[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

4-METHYLOCTANE.

BY LATHAM CLARKE.

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This hydrocarbon is the third nonane to be synthesized and studied in this laboratory.[1] The syntheses of normal nonane and two others are almost completed and accounts of the work will appear within the next few months.

4-Methyloctane is a liquid, boiling at 141.7–141.9° at 771 mm. It has, at 15°, the specific gravity 0.7320, compared to water at 15°. The index of refraction, N_D (25°) = 1.4027.

The method of preparation which seemed the best for 4-methyloctane was the following: Normal propyl iodide was condensed with ethyl sodium acetoacetate, giving ethyl normalpropylacetoacetate, which, on saponification with dilute alkali, yielded the ketone 2-hexanone. This, with normal propylmagnesium iodide, formed the alcohol 4-methyl-4-octanol, containing nine atoms of carbon. By treating the carbinol with iodine and red phosphorus, it was converted into the corresponding carbinol iodide, which last readily lost the elements of hydriodic acid when mixed with alcoholic potash, whereby a nonylene was produced which presumably was 4-metheneoctane, and which on reduction was saturated to 4-methyloctane.

Summary.

$CH_3COCH_2CO_2C_2H_5$. Ethyl acetoacetate + C_3H_7I ⟶
$CH_3COCH(CH_2CH_2CH_3)CO_2C_2H_5$. Ethyl *n*-propylacetoacetate ⟶
$CH_3COCH_2CH_2CH_2CH_3$. 2-Hexanone + C_3H_7MgI ⟶
$CH_3CH_2CH_2C(OH)(CH_3)CH_2CH_2CH_2CH_3$. 4-Methyl-4-octanol ⟶
$CH_3CH_2CH_2C(:CH_2)CH_2CH_2CH_2CH_3$. 4-Metheneoctane ⟶
$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_3$. 4 Methyloctane.

In the reaction between normal propylmagnesium iodide and 2-hexanone it was observed that by a slight variation in procedure, either 4-methyloctanol (the expected product) or 4-metheneoctane would be obtained, the latter resulting from a dehydration of the 4-methyloctanol. Ordinarily such reactions as this are carried out by dissolving the required amount of magnesium turnings in a slight excess over the theoretical amount of dry normal propyl iodide mixed with about three volumes of anhydrous ether. To the solution, after thoroughly cooling down in a bath of ice water, the ketone diluted with two volumes of anhydrous ether is added, the mixture allowed to stand a few moments, and the organo-magnesium compound decomposed by treatment with ice water, followed by neutralization with dilute hydrochloric acid. The ether

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[1] The first and second were 2,5-dimethylheptane, THIS JOURNAL, 34, 54, and 2,4-dimethylheptane, *Ibid.*, 34, 60.

layer is now drawn off, dried with potassium carbonate, the ether distilled off and the residue fractionated. This procedure in the case of normal propylmagnesium iodide and 2-hexanone gave a mixture of the nonylene and alcohol, in the proportion of about one of the former to three of the latter. The fractional separation was difficult. If the temperature was not kept down carefully during the addition of the ketone, the proportion of nonylene would increase, in one case reaching about three parts of the nonylene to one of alcohol. More concentrated solutions in ether as well as excess of acid at the finish were factors which increased the yield of nonylene. Conversely, carefully keeping the temperature in the neighborhood of 0°, and avoiding an excess of acid in the final steps considerably increased the amount of alcohol. In no case was either nonylene or alcohol obtained entirely. In concentrated solutions, the increased production of nonylene is probably due to the heat of reaction, which, being liberated in a smaller sphere, is more intense than in a dilute solution. That this is true is indicated by the fact that when the ketone was added in minute portions with vigorous shaking, thus avoiding any great heat of reaction in one place, the yield of carbinol was much greater.

Experimental Part.

Ethyl Normalpropylacetoacetate, $CH_3COCH(CH_2CH_2CH_3)CO_2C_2H_5$.—This was made from sodium ethylate, ethylacetoacetate and normalpropyliodide by the Conrad and Limpach method.[1] The normalpropyliodide was prepared from normalpropylalcohol by the action of red phosphorus and iodine and was dried over calcium chloride and redistilled before use. The crude ethyl normalpropylacetoacetate was not distilled but was converted directly into 2-hexanone.

2-Hexanone, $CH_3COCH_2CH_2CH_2CH_3$, was made from ethyl normalpropylacetoacetate by boiling for thirty minutes with four molecules of potassium hydroxide in 10% solution. At the end of that time, the ketone was distilled from the alkali with steam, the upper layer of the distillate separated, dried with calcium chloride and fractionated until a fraction was obtained which boiled at 126–126.5° at 760 mm. As a rule, the yield of pure 2-hexanone was about 35 grams from 130 grams of ethyl acetoacetate, from 5 to 15 grams were rejected during the fractional distillations. This ketone has already been described.[2]

4-Metheneoctane, $CH_3CH_2CH_2C(:CH_2)CH_2CH_2CH_2CH_3$.—As before noted in this paper, the action of normal propylmagnesium iodide and 2-hexanone results in the formation of a mixture of 4-methyloctanol and 4-metheneoctane, the amount of the two, depending on the conditions

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[1] *Ann.*, 192, 155.

[2] Erlenmeyer-Wanklyn, *Ann.*, 135, 144. Schorlemmer, *Ibid.*, 161, 273. Konovalov, *J. Russ. Phys. Chem. Soc.*, 25, 479.

of the experiment. Since 4-metheneoctane was the desired product, the conditions were so regulated as to produce this as far as possible.

The following procedure was usually employed: Twelve grams of magnesium turnings were dissolved in 90 grams of normal propyl iodide, diluted with three volumes of anhydrous ether. Fifty grams of 2-hexanone mixed with one volume of ether were added slowly, the temperature being held between 10° and 15°. The usual treatment with water and acid followed, and after separating and drying with potassium carbonate, the ether solution was fractionated. The separation of the nonylene from the alcohol was accomplished after several fractionations, the former boiling at 142–145°, the latter not very sharply at 178–183°. The yield of nonylene was usually 35–40 grams, of alcohol 20–22 grams. The nonylene was treated with 5% of its weight of iodine, and one-half of 1% of its weight of red phosphorus, and heated an hour or so to convert traces of alcohol into carbinol iodide, filtered to remove phosphorus, washed with water, and distilled with alcoholic potash. The distillate consisted of both nonylene and ethyl alcohol, as these form a soluble binary mixture which distils off on the steam bath. The distillate was treated with water, whereby the hydrocarbon separated as a floating layer which was removed, washed well with water, dried with metallic sodium and fractionated. The major portion boiled at 142–144° at 768 mm., while much of the fraction boiled at 143.6°. The carbinol mentioned above was mixed with one molecule of iodine and red phosphorus, one-tenth the weight of the iodine used being the weight of the phosphorus taken. The mixture was heated to 70° for three or four hours, filtered through glass wool, and washed with water. The resulting carbinol iodide was refluxed for an hour with alcoholic potash and distilled, the distillate was heated with water, which caused the nonylene to separate as a floating layer which was removed, dried with metallic sodium and distilled. The boiling point of the major fraction was 142–144° at 768 mm. The total yield of nonylene was usually about 80% of the theoretical or fifty grams, calculated from the fifty grams of hexanone used.

Subst., 0.1852; CO_2, 0.5807; H_2O, 0.1852.

Calculated for C_9H_{18}:	C, 85.71; H, 14.29.
Found:	C, 85.52; H, 14.32.

Properties.—Liquid boiling at 142–144° at 768 mm. It has a faint sweetish odor. It is miscible with the common organic solvents but not with water.

The carbinol was analyzed in the usual way.

Subst., 0.1554; CO_2, 0.4279; H_2O, 0.1920.

Calculated for $C_9H_{20}O$:	C, 75.00; H, 13.88.
Found:	C, 75.10; H, 13.83.

Properties.—Colorless, oily liquid with an aromatic sweetish odor. Boiling point, 178–183°. It is miscible with the common organic solvents.

4-Methyloctane, $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_2CH_2$, was prepared from 4-metheneoctane by reduction, the method being that of Sabatier and Senderens, wherein the unsaturated hydrocarbon was passed over freshly reduced nickel at a temperature of 160–180° in a stream of hydrogen. The process was exactly as that described by Clarke and Beggs[1] for the reduction of 2-methyl-5-metheneheptane to 2,5-dimethylheptane.

Twenty-one grams of 4-metheneoctane gave 19 grams of 4-methyloctane, which boiled at 141.7–141.9° at 771 mm. after a fractional distillation in which hardly a gram of hydrocarbon was rejected.

Subst., 0.1720; CO_2, 0.5334; H_2O, 0.2403.

Calculated for C_9H_{20}:	C, 84.37; H, 15.63.
Found:	C, 84.57; H, 15.62.

Properties.—Colorless, practically odorless, very mobil liquid. It boils at 141.7–141.9° under 771 mm. Its specific gravity at 15°, compared to water at 15°, is 0.7320 and its index of refraction as determined with the use of a Pulfrich refractometer, N_D (25°) = 1.4027.

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CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE HAVEMEYER LABORATORIES OF COLUMBIA UNIVERSITY No. 204.]

RESEARCHES ON QUINAZOLINES (THIRTY-FIRST PAPER). THE ACTION OF METHYL AND ETHYL IODIDES UPON 4-QUINAZOLONES.

BY MARSTON TAYLOR BOGERT AND GEORGE AUGUSTUS GEIGER.[2]

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But little information is on record concerning the action of alkyl iodides upon quinazolines.

Paal and Busch[3] heated 3-phenyldihydroquinazoline with methyl iodide for 2 hours at 100° and obtained an iodomethylate, another compound (apparently an isomeric iodomethylate), and an iodomethylate periodide.

Knape[4] heated a methyl alcohol solution of 3-methyl-4-quinazolone with methyl iodide in a sealed tube and obtained the iodomethylate. He also replaced the iodine by hydroxyl through contact with moist silver oxide.

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[1] THIS JOURNAL, 34, 59 (1912).

[2] Read at the Washington meeting of the Society, December 29, 1911.

[3] *Ber.*, 22, 2689 (1889).

[4] *J. prakt. Chem.*, [2] 43, 223 (1890).