanecarboxylic Acid.—Hydrolysis of 1-carboethoxy-1-isopropyl-2-methylcyclopentane was accomplished by heating 14 g. of the ester with 28 cc. of concentrated hydrochloric acid at 140–150° for twenty-four hours. After diluting with 100 cc. of water, the oil layer was extracted with ether. Extraction of the ether layer with dilute sodium hydroxide and acidification of the resulting basic solution at a low temperature gave a low-melting acid which on recrystallization from dilute acetic acid formed microscopic needles melting at 52–53°; yield, 10 g.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.62; H, 10.65.

1-Isopropyl-2-methylcyclopentanecarboxanilide.—By an identical procedure to that used in the preparation of 1-isopropylcyclohexanecarboxanilide, 1-isopropyl-2-methylcyclopentanecarboxanilide was prepared from 1 g. of the corresponding acid. Recrystallization from alcohol gave microscopic needles, m. p. 115–116°; yield, 0.5 g.

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

α,α,2-Trimethylcyclopentaneacetic Acid

2-Methylcyclopentanone.—Methylation of 2-carboethoxycyclopentanone was accomplished according to the procedure of Vavon and Horeau[12] by adding excess methyl iodide to the sodium derivative prepared by adding slowly with vigorous stirring sodium hydroxide in water to the ketoester in alcohol at −18°. A solution of 50 g. of 2-carboethoxy-2-methylcyclopentanone in 100 cc. of concentrated hydrochloric acid was diluted with water until slightly turbid, and the mixture was refluxed for twelve hours over a free flame in a flask connected to a reflux condenser by a ground joint, diluted to double its volume and extracted with ether. The ether layer, after drying with sodium sulfate, was fractionated to obtain 25 g. of 2-methylcyclopentanone, b. p. 139–140°.

Ethyl 1-Hydroxy-α,α,2-trimethylcyclopentaneacetate.—A solution of 25 g. of 2-methylcyclopentanone and 50 g. of ethyl α-bromoisobutyrate in 200 cc. of anhydrous ether was added dropwise to 6.1 g. of magnesium covered with 200 cc. of anhydrous ether. A few drops of methyl iodide was added to start the reaction, and the mixture of ketone and bromoester added at such a rate that the reflux of the ether did not become too violent. After refluxing for one hour following the addition, the reaction mixture was allowed to stand for several hours in order to complete the reaction. The mixture was poured into dilute sulfuric acid and ice and extracted with ether. After drying with sodium sulfate the ether layer was fractionated in a partial vacuum to obtain a liquid with the following physical properties: b. p. 122–123° at 12 mm.; n^{20}_D 1.4584; d^{20}_4 1.0036; yield, 30 g.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35. Found: C, 67.40; H, 10.28.

Ethyl α,α,2-Trimethylcyclopentene-1-acetate.—Refluxing 30 g. of ethyl 1-hydroxy-α,α,2-trimethylcyclopentaneacetate with a trace of iodine dehydrated only a relatively small portion of the compound. However, as the iodine did not appear in the first fraction on distillation, reaction with the compound probably removed it from further catalytic action. The mixture was then refluxed for two hours at atmospheric pressure with a double weight of freshly fused potassium acid sulfate and distilled under reduced pressure. The distillate in an equal volume of ether was washed with dilute sodium carbonate and water,

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(12) Vavon and Horeau, *Bull. soc. chim.*, [5] **1**, 1703 (1934).

dried over sodium sulfate and fractionated to give a liquid with the following physical properties: b. p. 224–225° at 753 mm.; n^{20}_D 1.4571; d^{20}_4 0.9475; yield, 16 g.

Anal. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.17; H, 10.27.

This product, however, was difficult to obtain free from hydroxyester as this latter compound apparently formed an azeotropic mixture with the unsaturated ester.

Ethyl α,α,2-Trimethylcyclopentaneacetate.—In glacial acetic acid, 16 g. of ethyl α,α,2-trimethylcyclopentene-1-acetate rapidly consumed the calculated quantity of hydrogen at atmospheric pressure in the presence of Adams platinum catalyst. Fractionation following removal of the catalyst and solvent gave a liquid with the following physical properties: b. p. 225–226° at 750 mm.; n^{20}_D 1.4468; d^{20}_4 0.9327; yield, 14 g.

Anal. Calcd. for $C_{12}H_{22}O_2$: C, 72.68; H, 11.18. Found: C, 72.50; H, 11.18.

α,α,2-Trimethylcyclopentaneacetic Acid.—A mixture of 14 g. of ethyl α,α,2-trimethylcylopentaneacetate and 28 cc. of concentrated hydrochloric acid was heated in a sealed tube for twenty-four hours at 140–150°, diluted to twice its volume and extracted with ether. The ether layer was extracted with dilute sodium hydroxide, and, upon acidification of the alkaline layer with dilute hydrochloric acid, the organic acid separated and was extracted with benzene. The benzene layer was dried with sodium sulfate and fractionated to obtain the liquid acid, b. p. 256–257° at 743 mm.; n^{20}_D 1.4612; d^{20}_4 0.9843; yield, 10 g.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.40; H, 10.56.

α,α,2-Trimethylcyclopentaneacetanilide.—Prepared by the same procedure employed in the preparation of 1-isopropylcyclohexanecarboxanilide, α,α,2-trimethylcyclopentaneacetanilide was recrystallized from alcohol in the form of colorless microscopic needles and melted at 102–103°.

Anal. Calcd. for $C_{16}H_{23}ON$: N, 5.71. Found: N, 5.82.

Summary

1. *dl*-1,2,2-Trimethylcyclohexanecarboxylic acid, 1-isopropylcyclohexanecarboxylic acid, 1-isopropyl-2-methylcyclopentanecarboxylic acid, and α,α,2-trimethylcyclopentaneacetic acid have been synthesized and characterized. These acids were not identical with the $C_{10}H_{18}O_2$ acid isolated from California petroleum by Shive, Horeczy, Wash and Lochte and obtained by Roberts and Bailey in degrading the $C_{16}H_{25}N$ base also isolated from California petroleum.

2. New general methods of synthesis of 1-alkylcycloalkanecarboxylic acids and 1,2-dialkylcycloalkanecarboxylic acids have been developed.

AUSTIN, TEXAS RECEIVED JULY 18, 1941

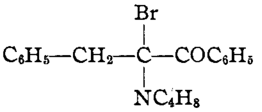
[CONTRIBUTION FROM AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

α,β-Unsaturated Aminoketones. V. Reaction of Pyrrolidine and Tetrahydroquinoline with Bromine Derivatives of Benzalacetophenone[1]

BY NORMAN H. CROMWELL

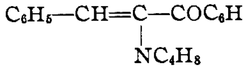
The only secondary amines that have been found to add to the carbon–carbon double bond of α-bromo-α,β-unsaturated ketones to form α-bromo-α-aminoketones are piperidine[2] and morpholine.[3,4] The present investigation was made in order to extend these studies to other heterocyclic amines for comparison with these previously mentioned experiments.

The strong heterocyclic base, pyrrolidine, has been found to resemble piperidine in these reactions. In cold anhydrous solutions pyrrolidine was found to add rapidly to α-bromobenzalacetophenone to give α-bromo-α-N-pyrrolidinobenzylacetophenone, I.



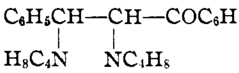
$C_6H_5—CH_2—C(Br)(NC_4H_8)—COC_6H_5$

I



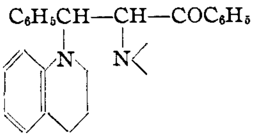
$C_6H_5—CH{=}C(NC_4H_8)—COC_6H_5$

II



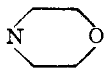
$C_6H_5CH(NC_4H_8)—CH(NC_4H_8)—COC_6H_5$

III



IV, N< = 

V, N< = 

VI, N< = 

The α-bromo-α-aminoketone I reacted in the usual way with sodium ethoxide to give the red α-N-pyrrolidinobenzalacetophenone, II. Pyrrolidine was also found to react rapidly with benzalacetophenone dibromide to give one equivalent

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[1] Presented before the Division of Organic Chemistry, American Chemical Society, Atlantic City, N. J., September, 1941. For paper IV in this series see Cromwell, THIS JOURNAL, **63**, 837 (1941).

[2] Dufraisse and Moureu, *Bull. soc. chim.*, (4) **41**, 466 (1927).

[3] Cromwell, THIS JOURNAL, **62**, 2897 (1940).

[4] Cromwell, *ibid.*, **62**, 3470 (1940).