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Tertiary Naphthenic Acids. I. Synthesis of 1,2,3,3-Tetramethylcyclopentanecarboxylic Acid from Camphor

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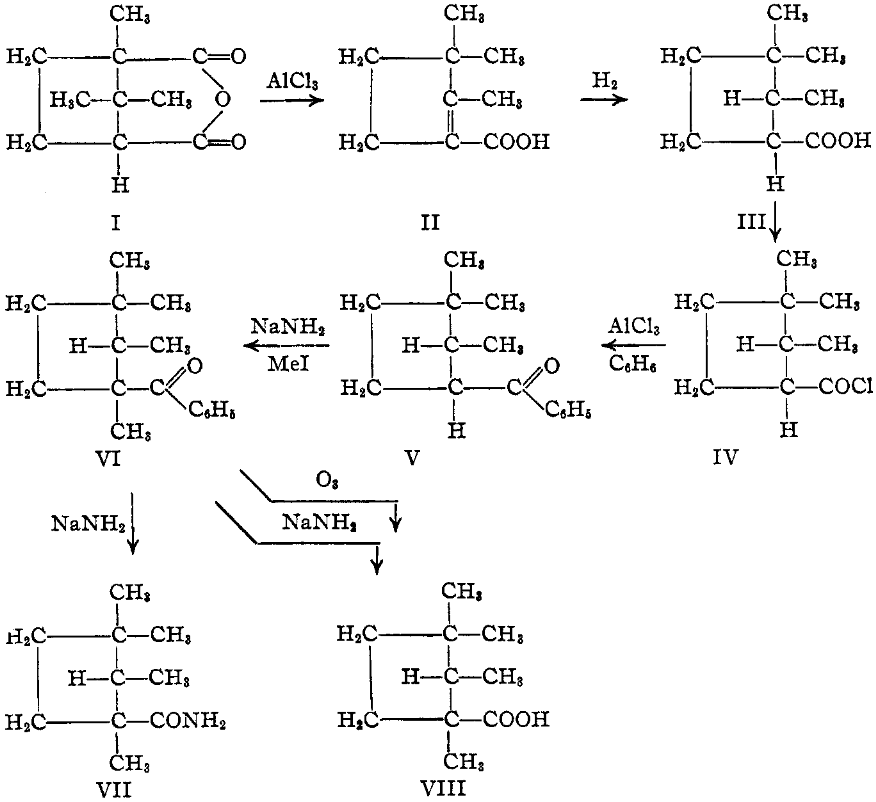
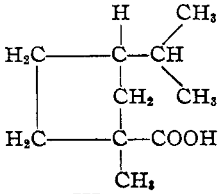
During the course of research on acidic constituents of petroleum, there have been encountered appreciable amounts of materials not esterifiable by alcoholic hydrogen chloride. Since little is known concerning the reactions and properties of tertiary naphthenic acids, the work upon such unesterifiable fractions is seriously hampered.

As shown by Shive and Bailey,[1] the $C_{10}H_{18}O_2$ acid isolated from straight-run California petroleum by Horeczy, Wash and Lochte[2] and apparently from Iranian petroleum by Kennedy[3] and obtained by degradation of a $C_{16}H_{25}N$ naphthenic base by Roberts and Bailey[4] gave degradation products which indicated that the acid was probably 1,2,3,3-tetramethylcyclopentanecarboxylic acid. Hence, the synthesis of this acid and determination of its properties was most important.

The series of reactions employed in the synthesis may be represented as follows



The above steps are essentially the same as those used by Bouveault and Levalois[5] who effected a partial synthesis of fencholic acid (IX).



IX

The isolauronolic acid (II) synthesis was worked out by Perkin[6] and improved by Bardhan, Baneri

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(1) Shive and Bailey, papers presented before the Meeting of the Petroleum Division, American Chemical Society, April, 1940, p. 81.

(2) Horeczy, Wash and Lochte, unpublished work, The University of Texas.

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

(4) Roberts and Bailey, paper presented before the Meeting of the Petroleum Division, American Chemical Society, April, 1939, Part II, v-1. "Structural Study of a $C_{16}H_{25}N$ Base from California Petroleum."

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

(6) Perkin, *J. Chem. Soc.*, **69**, 1476 (1896).

and Bose,[7] who noted that temperature played an important role. Extension of their observations and a somewhat better method of working up the product has been accomplished.

It was expected that alkylation of the ketone (V) by the method of Haller and Bauer[8] might present some difficulties. It was found that the temperature at which the reaction was carried out was a major factor, toluene as a solvent giving much better yields than benzene.

Haller and Bauer[9] also were the first to develop the splitting of a phenyl ketone with sodium amide. However, they did not determine how the ratio of acid and amide obtained might be controlled.

Ozonization of the benzene nucleus has been found to be a relatively slow reaction in most cases, and Noller and Kaneko[10] have reported that diphenyl does not form a hexaozonide. The yields of reactions involving the ozonization of a benzene nucleus as in the case of the methylated ketone (VI) would hence be expected to be relatively low and contaminated with unsaturated and keto acids, and such was found to be the case.

Since tertiary naphthenic halides decompose readily into the hydrogen halide and unsaturated hydrocarbon, yields of the corresponding acid by the Grignard reaction are poor if accomplished at all. Numerous attempts in this Laboratory have so far been disappointing. The ketone alkylation method of synthesis of tertiary naphthenic acids, especially those containing beta-alkylation, appears to be superior.

The acid of Horeczy, Wash and Lochte and of Bailey and Roberts was not identical with the synthesized 1,2,3,3-tetramethylcyclopentanecarboxylic acid. As the synthesis employed probably led to predominantly one of the two possible racemic forms, a search for the other racemic compound would have been of value, but a new degradation product obtained by the authors has led to the proof of structure and synthesis of the petroleum acid and base. Publication of this work will be forthcoming.

Experimental

Isolauronolic Acid (II).—A solution of 100 g. of dry camphoric anhydride in 400 cc. of pure anhydrous chloroform was added slowly to 100 g. of resublimed anhydrous aluminum chloride covered with chloroform. The temperature of the mixture was maintained at 23–25° during the course of the reaction which was carried out in a three-necked flask equipped with a stirrer, thermometer and reflux condenser. As the reaction was endothermic and little product was obtained if the temperature dropped below 20°, stirring and occasional application of heat to keep the temperature between 23 and 25° greatly increased the yields. The reaction mixture was allowed to stand one hour, after which water and hydrochloric acid were added until two homogeneous layers were obtained. The chloroform layer was extracted with dilute potassium hydroxide, and the extract acidified and steam distilled. The product was practically pure isolauronolic acid, m. p. 133–134°, yield, 72 g.

Dihydroisolauronolic Acid.—Hydrogenation of isolauronolic acid with copper chromite catalyst at 200° and 4500 lb./sq. in. pressure yielded the saturated alcohol. In glacial acetic acid solution, Adams catalyst at 1.5 atmospheres pressure caused a relatively slow reduction to the dihydro compound. Hydrogenation of 50 g. of the compound with 3 g. of Raney nickel catalyst in dioxane solution at 175° and 4500 lb./sq. in. pressure was complete in six hours. Extracted with dilute sodium carbonate, the acid was subjected to alkaline permanganate treatment at 0° until a coloration remained several minutes. After removal of manganese dioxide, the acid was liberated and distilled under reduced pressure to obtain a product with the following physical properties: b. p. 244° at 746 mm.; $n^{20}\text{D}$ 1.4590; d^{20}_4 0.9884; yield, 40 g. Amide: white plates from benzene–petroleum ether, m. p. 164°. Noyes[11] reported the following physical properties for the acid: b. p. 244°; d^{20} 0.9833. Amide, m. p. 161°, while Blanc[12] reported the amide as melting at 162°.

Dihydroisolauronolyl Chloride.—The acid chloride of the dihydro acid was prepared by the thionyl chloride method and fractionated out of the reaction mixture: b. p. 201° at 746 mm.; $n^{20}\text{D}$ 1.4607; d^{20}_4 1.0174; yield, 35 g. from 40 g. of acid.

Anilide.—To the acid chloride of the dihydro acid in ether solution was added two equivalents of aniline. After standing one hour, the reaction mixture was poured into water, and the anilide recrystallized three times from benzene–petroleum ether and once from dilute methyl alcohol to give long, slender needles, m. p. 156–157°.

Anal. Calcd. for $C_{15}H_{21}ON$: N, 6.06. Found: N, 6.19.

2,3,3-Trimethylcyclopentyl Phenyl Ketone.—In a small flask equipped with a reflux condenser and a dropping funnel were placed 25 g. of pulverized, anhydrous aluminum chloride and 65 cc. of anhydrous benzene. Through the dropping funnel was added drop by drop 30 g. of dihydroisolauronolyl chloride in 20 cc. of benzene. After addition of the acid chloride, the reaction mixture was refluxed over a water-bath for one hour.

The contents of the flask was dissolved in water and dilute hydrochloric acid and extracted with ether. The ether layer was washed with dilute sodium carbonate to remove any remaining acid chloride or acid. After drying over sodium sulfate, the ketone was fractionated *in vacuo*. The product, a colorless, slightly viscous liquid with an

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(7) Bardhan, Baneri and Bose, *J. Chem. Soc.*, 1127 (1935).

(8) Haller and Bauer, *Compt. rend.*, **148**, 70 (1909).

(9) Haller and Bauer, *ibid.*, **147**, 824 (1908).

(10) Noller and Kaneko, THIS JOURNAL, **57**, 2442 (1935).

(11) Noyes, *Am. Chem. J.*, **18**, 689 (1896).

(12) Blanc, *Bull. soc. chim.*, [4] **5**, 30 (1909).

odor resembling that of benzophenone, had the following physical properties: b. p. 299° at 751 mm.; n^{20}_D 1.5244; d^{20}_4 0.9913; yield, 30 g.

Anal. Calcd. for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.36; H, 9.28.

Oxime.—The oxime was prepared by dissolving 1.0 g. of hydroxylamine hydrochloride in 2 cc. of water, adding 4 cc. of 10% sodium hydroxide solution, 0.5 g. of the ketone and sufficient alcohol to form only one liquid phase. The mixture was refluxed on a water-bath for one hour, diluted with water and cooled. The resulting oxime was recrystallized from petroleum ether to give microscopic needles melting at 105–106°.

Anal. Calcd. for $C_{15}H_{21}ON$: N, 6.06. Found: N, 6.15.

1,2,3,3-Tetramethylcyclopentyl Phenyl Ketone.—To a flask equipped with a mercury-sealed stirrer, reflux condenser with a calcium chloride tube at the end, and a dropping funnel having a long stem was added 8.1 g. of sodium amide containing 40% benzene, and 30 cc. of anhydrous toluene. Benzene as a solvent gave inferior yields. Thirty grams of 2,3,3-trimethylcyclopentyl phenyl ketone was added through the dropping funnel and the reaction mixture refluxed on an oil-bath for twelve hours. Evolution of ammonia ceased at this point. After the mixture had cooled to room temperature, a slight excess of methyl iodide was added just above the surface of the reaction mixture with continuous stirring. After several minutes the precipitation of sodium iodide was apparent, but the mixture was allowed to stand overnight and refluxed an hour before final treatment with water and dilute sodium carbonate solution. After drying, the ketone was rectified *in vacuo* through a three-foot rotary column to give a colorless, slightly viscous liquid possessing an odor which also resembled benzophenone. The product was characterized by the following physical constants: b. p. 307–308° at 750 mm.; n^{20}_D 1.5242; d^{20}_4 0.9958; yield, 23 g.

Anal. Calcd. for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.65; H, 9.58.

Oxime.—The oxime was prepared by the method previously described. Recrystallization from petroleum ether–benzene gave microscopic needles, m. p. 154–155°.

Anal. Calcd. for $C_{16}H_{23}ON$: N, 5.71. Found: N, 5.65.

1,2,3,3-Tetramethylcyclopentanecarboxylic Acid.—A stream of ozonized oxygen was passed into a 20% solution of 4 g. of 1,2,3,3-tetramethylcyclopentyl phenyl ketone in anhydrous carbon tetrachloride 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, cooled and the resulting acid recrystallized from dilute acetone to give microscopic needles, m. p. 125–126°; yield, 0.3 g. This acid and the $C_{10}H_{18}O_2$ acid of Horeczy, Wash and Lochte[2] and Roberts and Bailey[4] were not identical, as the latter melts at 84°.

Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.32; H, 10.80.

The unreacted portion was recycled to obtain more of the acid. Attempts to improve the yield by ozonization at room temperature and in boiling carbon tetrachloride failed, the latter attempt giving only an extremely small yield.

1,2,3,3-Tetramethylcyclopentanecarboxylic Acid Amide.—Refluxing 2 g. of the ketone with an equivalent of sodium amide (containing 40% benzene which was partially removed on a water-bath) over a period of five hours gave on standing overnight with an equal volume of petroleum ether and water the amide of the acid. Recrystallized from petroleum ether–benzene, the leaflets melted at 85–86°; yield,1 g.

Anal. Calcd. for $C_{10}H_{19}ON$: N, 8.28. Found: N, 8.23.

Acidification of the water layer gave a small amount of acidic material which proved identical with that obtained from the ozonolysis of the ketone. By removing the benzene from the sodium amide and repeating the above procedure, an equal weight of acid and amide was obtained (0.5 g. each from 2 g. of ketone).

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Summary

1,2,3,3-Tetramethylcyclopentanecarboxylic acid has been synthesized from camphor. It proved to be different from the $C_{10}H_{18}O_2$ acid isolated from petroleum by Horeczy, Wash and Lochte and obtained as a degradation product by Roberts and Bailey.

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