

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

3-ETHYLHEXANE.

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Received March 4, 1912.

3-Ethylhexane, $\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_3$, has been synthesized and studied as a part of the researches of one of us on the paraffin hydrocarbons.¹ It is a liquid with a faint odor, boils at $118.8\text{--}119.0^\circ$, under 766 mm., has, at 15° , the specific gravity 0.7175, compared to water at 15° , and shows an index of refraction, $N_D(25^\circ) = 1.3993$.

Next to the normal, this octane probably has the highest boiling point of any, this statement being founded on the following reasoning: The boiling point of 2-methylheptane is 116° , of 3-methylheptane 117.6° , of 4-methylheptane 118° , so that in moving a methyl group from the end of the chain towards the center, a steady rise of boiling point is observed.

It is now true that an ethylhexane will have a higher boiling point than a methylheptane, for 2-methylheptane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, boils at 116° , while 2-ethylhexane (regarding 3-methylheptane for the moment as 2-ethylhexane), $\text{CH}_3\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{—CH}_2\text{CH}_3$, boils at 117.6° . Just as the boiling point of 3-methylheptane is higher than that of 2-methylheptane, so the boiling point of 3-ethylhexane should be higher than that of 2-ethylhexane, and, as a matter of fact, 3-ethylhexane boils at $118.8^\circ\text{--}119.0^\circ$. Since it is well known that hydrocarbons containing quaternary carbon atoms boil lower than those containing tertiary carbon atoms, all of the former class will have lower boiling points than the methylheptanes. It is apparent, therefore, that, next to normal octane, 3-ethylhexane has the highest boiling point of any octane.

The hydrocarbon isolated by Mabery² from Ohio petroleum and described by him as an octane of the boiling point 119.5° at 760 mm. was probably 3-ethylhexane. (In the same paper Mabery mentions another octane obtained from Ohio petroleum, boiling at $124\text{--}125^\circ$. This can be no other than normal octane.)

3-Ethylhexane contains a normal propyl chain—it may in fact be called diethyl-normal-propylmethane. The corresponding compound containing an isopropylmethane (or 2-methyl-3-ethylpentane), $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$, was prepared in this laboratory in 1908.³ The properties of the two compare as follows:

	Boiling point.	Mm.	Specific gravity $15^\circ/15^\circ$.	Index of refraction $N_D(25^\circ)$.
3-Ethylhexane	118.9°	766	0.7175	1.3993
2-Methyl-3-ethylpentane . . .	114	760	0.7084	1.3996

¹ See Clark, *THIS JOURNAL*, 33, 520 (1911). Clarke and Beggs, *Ibid.*, 34, 54 (1912).² Mabery and Hudson, *Am. Chem. J.*, 19, 255.³ Clarke, *Ibid.*, 39, 574.

The boiling points of these two liquids present an interesting relation.

It has been shown¹ in the case of the octanes previously synthesized, that when we have a methylheptane, and we substitute in one end of the chain a methyl group, the depression in boiling point which takes place is equal to the difference in boiling point between normal *heptane* and the corresponding *methylheptane*. To choose a specific example, the boiling point of 2-methylheptane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, is 116.0° . The boiling point of 2,5-dimethylhexane, $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{—CH}_2\text{CH}(\text{CH}_3)\text{CH}_3$, is 108.25° , but this is 7.75° lower than the boiling point of 2-methylheptane, and is very nearly equal to the difference in boiling point between normal heptane and 2-methylhexane, *viz.*, 8° . Other examples may be cited² to show that when a methylheptane is compared to a dimethylhexane, the boiling point of the latter is as much below the former as the boiling point of the corresponding methylhexane is below that of normal heptane. This rule appears to hold except in cases where the substituting methyl groups are on adjacent carbon atoms, when a boiling point several degrees higher than the "calculated" is observed. Thus the boiling point of 3-methylheptane, $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, is 117.6° . We should now calculate the boiling point of 2,3-dimethylhexane, $\text{CH}_3\text{CH}(\text{CH}_3)(\text{CH}_3)\text{CHCH}_2\text{CH}_2\text{CH}_3$, as 109.6° , since we change here from a C_7 straight chain to an "iso" chain, and so we should expect the boiling point of the second compound to be 8° lower than that of the first, or $117.6 - 8 = 109.6^\circ$, but the actual boiling point of 2,3-dimethylhexane is 114° , which is 4.6° higher than the "calculated." In the case of 3,4-dimethylhexane, the actual boiling point is 5.8° higher than the calculated.

Coming back to the case of 3-ethylhexane and 2-methyl-3-ethylpentane, we have in the second compound, on adjacent carbon atoms, a substituting methyl and a substituting ethyl group. By the method already described, we may calculate the boiling point of 2-methyl-3-ethylpentane, and see if this rule of the elevation of a boiling point by substituting methyl groups on adjacent carbon atoms holds also in the case of a methyl and an ethyl group. The boiling point of 3-ethylhexane is 118.9° . The boiling point of 2-methyl-3-ethylpentane should be as much below that of 3-ethylhexane as the boiling point of 2-methylpentane is below that of normal hexane, *viz.*, 6.8° , so that the boiling point of 2-methyl-3-ethylpentane should be 112.1° . The actual boiling point is 114° , or nearly two degrees higher. This shows then that when alkyl groups are substituted on adjacent carbon atoms, the boiling point of the compound will be several degrees higher than in compounds where the substituting alkyl groups are separated by one or more CH_2 groups.

¹ Clarke, *THIS JOURNAL*, **33**, 520.

² Clarke, *l. c.*

The boiling points of the xylenes are of interest in this connection. *p*-Xylene boils at 138°, *m*-xylene at 139.2°, while *o*-xylene, in which the methyl groups are on adjacent carbon atoms, boils at 142°.

It is worthy of note that the specific gravity of 3-ethylhexane is nearly the same as that of 3-methylheptane, the figures being 0.7175 and 0.7176, respectively, at 15°, compared to water at 15°. The specific gravity of 3-ethylhexane is greater than that of 2-methyl-3-ethylpentane, *viz.*, 0.7175 and 0.7084, but the indices of refraction ($N_D(25^\circ)$) are very close, 1.3993 for the first named, and 1.3996 for the second.

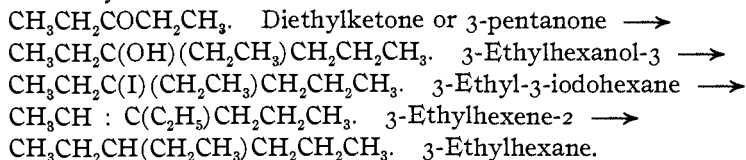
Special Theoretical.

Two methods were considered for the synthesis of 3-ethylhexane.

First Method.—The first consisted in subjecting diethylketone to the Barbier-Grignard reaction, using normal propylmagnesium iodide, by which the alcohol, 3-ethylhexanol-3 was formed. This was converted into the corresponding carbinol iodide and treated with alcoholic potash, which split off hydriodic acid and gave an octylene, 3-ethylhexane-2. By reduction the last was saturated to 3-ethylhexane.

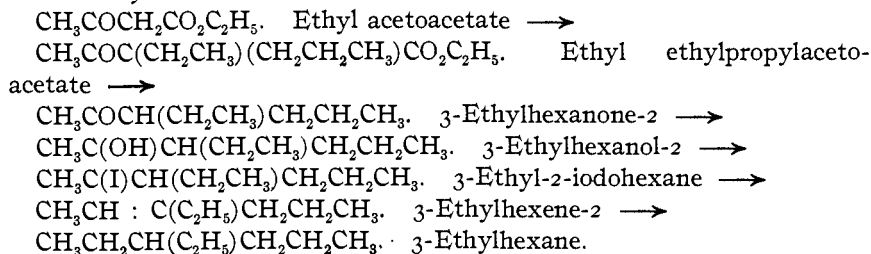
This method was very satisfactory, the yields were very good in all reactions, and the fractionation of each compound was carried on without trouble.

Summary.



Second Method.—This was not carried to a successful conclusion. The plan was as follows: Starting with ethyl acetoacetate, prepare the ethyl normal propyl derivative by replacement of the methylene hydrogen atoms in turn by ethyl and normal propyl groups. This could then be saponified giving the ketone, 3-ethylhexanone-2. By reduction an alcohol would be formed, 3-ethylhexanol-3, and the latter could be converted into the carbinol iodide, treated with alcoholic potash to produce the octylene, 3-ethylhexene-2, and reduced to 3-ethylhexane.

Summary.



This process was abandoned because of the difficulty in obtaining a sufficient quantity of the ketone, 3-ethylhexanone-2, in the proper grade of purity. The introduction of both an ethyl and a normal propyl group into ethyl acetoacetate is possible, but not easy, and gives a variety of products. For example, if the ethyl group be introduced first, a certain amount of the diethyl derivative is also formed, and the propyl group is very slow in substituting on later treatment, this mixture cannot be satisfactorily fractionated, so the whole must be saponified, and the resulting ketones fractionated. It did not seem worth while to prepare the hydrocarbon by this method, which is so laborious as compared to the first mentioned.

Experimental Part.

First Method.—3-Ethylhexanol-3, $\text{CH}_3\text{CH}_2\text{C}(\text{OH})(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, was made from diethylketone by the action of normal propylmagnesium iodide. The diethylketone was obtained from Kahlbaum and boiled at $101-103^\circ$. It was fractionated and that boiling at $101.2-101.8^\circ$ at 756 mm. was used in the subsequent Barbier-Grignard reaction.

Twelve grams of magnesium turnings were dissolved in a mixture of 90 grams of dry normal propyl iodide and 90 grams of anhydrous ether. To the solution 43 grams of diethylketone dissolved in two volumes of dry ether were added, allowed to remain at rest for thirty minutes, when the organo-magnesium compound was decomposed in the usual way with water and dilute hydrochloric acid. During the treatment with water and acid the reaction flask was kept cold by immersion in a tank of ice water. The ethereal layer, containing the desired carbinol, was separated and dried over potassium carbonate, the ether was distilled off and the residue fractionated, yielding 50 grams of 3-ethylhexanol-3, boiling at $155-159^\circ$ at 756 mm.

This experiment was repeated three times, giving a total yield of 150 grams of the carbinol.

Subst., 0.1969; CO_2 , 0.5316; and H_2O , 0.2430.

Calculated for $\text{C}_9\text{H}_{18}\text{O}$:	C, 73.85; H, 13.60
Found:	C, 73.63; H, 13.81

Properties.—This carbinol has an odor like that of musty apples. It is miscible with the common organic solvents but not with water.

3-Ethyl-3-iodohexane, $\text{CH}_3\text{CH}_2\text{C}(\text{I})(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, and its Conversion into 3-ethylhexene-2, $\text{CH}_3\text{CH} : \text{C}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_3$.—To 65 grams of 3-ethylhexanol-3, 6.5 grams of red phosphorus were added, and 64 grams of iodine gradually introduced into the mixture. During the addition of the iodine, the reaction flask was kept cool. At the end of one hour, the flask was heated on the steam bath for five hours. The resulting carbinol iodide was washed with water, and filtered to remove

unchanged phosphorus, but was not distilled. It was converted directly into the octylene.

The strong alcoholic potash solution was prepared and the carbinol iodide added to it with shaking. The mixture was heated on the water bath for two hours or so, the flask being fitted with a reflux condenser, after which a downward condenser was attached and the mixture distilled until no more octylene came over. Alcohol and this octylene form a soluble binary mixture of minimum boiling point and all the hydrocarbon passes off during the first part of the distillation. By dilution of the alcoholic distillate with water, the octylene separated as a floating layer, was separated, dried over calcium chloride and distilled. Thirty grams were obtained boiling at $119.6-120.5^{\circ}$ at 769 mm. This experiment was repeated and gave slightly more than 30 grams of octylene of the above boiling point.

Subst., 0.3157; CO_2 , 0.9868; H_2O , 0.4089.

Calculated for C_8H_{16} :	C, 85.71; H, 14.29
Found:	C, 85.27; H, 14.37

Properties.—Liquid with a rather strong odor, boiling at $119.6-120.5^{\circ}$ at 769 mm. It is miscible with the common organic solvents.

3-Ethylhexane, $\text{CH}_3\text{CH}_2\text{CH}(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_2\text{CH}_3$, was made from the preceding octylene by reduction according to the method of Sabatier and Senderens, by passing the octylene over freshly reduced nickel at a temperature of $160-180^{\circ}$ in a rapid stream of pure hydrogen.¹ The resulting octane was carefully fractionated, and thirty grams were finally obtained which boiled at $118.8-119^{\circ}$ under 766 mm. Thirty-five grams of octylene were reduced, and as this was run through the reducing apparatus twice, some was lost through incomplete condensation. Less than a gram of material was rejected in the distillations.

Subst., 0.2935; CO_2 , 0.9012; H_2O , 0.4128.

Calculated for C_8H_{18} :	C, 84.21; H, 15.79
Found:	C, 83.74; H, 15.74

Properties.—Colorless, very mobil liquid, practically without odor. It boils at $118.8-119.0^{\circ}$ at 766 mm.; has, at 15° , the specific gravity 0.7175 compared to water at 15° . The index of refraction $N_D(25^{\circ}) = 1.3993$.

Second Method.—Ethyl ethylacetoacetate was made by the method of Conrad,² using sodium ethylate, ethyl acetoacetate and ethyl iodide, and in the usual fashion ethyl ethylacetoacetate was isolated and dried with potassium carbonate. This was treated with sodium ethylate and normal propyl iodide, and the reaction product isolated in the usual way.

¹ See Clarke and Beggs, *THIS JOURNAL*, 34, 59 (1912).

² Conrad and Limpach, *Ann.*, 192, 155.

It was found, however, that the introduction of the propyl group into ethyl ethylacetoacetate was no easy matter and even when the reaction mixture was allowed to stand a week before working up, the yield of ethyl ethylnormalpropylacetoacetate was poor. Somewhat better results were obtained when the propyl group was introduced first, but in no case was the yield satisfactory. The substituted acetoacetate was not purified by distillation but was at once converted into the ketone, or rather a mixture of ketones, since there were several acetoacetic ester derivatives.

Fifty grams of the crude acetoacetate were boiled for ten hours with 75 grams of caustic potash dissolved in 750 cc. of water, the mixture was distilled with steam, the upper layer of the distillate was removed, and dried with calcium chloride. Ten such distillates were then united and carefully fractionated. The products were: 2-pentanone, boiling at 101–104°; 3-ethylpentanone-2, boiling at 136–139°; 2-hexanone, boiling at 126–129°; a small amount of 3-propylhexanone-2, boiling at 173–175°, and (from 500 grams of crude acetoacetate) 25 grams of the desired ketone, 3-ethylhexanone-2, $\text{CH}_3\text{COCH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$, boiling at 157.5–158.5° at 761 mm. There was a residue of unketonized acetoacetates.

Properties of 3-Ethylhexanone-2.—Liquid with peppermint-like odor. Boiling point 157.5–158.5° at 761 mm. Miscible with the common organic solvents, but immiscible with water.

3-Ethylhexanol-2, $\text{CH}_3\text{C}(\text{OH})\text{CH}(\text{CH}_2\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$.—Twenty grams of ketone were dissolved in 40 grams of ether and placed in a flask fitted with a long reflux condenser together with 35 grams of water. In small pieces during half an hour, 10 grams of sodium were added. When the sodium had all dissolved, the ether layer was removed, the ether was distilled off, and the residue fractionated, which yielded 19 grams of ethylhexanol-2, boiling at 167.5°–168.5° at 760 mm., and a high-boiling residue of 3 grams, probably a pinacone.

Properties of 3-Ethylhexanol-2.—Liquid with an odor like musty apples, boiling at 167.5–168.5° at 760 mm.; miscible with the common organic solvents; not miscible with water.

On account of the difficulty in preparing a sufficient amount of material, the synthesis of 3-ethylhexane was abandoned at this point, and the study of the hydrocarbon was made with the hydrocarbon prepared by Method I.

Part of the expense of this research was defrayed by a grant from the C. M. Warren Fund for Research, for which we wish to express our gratitude.