

after some time. Traube¹ found that the density of ethyl acetate 15 minutes after distillation was 1.02443, and 20 hours later, 1.02467, evidently a change exactly similar to the one described here. These densities as found by Traube are somewhat lower than those given by others, but since the change is the important factor, the comparative values will serve. For the density right after distillation, the value 1.0244 will be taken, and after equilibrium is reached 1.0247. The refractive powers then for the C line calculated from formulas II and III will be:

	$(n_c - 1)/d.$	$(n_c^2 - 1)/(n_c^2 + 2)d.$
Immediately after distillation.....	0.4066	0.2452
At equilibrium.....	0.4070	0.2455

There is evidently a change in structure taking place, manifesting itself by the change in refractive power. The molecular refraction calculated according to Brühl would be 31.382 for the keto form and 32.545 for the enol form. From the above (last column) the molecular refraction is found to be 31.876 immediately after distillation and 31.915 at equilibrium, indicating that, at ordinary temperatures, very nearly equal amounts of the two isomers are present, while at higher temperatures, more of the keto form is present than at lower, the difference, however, being small. The matter cannot of course be considered settled satisfactorily as yet, owing to the more or less approximate nature of some of the data used, but the results given point to interesting possibilities.

PHOENIX PHYSICAL LABORATORY, COLUMBIA UNIVERSITY,
September, 1908.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

ISO-OCTANE.

BY LATHAM CLARKE.

Received November 9, 1908.

In this paper are described the preparation and properties of iso-octane or 2-methyl heptane, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, the study of which has been taken up in the continuation of a research on the octanes begun some time ago in this laboratory.

Iso-octane is the ninth hydrocarbon to be prepared in the series C_8H_{18} , of which there are eighteen possible members. A list of the nine octanes so far prepared is given herewith.

Normal octane,² $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

Iso-octane, or 2-methyl heptane, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$.

¹ *Ber.*, 29, 1719 (1898).

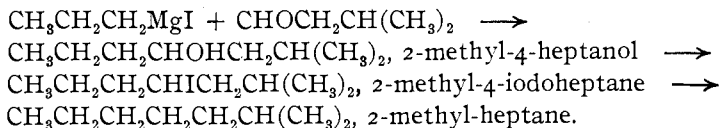
² Riche, *Ann. Chem.* (Liebig), 117, 265. Schorlemmer, *Ibid.*, 161, 280; 147, 227; 152, 152. Zincke, *Ibid.*, 152, 15. Paterno and Peratoner, *Ber. d. Chem. Ges.*, 22, 467.

In preparing iso-octane by the second method, normal propyl magnesium iodide was made to react with isovaleric aldehyde, forming the carbinol, 2-methyl-4-heptanol, $\text{CH}_3\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3$.

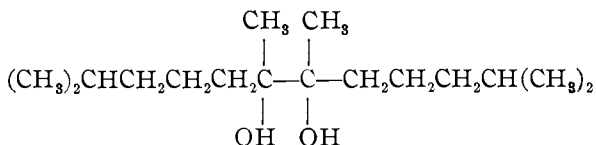
$$\begin{array}{c} \text{CH}_3 \qquad \qquad \text{OH} \\ | \qquad \qquad | \\ \text{CH}_3\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3 \end{array}$$

This on conversion into the corresponding carbinol iodide and subsequent reduction, produced iso-octane.

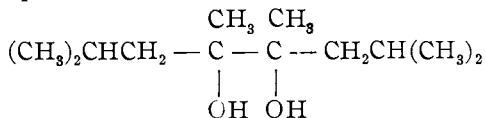
Summarizing these reactions:



In the first method, in reducing methyl isohexyl ketone to the corresponding carbinol, a certain amount of pinacone was obtained as a by-product. The pinacone itself was of no use in this research and the formation of it cut down the yield of carbinol very much. An experiment was tried for the purpose of converting this pinacone, which had the formula



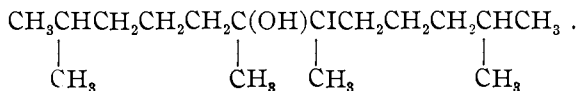
into the alkyl iodide, $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{CHICH}_3$ by the action of hydriodic acid. This reaction has a precedent in a reaction which was discovered two years ago in this laboratory when it was found that methyl isobutyl pinacone,



(which is exactly analogous in structure to the one under investigation), when treated with gaseous hydriodic acid, was transformed into methyl carbinol iodide, or 2-iodo-4-methyl pentane,



It was found that gaseous hydriodic acid acted very readily on methyl isohexyl pinacone, but it attacked only one hydroxyl group; the resulting body, therefore, was a monoiodo derivative: 7-iodo-2,6,7,11-tetramethyl-6-dodecanol,



¹ Clarke and Shreve, *Amer. Chem. J.*, **35**, 513.

A method for the reduction of 6-methyl-2-iodo heptane to the hydrocarbon was tried in this research with considerable success. This consisted in treating the above-mentioned iodo compound with magnesium to form the organo-magnesium body and decomposing the latter with water, producing iso-octane and a mixture of magnesium iodide and hydroxide. This reaction was originally worked out by Grignard and has been used by Spencer,¹ for the reduction of amyl iodide, iodobenzene, and bromnaphthalene to the corresponding hydrocarbons.

The observation was made several months ago in this laboratory that tertiary carbinol iodides react in a complex way and reduction to the hydrocarbon cannot be effected through this agency. The reason for this action is not entirely understood and is now being studied. Our observation so far shows that this method of reduction with primary and secondary carbinol iodides is practical, but with tertiary carbinol iodides it is not. This statement includes only iodides of the formula $C_8H_{17}I$, as no others have been investigated.

Experimental.

First Method: Isoamylacetic Ester.—The isoamyl alcohol used in this research was obtained from Kahlbaum and was pyridine-free. Work was started towards purifying this by the method of Udransky,² but subsequent work showed that this process could be dispensed with, for by careful fractionation, the derivative, methyl isohexyl ketone, obtained later in the research, could be purified completely, and much time and material was, therefore, saved by this procedure.

From isoamyl alcohol, the corresponding carbinol iodide was obtained by treatment with red phosphorus and iodine. 88 grams of the alcohol were mixed with 20 grams of red phosphorus and 128 grams of iodine were gradually added with cooling of the flask in cold water. After standing an hour, the flask was heated on the free flame with a reflux condenser for an hour, after which the isoamyl iodide was distilled off, washed with water and dried over calcium chloride. The yield was between 98 and 99 per cent. of the theoretical.

From isoamyl iodide, sodium and acetic ester, isoamylacetic ester was prepared by the method of Conrad.³ The yield was very large, usually over ninety-five per cent.

The isoamylacetic ester obtained by the above process was distilled *in vacuo*. This compound was a colorless liquid with a characteristic odor, and was soluble in the common organic solvents.

Calculated for $C_{11}H_{18}O_2$:
Found:

C, 66.00; H, 10.00
C, 65.71; H, 10.32

¹ Ber., 41, 2302.

² H., 13, 251.

³ Conrad and Limpach, *Ann. Chem. (Liebig)*, 192, 153.

Methyl Isohexyl Ketone, $\text{CH}_3\text{COCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$.—This ketone has already been made by Welt,¹ from isoamylacetacetic ester by saponification with potassium hydroxide. It has also been obtained by Andren, Perkin and Rose² by splitting α -isoamyl- β -hydroxy- β -cyanbutyric ester with hydrochloric acid. In this research it was prepared by boiling isoamylacetacetic ester for 10 hours with 3 molecules of caustic potash in 10 per cent. aqueous solution, distilling with steam, when the upper layer was separated and dried with calcium chloride. The fractionation of the impure methyl isohexyl ketone was carried out with great care with a Hempel column, and was repeated three times. The boiling point of the methyl isohexyl ketone was 165° at 764 millimeters pressure.

Calculated for $\text{C}_8\text{H}_{16}\text{O}$:

C, 75.00; H, 12.50

Found:

C, 74.89; H, 12.62

Properties: Methyl isohexyl ketone boils at 165° at 764 millimeters pressure.³ It has a strong, pleasant, very characteristic odor which reminds one somewhat of caraway seed. It is miscible with the common organic solvents.

Methyl Isohexyl Carbinol, $\text{CH}_3\text{CHOHCH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$.—This compound has been obtained by Mlle. Welt⁴ by reduction of methyl isohexyl ketone in alcohol solution with sodium. The method employed in this research differed somewhat and was as follows: 60 grams of methyl isohexyl ketone were dissolved in 120 grams of ethyl ether and placed in a flask with 110 grams of water. Metallic sodium in small pieces was introduced through the condenser tube, until 30 grams in all had been added. The sodium was put in a small amount at a time and after each portion had disappeared, the flask was thoroughly shaken in order to decompose the sodium salt of the methyl carbinol, which causes a milky turbidity and retards the smoothness of the reduction by making the reaction mixture thick and pasty. Finally, the ether layer was separated, and fractionated without drying, as the solution of sodium hydroxide produced by the action of the sodium on the water, was a sufficiently good desiccating agent to dry the ether solution. On fractionating, the ether residue was separated into two portions, the first boiling at 170° – 185° and the second at 290° – 297° . The first fraction on being twice redistilled boiled at 176° at 765 millimeters pressure and was methyl isohexyl carbinol, while the second fraction on being refractionated, boiled at 293° – 295° at 765 millimeters and was methyl isohexyl pinacone. The yield

¹ *Ann. chim. phys.* [7], 6, 134.

² *Soc.*, 75, 973.

³ Mlle. Welt (*loc. cit.*) gives 167 – 8° as the boiling point, but all the several samples in this research boiled at 165° quite sharply, so undoubtedly the latter is the correct figure.

⁴ *Ann. chim. phys.* [7], 6, 135.

of the carbinol was about 47 grams and the yield of pinacone about 8 grams.

Calculated for $C_8H_{18}O$:	C, 73.85; H, 13.85
Found:	C, 73.61; H, 13.08
Calculated for $C_{10}H_{20}O_2$:	C, 74.41; H, 13.17
Found:	C, 74.20; H, 13.43

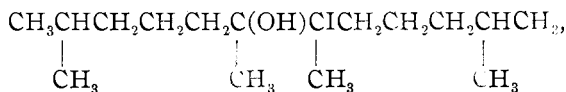
Properties of Methyl Isohexyl Carbinol, $CH_3CHOHCH_2CH_2CH_2CH(CH_3)_2$.—This liquid boils at 176 at 765 millimeters.¹ It has a strong characteristic odor, disagreeable when strong but rather pleasant when dilute. It is miscible with the common organic solvents, but is essentially insoluble in water. It dissolves in concentrated sulphuric acid with evolution of heat and forms a yellowish turbid solution.

Properties of Methyl Isohexyl Pinacone.—Liquid which does not solidify even in the ice-chest. It boils at 293–295° at 765 millimeters. It has a weak but rather pleasant odor and dissolved in alcohol, ether, and benzene.

Action of Hydriodic Acid on Methyl Isohexyl Pinacone.—In an earlier research² the observation was made that methyl isobutyl pinacone by the action of hydriodic acid was transformed into methyl isobutyl carbinol iodide. It was thought that methyl isohexyl pinacone might be capable of a similar reaction and, if so, would result in a considerable saving of material otherwise wasted in the research.

Five grams of the pinacone contained in a round-bottom flask were saturated with gaseous hydriodic acid, made by the method of Gattermann,³ and the solution was allowed to stand over-night. Next day more hydriodic acid was passed in and the temperature was raised to 60°. After standing two hours, the thick red oil was poured into ethyl alcohol. A colorless oil sank to the bottom of the flask and was extracted a few times with alcohol in which the oil itself was insoluble. It could not be made to solidify and it decomposed on attempted distillation. A sample was, therefore, analyzed directly, after drying thoroughly in a desiccator, giving by Carius method 34.08 per cent. I; calculated for $C_{16}H_{33}OI$, 34.51.

The analysis and its insolubility in alcohol show this compound to have the formula



and it is, therefore, 7-iodo-2,6,7,11-tetramethyl-6-dodecanol.

This compound is a colorless oil. On account of its instability, no boil-

¹ Mlle. Welt (*loc. cit.*) gives the boiling point as 167–9°.

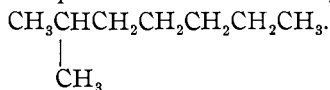
² Clarke and Shreve, *Amer. Chem. J.*, 35, 513.

³ *Pract. Meth. Org. Chem.*, 2nd Am. ed., p. 345.

ing point could be observed. It is not soluble in alcohol, but is somewhat soluble in ether and fairly soluble in chloroform. On standing, it slowly decomposes.

Preparation and Reduction of 6-Methyl-2-iodo Heptane.—Forty grams of methyl isohexyl carbinol were placed in a flask together with 10 grams of red phosphorus, and to the mixture 40 grams of iodine were slowly added, the flask all the while being kept cool by immersion in a bath of water at room temperature. After standing an hour, the reaction mixture was heated on a steam bath for four hours and then the 6-methyl-2-iodo heptane was distilled off over the free flame. It suffered no decomposition by the treatment and collected in the receiver as a clear, colorless, rather heavy oil. The yield was practically quantitative and the whole was then subjected to reduction for the purpose of obtaining the hydrocarbon, 2-methyl heptane.

The carbinol iodide was mixed with 200 grams of finely divided zinc (not zinc dust) which had previously been treated with a few cubic centimeters of a dilute solution of copper sulphate. A long condenser was attached to the flask and through the condenser tube, concentrated hydrochloric acid (38 per cent.) was poured, a few cubic centimeters at a time, rapidly enough to produce a mild effervescence. The reduction proceeded rapidly and a floating oily layer of octane soon collected on the surface. After two hours, the thickness of the floating layer had apparently reached a maximum, so the flask was cooled and disconnected and several pieces of scrap magnesium introduced, the flask again connected to the condenser and warmed. The magnesium reacted with the acid at the plane of contact of the two layers and completely reduced all unchanged iodide which was dissolved in the octane. After 30 minutes, the reaction had stopped, so the octane was separated, dried over calcium chloride and distilled. Practically all passed over between 110° and 125° , which fraction was treated with concentrated sulphuric acid a few days; then was allowed to stand over sodium a month. (It is rather a better procedure to boil over sodium with a reflux condenser, until finally the surface of a fresh piece of sodium remains untarnished.) It was distilled over sodium and boiled at 116.1° at 762 millimeters pressure. The yield was about fifty per cent. of the theoretical. The octane was entirely free from halogen and contained no unsaturated hydrocarbon. The method of formation proves the constitution, *viz.*,



Calculated for C_8H_{18} :

Found:

C, 84.21; H, 15.79

C, 84.08; H, 16.89

Properties: Isooctane is a colorless liquid with a mild but characteristic

odor. The boiling point is 116° at 761 millimeters. Its specific gravity at 15° compared to water at 15° is 0.7035. Its index of refraction was determined, using a fine Pulfrich refractometer, *viz.*, $N_D(25^{\circ}) = 1.3944$.

Reduction of 6-Methyl-2-iodo Heptane through the Organo-magnesium Body.—In a flask was placed 2.4 grams of magnesium turnings, and to it 24 grams of anhydrous ether and 24 grams of 6-methyl-2-iodo heptane, which had previously been distilled and dried over calcium chloride, were added. The magnesium dissolved slowly and when solution was complete, the reaction mixture was cooled by immersion in a water bath, and water was added drop by drop until there was no further action. The ether layer was separated and fractionated, yielding four grams of octane boiling at 112° to 120° , which was purified by the procedure already described in this paper, and redistilled. A boiling point, 116° at 760 millimeters, was found.

A study will be made of this method of reduction in the near future, some work being directed to the betterment of the yield, and some to the application of the method to tertiary carbinol iodides.

Second Method for the Preparation of Isooctane.—Normal propyl iodide was prepared from pure normal propyl alcohol by treating 60 grams of the latter with 15 grams of red phosphorus and 128 grams of iodine. After an hour's standing at room temperature, the mixture was heated two hours on the water bath and the normal propyl iodide distilled off, dried with calcium chloride, and fractionated. Boiling point, 102° . The yield was practically quantitative.

Isovalerianic aldehyde was made by the oxidation of purified isoamyl alcohol according to the method of Bouveault and Rousset.¹ The carefully fractionated product boiled at 93° .

2-Methyl-4-heptanol, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHOHCH}_2\text{CH}_2(\text{CH}_3)_2$.—This alcohol was synthesized by the use of normal propyl magnesium iodide and isovalerianic aldehyde.

The organo-magnesium compound was made by dissolving 20 grams of magnesium turnings in a mixture of 136 grams of normal propyl iodide and 150 grams of anhydrous ether. To this solution, 69 grams of iso-valerianic aldehyde, together with an equal volume of ether, was slowly added and in due time the carbinol was extracted by the customary procedure of treating with water, dilute hydrochloric acid, and separation of the ether layer. The ether residue, after drying with potassium carbonate, was fractionated and the greater part of the portion boiling at 160° to 166° on thrice being distilled, finally came over at 164° at 760 millimeters.

The yield was very good and by-products were almost entirely absent.

¹ BI [3], 11, 301.

Calculated for $C_8H_{18}O$:

C, 73.85; H, 13.85

Found:

C, 73.63; H, 14.08

This experiment was repeated several times on a smaller scale and very high yields of the carbinol were obtained in some cases. It was found, however, that the isovalerianic aldehyde was very hard to dry perfectly, and the admixture of a very small amount of water interfered very seriously with the reaction. For example, in one case a very considerable reduction took place, instead of a true Grignard reaction; and the reaction produced, not 2-methyl-4-heptanol, but a mixture of much unchanged aldehyde, isoamyl alcohol and a glycol, $(CH_3)_2CHCH_2CHOHCHOHCH_2CH(CH_3)_2$, these two latter, of course, being reduction products of the aldehyde.

The glycol, $(CH_3)_2CHCH_2CHOHCHOHCH_2CH(CH_3)_2$, or 4,5-dihydroxy-2,7-dimethyl octane was a colorless viscid oil, boiling at 238° – 242° at 760 millimeters. It was soluble in the common organic solvents.

Calculated $C_{10}H_{22}O_2$:

C, 68.96; H, 12.63

Found:

C, 68.72; H, 12.84

Properties of 2-Methyl-4-heptanol.—This is a colorless liquid boiling at 164° at 760 millimeters. It has a rather strong odor similar to ordinary amyl alcohol, but not so pungent. It is miscible with alcohol, ether, chloroform, benzene, acetone and glacial acetic acid; not miscible with water, but dissolves in concentrated sulphuric acid to form a somewhat turbid solution.

Preparation and Reduction of 2-Methyl-4-iodo Heptane.—Fifteen grams of 2-methyl-4-heptanol were mixed with five grams of red phosphorus and fifteen grams of iodine, the reaction mixture being kept cool. After standing at room temperature an hour, the flask was heated on the water bath three hours, at the end of which time, the 2-methyl-4-iodo heptane was distilled off with the free flame. Since the carbinol iodide is a derivative of a secondary alcohol, it is relatively very stable towards heat and undergoes distillation under atmospheric pressure with practically no decomposition. The yield was nearly theoretical.

The reduction of the 2-methyl-4-iodo heptane was carried out under the same conditions and with the same proportional parts of zinc, etc., that were used in the reduction of 6-methyl-2-iodo heptane described earlier in this paper. It is unnecessary, therefore, to repeat the directions here.

The iso-octane produced by this second method boiled at 116° at 761 millimeters. The product was halogen-free and contained no unsaturated hydrocarbon after the customary treatment with concentrated sulphuric acid and metallic sodium.

Calculated for C_8H_{18} :

C, 84.21; H, 15.79

Found:

C, 84.11; H, 15.98

Properties: Iso-octane, made by the second method, is a colorless liquid boiling at 116° at 761 millimeters, and has a slight characteristic odor. Its specific gravity at 15° compared to water at 15° is 0.7035. Its index of refraction is $N_D(25^{\circ})$, 1.3944. It is, therefore, identical in properties with that obtained by the first method.

The expenses of this research were defrayed by a grant from the C. M. Warren Research Fund, for which I wish to express my appreciation.

HARVARD UNIVERSITY, CAMBRIDGE, MASS.,
July 20, 1908.

THE PRESENCE OF A CHOLESTEROL SUBSTANCE IN SOILS; AGROSTEROL.¹

BY OSWALD SCHREINER AND EDMUND C. SHOREY.

Received November 23, 1908.

In the attempts which have been made to isolate definite organic compounds from soils it has been found that in most cases treatment of the soil with alcohol even at boiling temperature does not give a solution of soil organic matter from which definite results could be obtained.

However with some soils, characterized usually by a high content of organic matter, this treatment has led to the isolation and identification of definite organic compounds.

The details of the method and the properties of one of the compounds obtained are the subject of this paper.

The soil from which this compound was obtained was the Marshall clay from North Dakota, a black soil containing 10.6 per cent. organic matter and 0.51 per cent. nitrogen.

When this soil was treated with boiling 95 per cent. alcohol there was obtained a greenish-brown colored extract from which on cooling a yellowish microcrystalline precipitate separated. On treating the soil with successive portions of boiling alcohol, the extracts combined and concentrated to smaller volume and allowed to cool yielded this precipitate in considerable quantity, 250-300 parts per million of soil. This precipitate contained both mineral and organic matter and is at present the subject of further investigation. The mineral matter is alumina for the most part, and the organic portion is a mixture, some of the so-called waxy acids being present.

The filtrate from this precipitate was a dark greenish-brown solution which on evaporation of the alcohol became a thick resinous mass. On treating this residue with cold ether nearly all of the coloring matter went into solution leaving a small quantity of a yellowish wax-like substance, the nature of which is yet unknown.

¹ Presented at the New Haven meeting, June, 1908, of the American Chemical Society by permission of the Secretary of Agriculture.