From these experiments the conclusion is reached that the method described by Kober for urine, if modified as described, will give good results with other nitrogen-containing bodies. R. O. E. DAVIS.

LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA.

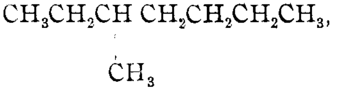
[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

3-METHYL-HEPTANE.

BY LATHAM CLARKE.

Received March 2, 1909.

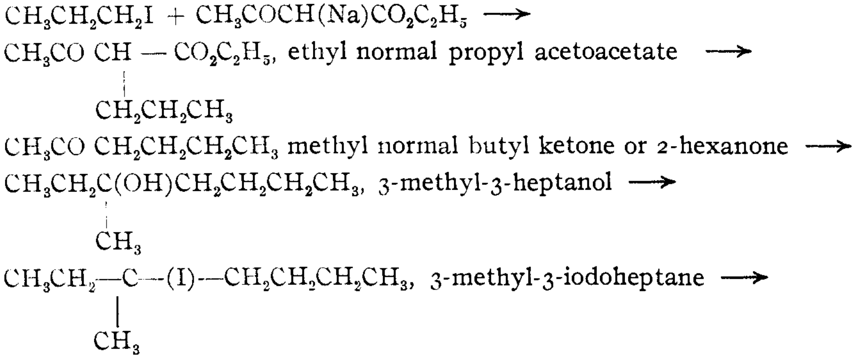
This paper contains an account of the synthesis and properties of the octane, 3-methyl-heptane, $CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}\,CH_2CH_2CH_2CH_3$, and forms a continuation of the study of the octanes which was begun some time ago in this laboratory.[1]



3-Methyl-heptane has already been prepared and described by Mlle. Welt,[2] but as her product boiled from 110° to 120°, it was evidently too impure for the careful study of the physical constants, which is one of the objects of this research. The method of preparation according to Wurtz was employed by Mlle. Welt, who treated amyl iodide and ethyl iodide with sodium.

In this study of 3-methyl-heptane one method was used, which guaranteed a pure product, and alone of those considered was simple enough to be used with ease. It consisted of the following reactions: Ethyl normal propyl acetoacetate was made and saponified, forming methyl normal butyl ketone, which on treatment with ethyl magnesium bromide produced 3-methyl-heptanol. This last compound was converted into the corresponding iodide and reduced, yielding the desired octane.

Summary of Reactions.



$CH_3CH_2CH_2I + CH_3COCH(Na)CO_2C_2H_5 \longrightarrow$

$CH_3CO\,\underset{\displaystyle CH_2CH_2CH_3}{\underset{|}{CH}} - CO_2C_2H_5$, ethyl normal propyl acetoacetate $\longrightarrow$

$CH_3CO\,CH_2CH_2CH_2CH_3$ methyl normal butyl ketone or 2-hexanone $\longrightarrow$

$CH_3CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}(OH)CH_2CH_2CH_2CH_3$, 3-methyl-3-heptanol $\longrightarrow$

$CH_3CH_2-\underset{\displaystyle CH_3}{\underset{|}{C}}-(I)-CH_2CH_2CH_2CH_3$, 3-methyl-3-iodoheptane $\longrightarrow$

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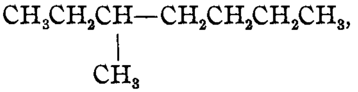
[1] A full list of the octanes hitherto described will be found in the January, 1909, number of THIS JOURNAL, 31, 107.

[2] *Ann. Chim. Phys.* [7], 6, 121.



$$\underset{\displaystyle CH_3}{CH_3CH_2\overset{}{CH}}\!-\!CH_2CH_2CH_2CH_3$$

, 3-methyl-heptane.

The 3-methyl-heptane obtained by the foregoing procedure was purified by treating in the cold with concentrated sulphuric acid, after which it was separated and boiled over metallic sodium for an hour with a return condenser and twice distilled. The boiling point on both distillations was the same and was constant, *viz.*, 117.6° at 760 mm., and therefore the hydrocarbon was supposed to be pure.

A sample of this was lent to Professor Richards in order that his assistant, Professor Speyers, might make a determination of its compressibility. Professor Speyers found that the mercury which he used in his compressibility apparatus was attacked by the hydrocarbon and a small amount of a black substance was formed on the plane of contact of the two liquids—the mercury and the hydrocarbon. Subsequent investigation showed that boiling ten grams of octane together with mercury in a flask with a return condenser yielded several milligrams of this black substance, the nature of which has not yet been determined. It, however, is an organic derivative, contains neither halogen nor sulphur and is soluble in dilute acetic acid, but not in water. On account of the small quantity obtainable, work on it is slow and difficult, but it is hoped that its identity will soon be discovered.

In the new purification of the octane after treatment with sulphuric acid and sodium as before mentioned, it was boiled with a return condenser over metallic mercury and then twice redistilled. Or better, instead of the mercury treatment, the hydrocarbon was shaken out with dilute potassium permanganate solution which oxidized the impurity that caused the action on the mercury.

The effect of this impurity on the physical properties of the octane was negligible. The specific gravity, for example, before and after purification by mercury or permanganate was found to agree to the fourth decimal place.

Properties: 3-Methyl heptane is a clear colorless very mobile liquid, possessing a mild but quite characteristic odor. It boils at 117.6° at 760 mm. pressure. At 15° it has the specific gravity compared to water at 15°, 0.7167. At 25° it has the following index of refraction: $N_D(25°) = 1.4022$, in the determination of which much aid was given by Mr. F. W. Barry.

Experimental.

Normal propyl iodide and sodium ethylacetoacetate by the use of Conrad's method[1] yielded ethyl normal propyl acetoacetate. This was not purified by distillation, but the crude product of the reaction was converted into normal butyl ketone or 2-hexanone.

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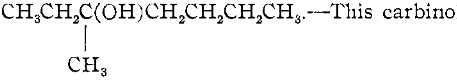
[1] Conrad and Limpach, *Ann.*, **192**, 153.

Methyl Normal Butyl Ketone or 2-Hexanone, $CH_3COCH_2CH_2CH_2CH_3$.—This was made from normal propyl acetacetate by boiling for eight hours with 3 molecules of potassium hydroxide in 10 per cent. solution, and distilling with steam at the end of the eight-hour period. The upper layer of the distillate was separated, dried over calcium chloride and redistilled until a fraction boiling at 126–126.5° at 760 mm. was obtained. The usual yield was 40 per cent. of the theoretical, or about 40 grams reckoning through two reactions, that is, from 130 grams of acetoacetic ester.

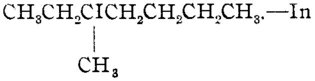
2-Hexanone has already been described so it was properly identified without the necessity of an analysis.[1]

3-Methyl-3-heptanol,  $CH_3CH_2\underset{CH_3}{\underset{|}{C}}(OH)CH_2CH_2CH_2CH_3$.—This carbinol was synthesized from ethyl magnesium bromide and 2-hexanone by the Grignard reaction.

Twelve grams of magnesium turnings were dissolved in a mixture of 60 grams of ethyl bromide and 60 grams of anhydrous ether, and to the cold reaction product 50 grams of 2-hexanone dissolved in an equal volume of dry ether were slowly added. After standing fifteen minutes, the carbinol was set free by treatment with water and hydrochloric acid and the ether layer containing it, was separated and dried over potassium carbonate. On distilling off the ether, the carbinol was obtained as a residue, and thus was fractionated until a portion boiling at 161–2° at 763 mm. was obtained. The yield was practically quantitative.

Analysis—Calculated for $C_8H_{18}O$: C, 73.85; H, 13.85
Found: C, 73.08; H, 13.60

Properties.—Colorless liquid with an odor much like oil of eucalyptus. It is insoluble in water but readily miscible with the common organic solvents. Boiling point 161–2° at 763 mm.

3-Methyl-3-iodoheptane,  $CH_3CH_2\underset{CH_3}{\underset{|}{C}}ICH_2CH_2CH_2CH_3$.—In a typical experiment, 65 grams of 3-methyl-3-heptanol were mixed with 10 grams of red phosphorus and 63 grams of iodine added in small portions, the reaction flask all the time being kept cool by a bath of cold water. At the end of an hour the bath was warmed slowly until 80° was reached at which point the temperature was held constant four hours. The carbinol iodide was poured into water, washed once by decantation, filtered from unchanged red phosphorus and transferred to the flask in which it was to be reduced to the hydrocarbon.

Reduction of 3-Methyl-3-iodoheptane.—The 3-methyl-3-iodoheptane from the foregoing experiment was transferred to a round bottom flask of 250 cc. capacity—which was fitted with a reflux condenser—and mixed with 200 grams of finely divided zinc, which had previously been treated with 10 cc. of copper sulphate solution. Through the condenser tube, concentrated hydrochloric acid was added a few cubic centimeters at a time, and heat was supplied to the flask, so the temperature was about 80° and the effervescence produced by the acid was very lively. This treatment was continued until the floating layer of octane had apparently reached a maximum. No more acid was then added, but a piece of scrap magnesium weighing about 5 grams was introduced, and this, reacting on the plane of contact between the lower aqueous solution and the upper hydrocarbon layer completed the reduction of the small amount of alkyl iodide which was still present in the latter. As soon as the magnesium was used up, the reaction flask was attached to a downward condenser and the octane

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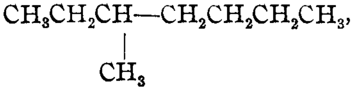
[1] Erlenmeyer, Wanklyn, *Ann.*, **135**, 144. Schorlemmer, *Ann.*, **161**, 273. Konovalov, *J. Russ. Phys.-Chem. Soc.*, **25**, 479.

distilled off with steam, separated, treated with concentrated sulphuric acid and boiled over metallic sodium with a reflux condenser until all traces of halogen were removed. On distillation the octane boiled at 117.8° at 760 mm. and on analysis gave the following result:

Calculated for C_8H_{18}: C, 84.21; H, 15.79
Found: C, 84.11; H, 15.96

The constitution of 3-methyl-heptane,  $\mathrm{CH_3CH_2}\underset{\substack{|\\ \mathrm{CH_3}}}{\mathrm{CH}}\text{—}\mathrm{CH_2CH_2CH_2CH_3}$, is shown by the method of preparation.

I am deeply indebted to the C. M. Warren Fund for materials used in this research.

CAMBRIDGE, MASS., February 17, 1909.

CONTRIBUTIONS TO OUR KNOWLEDGE OF AMERICAN COLOPHONIUM. I. THE RESIN OF THE NORWAY PINE.

BY GEORGE B. FRANKFORTER.

Received March 9, 1909.

The first important work on the resins was begun by Baup[1] in 1826. He obtained from *Pinus abies*, a crystallized substance to which he gave the name abietic acid. From another species, *Pinus maritima*, he obtained a second substance which he called pinic acid. Later, Unverdorben[2] obtained two acids from common colophonium. One seemed to be identical with abietic acid although it was called sylvic acid; the other, an amorphous substance, was called pinic acid, differing in its general properties, however, from Baup's pinic acid. Immediately following the work of Unverdorben, Trommsdorff[3] obtained from American colophonium a crystallized acid which he regarded as sylvic acid and to which he assigned the formula $C_{40}H_{60}O_4$. Some years later Siewert[4] repeated the work of Trommsdorff and assigned to sylvic acid the formula $C_{20}H_{30}O_2$, showing incidentally that abietic acid is isomeric with Baup's pinic and with pimaric acid described by Laurent,[5] differing, however, in its physical properties and especially with regard to its solubility in alcohol.

Maly[6] again studied American colophonium exhaustively, obtaining a crystallized acid by a slightly modified form of the Unverdorben method. Maly's process for the purification of the resin acids has been of the greatest importance, inasmuch as it has been practically the only process used

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[1] *Ann. chim. phys.*, **31**, 108.

[2] *Pogg. Ann.*, **11-20**, 239.

[3] *Ann.*, **13**, 169.

[4] *Z. gesammten Naturwissenschaften*, **14**, 311.

[5] *Ann.*, **34**, 372.

[6] *J. prakt. Chem.*, **96**, 145.