

chloroform, acetone or hot alcohol; very difficultly soluble in boiling water, carbon bisulphide, ether, petroleum ether, dilute acid or alkalis.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

METHYL ETHYL ISOBUTYL METHANE.

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In continuing the research on the octanes undertaken some time ago in this laboratory,¹ the synthesis of methylethyl isobutyl methane,

$$\begin{array}{l} \text{C H}_3 \\ \text{C}_2\text{H}_5 \end{array} \left. \begin{array}{l} \diagup \\ \diagdown \end{array} \right\} \text{CH} - \text{CH}_2 - \text{CH}(\text{CH}_3)_2, \text{ or } 2\text{-}4\text{-dimethyl hexane has been accomplished.}$$

In the preparation of this hydrocarbon the two following series of reactions promised a pure product and both were therefore used.

First Method.—From isopropyl acetacetic ester by saponification methyl isobutyl ketone was obtained. This, when treated with ethyl magnesium bromide, yielded 2-4-methyl-4-hexanol, $\text{CH}_3\text{CH}_2 - \underset{\text{CH}_3}{\text{C}}(\text{OH}) - \underset{\text{CH}_3}{\text{CH}_2}\text{CH} - \text{CH}_3$.

This carbinol, on transforming into the corresponding iodide and reducing, gave the desired octane.

These reactions are herewith summarized:

$\text{CH}_3\text{COCH}(\text{CH}_3) - \text{CO}_2\text{C}_2\text{H}_5$, isopropyl acetacetic ester \rightleftharpoons

$$\begin{array}{c} | \\ \text{CH}(\text{CH}_3)_2 \\ | \\ \text{CH}_3\text{COCH}_2 - \text{CH}(\text{CH}_3)_2, \text{ methylisobutyl ketone } \rightleftharpoons \end{array}$$

$\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{CH}_3) - \text{CH}_2\text{CH}(\text{CH}_3)_2$, 2-4-methyl-4-hexanol \rightleftharpoons

$$\begin{array}{c} | \\ \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2 - \text{C}(\text{I}) - \text{CH}_2\text{CH}(\text{CH}_3)_2, \text{ 2-4-methyl-4-iodohexane } \rightleftharpoons \end{array}$$

$$\begin{array}{c} | \\ \text{CH}_3 \\ | \\ \text{CH}_3\text{CH}_2 - \text{CH} - \text{CH}_2\text{CH}(\text{CH}_3)_2, \text{ methyl ethyl isobutyl methane or 2-4-dimethyl hexane.} \\ | \\ \text{CH}_3 \end{array}$$

methyl hexane.

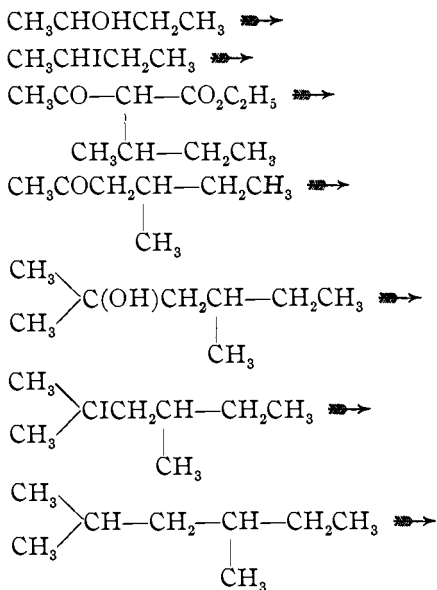
Second Method.—Secondary butyl alcohol was converted into the corresponding iodide and made to react with sodium acetacetic ester, thus forming ethyl secondary butyl acetacetate, $\text{CH}_3\text{COCHCO}_2\text{C}_2\text{H}_5$.



¹ Preliminary notice. *Ber.*, 40, 352.

From this the ketone 4-methyl-2-hexanone, $\text{CH}_3\text{COCH}_2\text{CH}-\text{C}_2\text{H}_5$, was prepared, which by treating with methyl magnesium iodide was transformed into the carbinol, 2-4-methyl-2-hexanol, $\begin{array}{c} \text{CH}_3 \\ | \\ \text{C}(\text{OH})-\text{CH}_2-\text{CH} \\ | \\ \text{CH}_3 \end{array} (\text{CH}_3)-\text{CH}_2\text{CH}_3$. The corresponding carbinol was next made, and by reduction the octane, methyl ethyl isobutyl methane, was formed.

Summarizing these reactions:



The ketone 4-methyl-2-hexanone possessed an odor much like that of bananas. The ketone 4-methyl-2-heptanone described in an earlier paper¹ also had an odor like bananas. This is an interesting observation in view of the similarity of structure of these compounds, the first-mentioned having the configuration, $\text{CH}_3\text{COCH}_2-\text{CH}-\text{CH}_2\text{CH}_3$, and the

second, $\text{CH}_3\text{COCH}_2-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3$.

In this paper is also described a device to serve as a small Hempel column in the fractional distillation of small quantities of liquids and which consists of a platinum wire with small glass beads strung on it. By folding the wire back and forth a column can be obtained of various lengths and of such a thickness as to fit flask necks of various diameters.

¹ Clarke, *Amer. Chem. J.*, 39, 93 (1908).

An improvement in this method of reduction of an iodide to the hydrocarbon is also described and also a description given of a new unsaturated alkyl chloride.

Experimental.

First Method.—Ethyl isopropylacetate was prepared from sodium ethyl acetate by the method of Conrad.¹ This was converted into methyl isobutyl ketone by the method described in a former paper² by boiling with a 10 per cent. solution of caustic potash using, however, 3 molecules of alkali instead of 2, as was erroneously printed in the paper referred to. This process yielded methyl isobutyl ketone which boiled at 118–118.2° at 758 mm. pressure.

A certain line of work was planned on this ketone which, however, failed to produce satisfactory results and was abandoned. The preliminary experiment on this projected research was the preparation of *2-chlor-4-methyl-Δ^{1,2}-amylene*, $(\text{CH}_3)_2\text{CH}-\text{CH}_2-\overset{\text{Cl}}{\underset{|}{\text{C}}}=\text{CH}_2$. As this work will proceed



no further, a description of this compound will be inserted here. The compound was prepared by the action of phosphorus pentachloride on methyl isobutyl ketone. Twenty grams of methyl isobutyl ketone were treated with 44 grams of phosphorus pentachloride in small portions, the ketone being kept cool by a bath of cold water. The pentachloride dissolved slowly in the liquid and when finally the solution became complete, it was poured into 100 grams of cold water, which removed the phosphorus oxychloride and extracted one molecule of hydrogen chloride from the *2-dichlor-4-methyl pentane*, $(\text{CH}_3)_2\text{CHCH}_2-\overset{\text{Cl}}{\underset{|}{\text{C}}}-\text{CH}_3$, and formed



2-chlor-4-methyl-Δ^{1,2}-amylene. This reaction was attended by some heat. The amylene compound was washed with water till the wash water was free from hydrochloric acid, dried with calcium chloride and distilled. It boiled at 102.5° at 760 mm. pressure.

Analysis by Carius's method gave Cl, 29.89; calculated, 29.24.

Properties.—Colorless mobile liquid boiling at 102.5° at 760 mm. It is miscible with methyl alcohol, ethyl alcohol, benzene and chloroform. The dry liquid mixed with anhydrous ether is almost without action on magnesium turnings even after 10 hours' boiling with a reflux condenser. Oxidation by potassium permanganate in aqueous solution, brought about by shaking thoroughly in a closed flask, yielded isovaleric acid, $(\text{CH}_3)_2\text{CHCH}_2-\text{CO}_2\text{H}$, and thereby proved the constitution to be that given above.

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

² Clarke and Shreve, *Amer. Chem. J.*, **35**, 514.

2,4-Methyl-4-hexanol, $(\text{CH}_3)_2\text{CH}-\text{CH}_2\text{C}(\text{CH}_3)(\text{OH})-\text{CH}_2\text{CH}_3$, was made from methyl isobutyl ketone by the use of ethyl magnesium bromide.

The organo magnesium compound made from 6.2 grams of magnesium turnings and 25 grams of ethyl bromide was treated with 20 grams of the ketone and the carbinol extracted in the usual manner by subsequent treatment with water and hydrochloric acid, and separation of the ether layer.

In this experiment the ether residue after drying with a small amount of potassium carbonate was fractionated with great care. The small amount of material (20 grams) did not permit the use of a large Hempel column, so a small and convenient modification of this apparatus was devised and was used in the fractionation of small quantities of liquids.

A piece of small platinum wire (No. 27 B. & S.) about a meter long was strung with fine glass beads (5 mm. long by 2 mm. in diameter). This was then folded back and forth in lengths of 7 or 8 cm. to form a cylinder which would just fit snugly into the neck of the distilling flask and was lowered so that it was between the entrance to the bulb and a distance of about 2 cm. below the side neck—so that it should not interfere with the bulb of the thermometer. Ten cm. of the platinum wire were left bare and were allowed to protrude from the top of the flask neck, the whole column being thus held in position by the cork. The column could therefore be raised or lowered at will. By varying the number of folds it could be made short and thick or long and slender and could be made to fit various distilling flask necks of different diameters. This device was found to be very satisfactory.

In fractionating the above-mentioned carbinol, three portions were obtained: the first consisted of but a few drops of liquid boiling at about 120° and was unchanged ketone; the second weighed 20 grams and after being thrice distilled, boiled at 151° at 768 mm.; the third fraction boiled vaguely between 175° and 190° . but weighed less than a gram so no further study was made of it. The yield of 2,4-methyl-4-hexanol was 77 per cent. of the theoretical.

Calculated for $\text{C}_8\text{H}_{18}\text{O}$: C, 73.85; H, 13.85.

Found: C, 73.59; H, 13.98.

Properties.—This carbinol is a liquid boiling at 151° at 768 mm. It has a pronounced odor, reminding one of oil of *Eucalyptus*. It is soluble in ethyl alcohol, methyl alcohol, ether, benzene, toluene, chloroform and carbon tetrachloride.

Preparation and Reduction of 2,4-methyl-4-iodohexane.—To 18 grams of 2,4-methyl-4-hexanol, 5 grams of red phosphorus and 18 grams of iodine were added, the mixture being kept cool for an hour by immersion of the flask in cold water. The flask was heated on the steam bath for four hours, and 20 grams of constant boiling aqueous hydriodic acid (boiling

point 126°) were poured into the flask and the heating on the steam bath continued for an hour. This brought about no reduction of the carbinol iodide to octane. Another test portion of the carbinol itself was boiled with hydriodic acid and red phosphorus, but no reduction followed. The above-mentioned hydriodic acid and carbinol iodide were subjected to distillation with the free flame, whereby the 2,4-methyl-4-iodohexane passed over with the hydriodic acid and condensed as a colorless liquid. The separation from the unchanged red phosphorus and phosphoric acid was effected completely in this way. By means of a separatory funnel the iodide was removed and transferred to a round-bottomed flask of 250 cc. capacity. 200 grams of finely divided zinc were mixed with it to form a thick paste and the flask was attached to a long return condenser.

Strong hydrochloric acid was poured through the condenser a few cubic centimeters at a time and the flask thoroughly shaken until after about two hours a floating layer of octane had collected on the surface of the solution. This still contained unreduced iodide which was completely reduced by adding a few pieces of scrap magnesium which floated on the acid solution and stayed at the plane of contact of the two liquids. The liquids were decanted from the unchanged zinc after standing about half an hour from the time of putting in the magnesium, and were separated and the octane layer dried with calcium chloride.

The zinc left in the reduction flask was treated again with 100 cc. of 38 per cent. hydrochloric acid in small portions with very thorough shaking and, as before, an oily floating layer separated out and was treated with a gram or so of magnesium scrap after which it was separated and put into the flask with the first lot. A third and a fourth time this procedure was repeated. Finally the collected octane was fractionated and boiled mostly between 105° and 115°. Some unchanged iodide and carbinol were also recovered. The fraction 105–115° was redistilled and a new fraction, 109–111°, obtained. This was dried two weeks over sodium, and was allowed to stand two weeks over concentrated sulphuric acid, then over sodium again for a week and finally was boiled over sodium, using a return condenser. On distillation, 8 grams of the octane collected in a fraction boiling at 109.8° to 110° at 762 mm. It was halogen-free and contained no unsaturated hydrocarbon. The method of formation proves this hydrocarbon to be methyl ethyl isobutyl methane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$.

Calculated for C_8H_{18} :	C, 84.21; H, 15.79.
Found:	C, 84.10; H, 15.90.

Properties.—This octane forms an almost odorless, very mobile liquid boiling at 109.8° to 110.0° at 762 mm. Its specific gravity at 15° is 0.7083, compared to water at 15°. The index of refraction, determined with a Pulfrich refractometer, is $n_D(25^\circ) = 1.3986$.

Second Method.—Secondary butyl alcohol was prepared by the action of ethyl magnesium bromide on acetaldehyde. This was deemed the best way of making it, because the reduction of methyl ethyl ketone is attended by many difficulties and gives a poor yield.¹

Twenty-four grams of magnesium turnings were dissolved in 115 grams of pure ethyl bromide mixed with 100 grams of dry ether and to the solution—cooled by immersion of the flask in ice water—44 grams of anhydrous acetaldehyde dissolved in 50 grams of ether were added. The reaction is quite violent but the flask was kept cool by ice water and the aldehyde added very gradually. The reaction mixture was allowed to stand for half an hour, when it was treated with water and dilute hydrochloric acid, and the ether layer separated, dried with potassium carbonate and fractionated in the usual fashion. The yield of secondary butyl alcohol was about 80 per cent. of the theoretical (reckoned from the acetaldehyde)—in the above experiment, 59 grams—but a small amount of a higher boiling compound was also obtained, which will be investigated when opportunity offers.

The boiling point of the secondary butyl alcohol was 99° at 762 mm. Norris and Green² give 99.7° to 99.9° at 756 mm. Our product, however, boiled very sharply and must have been pure.

Secondary Butyl Iodide was prepared from the carbinol by the action of iodine and red phosphorus. Seventy-four grams of secondary butyl alcohol were mixed with 20 grams of red phosphorus and treated with 128 grams of iodine in small portions with cooling. To complete the reaction, after standing an hour, the mixture was heated for two hours on the steam bath with a return condenser. Finally by distillation with the free flame the carbinol iodide was obtained, and was washed with water, dried with calcium chloride and redistilled. Boiling point, 118–120°. The yield was nearly quantitative.

Ethyl Secondary Butyl Acetacetate, $\text{CH}_3\text{COCH}-\text{CO}_2\text{C}_2\text{H}_5$, was made by



the procedure generally employed in the preparation of acetacetic ester derivatives. Twenty-three grams of sodium were dissolved in 300 grams of absolute alcohol, and to the solution 130 grams of acetacetic ester and 185 grams of secondary butyl iodide were added, after which the flask was placed on the steam bath and heated for ten hours, by which time the contents became neutral. The major part of the alcohol was distilled off over the free flame, the flask being incessantly agitated, and then the residue was poured into a liter of water, which caused the ethyl secondary butyl acetacetate to separate out as a floating oily layer. By drying

¹Norris and Green, *Amer. Chem. J.*, **26**, 293.

²*Amer. Chem. J.*, **26**, 307.

this with potassium carbonate and distilling, it was obtained as a colorless, oily liquid boiling at 210–211° at 762 mm.

Analysis: 1121 grams substance gave 2643 grams CO₂ and 0.0994 gram H₂O.

Calculated for C₁₀H₁₈O₃: C, 64.51; H, 9.67.

Found: C, 64.29; H, 9.88.

Properties.—Colorless oily liquid boiling at 210–211° at 762 mm. and having a rather strong characteristic odor. It is miscible with methyl alcohol, ethyl alcohol, ether, toluene, benzene, chloroform, acetone and glacial acetic acid. It dissolves readily in cold concentrated nitric acid, hydrochloric acid, and sulphuric acid without change of color or apparent decomposition.

4-Methyl-2-Hexanone, CH₃COCH₂CH(CH₃)CH₂CH₃, was produced when ethyl secondary butyl acetate was hydrolyzed with caustic potash. The acetate was boiled for fifteen hours with three molecules of caustic potash in 10 per cent. solution, using a flask with a return condenser, after which the mixture was distilled with steam and the upper layer of the distillate separated, dried over calcium chloride and distilled with a Hempel column. A fraction was obtained boiling at 130–145° which contained the largest part of the above-mentioned distillate, but a small amount of unchanged ethyl secondary butyl acetate was also recovered. On careful redistillation of the 130–145° fraction, the 4-methyl-2-hexanone came over at 139° at 762 mm. The yield was usually about 50 per cent. of the theoretical on the assumption that the ketone splitting is the only reaction.

Calculated for C₇H₁₄O: C, 73.68; H, 12.27.

Found: C, 73.52; H, 12.45.

Properties.—4-Methyl-2-hexanone, CH₃COCH₂CH(CH₃)CH₂CH₃, boils at 139° at 762 mm. It has an odor something like oil of tansy and very similar in nature to that of 4-methyl-2-heptanone,¹ which smells like oil of bananas. These odors are by no means exactly the same but are of the same general order and have much in common which it is hard to describe.

This ketone is soluble in ether, ethyl alcohol, methyl alcohol, benzene, toluene, acetone, chloroform and glacial acetic acid. It dissolves without coloration or decomposition in concentrated nitric, hydrochloric and sulphuric acids.

2,4-Methyl-2-hexanol, CH₃—C—(CH₃)(OH)CH₂—CH(CH₃)—CH₂CH₃, was prepared from 4-methyl-2-hexanone by the action of methyl magnesium iodide. A solution of 12 grams of magnesium in 75 grams of methyl iodide and 75 grams of ether was treated with 57 grams of the C₇-ketone and after standing for half an hour, the C₈-carbinol was extracted by the customary procedure, by adding first water, then dilute

¹ Clarke, *Amer. Chem. J.*, **39**, 93 (1908).

hydrochloric acid, separating the ether layer and drying the latter over potassium carbonate. Fractionation of the ether residue gave a fraction weighing 65 grams and boiling between 150° and 154° . This was four times redistilled with the modified Hempel column already described in this paper and at the last distillation practically all boiled at 150.0 – 150.5° at 766 mm. The yield was 59 grams or about 90 per cent. of the theoretical.

Calculated for $C_8H_{18}O$: C, 73.85; H, 13.85.

Found: C, 73.60; H, 14.02.

Properties.—2,4-Methyl-2-hexanol boils at 150.0 – 150.5° at 766 mm. It has an odor like that of oil of *Eucalyptus*. It is soluble in ethyl alcohol, methyl alcohol, benzene, toluene, acetone, chloroform and glacial acetic acid.

Preparation and Reduction of 2,4-Methyl-2-Iodohexane.—Twenty-six grams of 2,4-methyl-2-hexanol were mixed with 7 grams of red phosphorus, and 26 grams of iodine slowly added with cooling. After standing an hour in cold water, the flask was heated to 80° on the steam bath for four hours, after which the resulting iodide was poured into water, washed three times by decantation and filtered to free it from red phosphorus. The 2,4-methyl-2-iodohexane was then reduced to the octane by the same method and under the same conditions that were employed in the reduction of 2,4-methyl-4-iodohexane previously described in this paper. The crude octane in this case boiled at 108 – 112° but after standing over sodium for a month, concentrated sulphuric acid for a week, and sodium again for a week, it boiled sharply at 110° at 763 mm. pressure. This octane was entirely halogen-free and contained no unsaturated hydrocarbon. Its method of formation shows it to be methyl ethyl isobutyl methane, $CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH_3$.

Calculated for C_8H_{18} : C, 84.21; H, 15.79.

Found: C, 84.12; H, 15.88.

Properties.—Methyl ethyl isobutyl methane or dimethyl-2,4-hexane prepared by this second method was apparently identical with that obtained by the first method. It forms a colorless, almost odorless, very mobile, liquid boiling at 110° at 763 mm. Its specific gravity at 15° compared to water at 15° is 0.7083. Its index of refraction, $n_D(25^{\circ}) = 1.3986$.

This agreement in properties of the hydrocarbons, produced by these two methods, shows that in the compounds leading up to the octane and in the octane itself, the configurations of the atoms are stable and are not transposed by the chemical processes made use of, and this is a proof that the constitution assigned is correct.

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