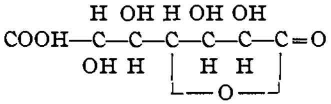
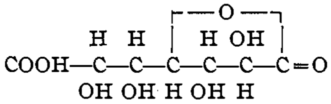
The above-described relation between configuration and rotation affords a new method for determining the configuration of the lactones formed by some dibasic acids. Thus, β pentahydroxy pimelic[1] acid forms a mono lactone which has either configuration, I or II.

I.



$$\begin{array}{l} \qquad\quad \mathrm{H\ \ OH\ H\ OH\ OH} \\ \mathrm{COOH{-}C{-}C{-}C{-}C{-}C{=}O} \\ \qquad\quad \mathrm{OH\ H\ \ |\ \ H\ \ H\ \ |} \\ \qquad\qquad\qquad \mathrm{\llcorner{-}O{-}\lrcorner} \end{array}$$

II.



$$\begin{array}{l} \qquad\qquad\qquad \mathrm{\ulcorner{-}O{-}\urcorner} \\ \qquad\quad \mathrm{H\ \ H\ \ |\ \ H\ OH\ |} \\ \mathrm{COOH{-}C{-}C{-}C{-}C{-}C{=}O} \\ \qquad\quad \mathrm{OH\ OH\ H\ OH\ H} \end{array}$$

Since the specific rotation of the lactone is +68°, it must have configuration I.

The data given above furnish additional evidence for the hypothesis advanced by Hudson. They show how varied the lactone structure may be and that hypothesis still apply.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

2,5-DIMETHYLHEPTANE.

BY LATHAM CLARKE AND SYDNEY A. BEGGS.

Received November 6, 1911.

In the study of the octanes, which for some years has been in process in this Laboratory, certain relationships have been discovered between chemical constitution and physical properties, an account of which has been included in an earlier paper.[2] It is of considerable interest to ascertain whether these relationships hold true in the series of nonanes as well as in the series of octanes, and the study of the nonanes has therefore been taken up; meanwhile, the researches on those octanes which are yet to be synthesized are being pushed on as actively as possible. In this paper is given a description of the synthesis and properties of 2,5-dimethylheptane, the first nonane to be prepared in this laboratory.

This hydrocarbon has been made by Mlle. Welt,[3] who used the Wurtz reaction; but the compound prepared by her was apparently not at all pure since the boiling point is given as 128–134°. The 2,5-dimethylheptane prepared in this research boiled at 135.6–135.9° at 760 millimeters pressure and had at 15° the specific gravity 0.7190, compared with water at 15°.

The literature records four nonanes in addition to that of Mlle. Welt:

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[1] Fischer, *Ann.*, 270, 90.

[2] THIS JOURNAL, 33, 520 (1911).

[3] *Ann. chim. phys.*. [7] 6, 122.

1. Normal nonane.[1]
2. 2,6-Dimethylheptane.[2]
3. 4-Ethylheptane.[3]
4. 2-Methyl-3,3-dimethyl-4-methylpentane.[4]

As pointed out in the earlier paper on octanes,[5] the hydrocarbons fall in classes according to their constitution. Thus normal octane stands by itself, the three monomethylheptanes form a class by themselves, as do the four dimethylhexanes, and the physical properties of each of these different classes exhibit certain regularities. To show these a table of the physical constants of the first eight octanes is given herewith.

		Boiling point. Degrees.	Mm.	Specific gravity 15/15.	Index of refraction N_D (25°).
1.	Normal octane	124.7	at 760	0.7068	1.3963
2.	2-Methylheptane	116.0	at 761	0.7035	1.3944
3.	3-Methylheptane	117.6	at 760	0.7167	1.4022
4.	4-Methylheptane	118.0	at 760	0.7217	1.3978
5.	2,3-Dimethylhexane	113.9	at 758	0.7246	1.4075
6.	2,4-Dimethylhexane	110.0	at 763	0.7083	1.3986
7.	2,5-Dimethylhexane	108.25	at 760	0.6991	1.3930
8.	3,4-Dimethylhexane	116.5	at 759	0.7270	1.4038

By substituting a normal chain with an "iso" group, that is, in going from normal octane to 2 methylheptane, we observe a depression in boiling point of 8.7°; but as we move the substituting methyl group along from the 2- to the 3- and again to the 4-position a slight elevation in boiling points occurs. With increasing boiling point, we find a rise in the specific gravity in the case of these three methylheptanes. Considering now the dimethylhexanes, that which has the lowest boiling point is 2,5-dimethylhexane, where we have two "iso" groups, one at each end of the chain. We should expect that since, in the case above noted, we move one methyl group from the 5- to the 4-position, and observe an elevation of boiling point, we should likewise find an elevation of boiling point when we change one methyl group of 2,5-dimethylhexane from the 5- to the 4-position and we do find a slight increase, in the first case 1.6°, in the second 1.75°.

But when we again move our methyl group, this time from the 4- to the 3-position, giving 2-3-dimethylhexane, we get a relatively very considerable rise. Here, however, we have the substituting methyl groups in adjacent positions. In 3,4-dimethylhexane, when again the methyl groups are on adjacent carbon atoms, we observe a still higher boiling point.

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[1] Thorpe and Young, *Ann.*, **165**, 19 (1873). Krafft, *Ber.*, **15**, 1692 (1882).

[2] Wurtz, *Jahresb.*, **1855**, 575.

[3] Oberreit, *Ber.*, **29**, 2003.

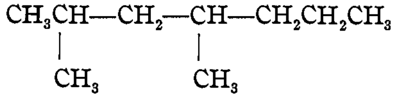
[4] Silva, *Ibid.*, **5**, 984.

[5] *Loc. cit.*

The specific gravities of the methylheptanes rise in relation to the boiling points and the same is true of the dimethylhexanes, without exception, in each class the higher the boiling point, the greater the specific gravity.

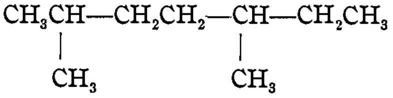
Let us now examin the properties of the nonanes. As none of the methyl octanes have yet been made, we cannot include them, but there are three of the dimethylheptanes, *viz*:

1. 2,4-Dimethylheptane,[1]



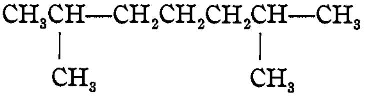
$CH_3\underset{\substack{|\\ CH_3}}{CH}—CH_2—\underset{\substack{|\\ CH_3}}{CH}—CH_2CH_2CH_3$

2. 2,5-Dimethylheptane,



$CH_3\underset{\substack{|\\ CH_3}}{CH}—CH_2CH_2—\underset{\substack{|\\ CH_3}}{CH}—CH_2CH_3$

3. 2,6-Dimethylheptane,



$CH_3\underset{\substack{|\\ CH_3}}{CH}—CH_2CH_2CH_2\underset{\substack{|\\ CH_3}}{CH}—CH_3$

		Boiling point. Degrees.	Mm.	Specific gravity 15°/15°.	Index of refraction N_D (25°).
1.	2,4-Dimethylheptane[2]	132.9–133	at 752	0.7206	1.4014
2.	2,5-Dimethylheptane[3]	135 –135.9	at 760	0.7190	1.4020
3.	2,6-Dimethylheptane[4]	132		0.7122	..

2,6-Dimethylheptane has the lowest boiling point and the smallest specific gravity. 2,5-Dimethylheptane should by analogy to the octanes come next but, very strange to say, the boiling point is very much higher than we should expect, it being about 3.7° higher, when we should anticipate a difference of about 1.7°, while the specific gravity is about as much greater as we should look for. But in the case of 2,4-dimethylheptane, the boiling point is *lower* than that of 2,5-dimethylheptane by practically 2.7°, and is only one degree higher than that of 2,6-dimethylheptane. This surprizing exception is all the more noteworthy, because the specific gravity is normal, that is, somewhat greater than the specific gravity of 2,5-dimethylheptane.

It will be decidedly interesting in view of the above facts to see how the properties of the other nonanes compare and to this end their syntheses will be accomplished as soon as possible, and all attempts to explain postponed until further data are at hand.

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[1] An account of the preparation and properties of 2-4-dimethylheptane is given in the succeeding paper.

[2] From data in the succeeding paper.

[3] From data determined in this research and given later in the paper.

[4] Wurtz, *Jahresb.*, 1855, 575. In his paper Wurtz gives the specific gravity at 0° as 0.7247. The value above is a theoretical approximation calculated from Wurtz's figures.

2,5-Dimethylheptane.—The starting point of this research in the synthesis of 2,5-dimethylheptane was ethyl acetoacetate, which was converted into ethyl isobutylacetoacetate by the usual procedure of conversion into the sodium salt and treatment with isobutyl iodide. The ethyl isobutylacetoacetate was then saponified, giving the ketone, 2-methyl-5-hexanone, which was subjected to the Barbier-Grignard reaction, using ethyl magnesium bromide, thus producing an alcohol containing nine atoms of carbon, *viz.*, 2-methyl-5-methyl-5-heptanol. From the last the corresponding carbinol iodide was obtained, and by boiling this with alcohol potash, the nonylene 2-methyl-5-metheneheptane was formed, which was then reduced to 2,5-dimethylheptane.

To summarize these reactions:

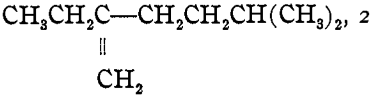
$CH_3COCH_2CO_2C_2H_5$, Ethyl acetoacetate $\longrightarrow$

$CH_3COCH\{(CH_2CH)(CH_3)_2\}CO_2C_2H_5$, Ethyl isobutylacetoacetate $\longrightarrow$

$CH_3COCH_2CH_2CH(CH_3)_2$, 2-Methyl-5-hexanone + C_2H_5MgBr $\longrightarrow$

$CH_3CH_2C(OH)(CH_3)CH_2CH_2CH(CH_3)_2$, 2-Methyl-5-methylheptanol $\longrightarrow$

$CH_3CH_2C(I)(CH_3)CH_3CH_2CH(CH_3)_2$, 2-Methyl-5-methyl-5-iodoheptane$\longrightarrow$



$CH_3CH_2\underset{\underset{CH_2}{\|}}{C}—CH_2CH_2CH(CH_3)_2$, 2-Methyl-5-metheneheptane

$CH_3CH_2(CH)(CH_3)CH_2CH_2CH(CH_3)_2$, 2,5-Dimethylheptane.

Owing to lack of time, the constitution of the nonylene, although probably that given above, was not determined, but the only point in question is the position of the double bond, and since it is reduced to a saturated single bond in the final hydrocarbon, it has nothing to do with the constitution of the nonane.

A noteworthy fact in connection with this nonylene is that it forms a binary mixture with ethyl alcohol which boils at 80°, while the boiling point of the nonylene itself is 139–140°. The two liquids are perfectly miscible. This recalls the mixtures of minimum boiling point which normal hexane forms with the lower alcohols.[1]

Experimental Part.

Ethyl isobutylacetoacetate, $CH_3COCH\{CH_2CH(CH_3)_2\}CO_2C_2H_5$, was prepared from ethyl acetoacetate and isobutyliodide by the method of Conrad,[2] the condensation being effected through the sodium salt of the ethyl acetoacetate. The ethyl isobutylacetoacetate was saponified by boiling with a return condenser for eight hours with a 10% solution of caustic potash, using four molecules of caustic potash to each molecule of the acetoacetate. The resulting ketone was distilled with steam, separated, washed with water, dried with calcium chloride and fractionated until the boiling point extended over but one degree, *viz.*, 143–144°. The

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[1] See page 268, *et seq.*, in "Stoichiometry," by Sydney Young.

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

yield of the ketone, which was 5-methyl-2-hexanone, $CH_3COCH_2CH_2CH(CH_3)_2$, was usually about 40% of the theoretical, 100 grams of the acetoacetate giving 25 grams of ketone. This is not a new ketone, the conditions of preparation only, are new.[1]

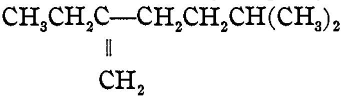
2,5 - Dimethyl - 5 - heptanol, $CH_3CH_2C(OH)(CH_3)CH_2CH_2CH(CH_3)_2$. 5-Methyl-2-hexanone, a ketone containing seven carbon atoms, was converted into 2,5-dimethyl-5-heptanol containing nine atoms of carbon by the Barbier-Grignard reaction.

Twenty grams of magnesium were dissolved in a mixture of 100 grams ethyl bromide and an equal volume of ether. To this were added ninety-one grams of ketone in an equal volume of ether and the whole heated on the steam bath for one hour. The organo-magnesium compound was then carefully decomposed by ice and water and the mixture neutralized by hydrochloric acid. The ether layer was separated and dried over potassium carbonate. Finally the ether was evaporated off and the remaining liquid fractionated. It gave sixty-one grams boiling from 172–174°. This was 2,5-dimethylheptanol.

Calculated for $C_9H_{20}O$: C, 75.0 ; H, 13.88
Found: C, 75.11; H, 14.03

Properties: Colorless liquid boiling at 172–174°. Odor of musty apples. Miscible in the common organic solvents, but not miscible in water.

2,5-Dimethyl-5-iodoheptane, $CH_3CH_2C(I)(CH_3)CH_2CH_2CH(CH_3)_2$ *and its conversion into the nonylene,*



$$CH_3CH_2\underset{\underset{CH_2}{\|}}{C}—CH_2CH_2CH(CH_3)_2$$

For the preparation of 2,5-dimethyl-5-iodoheptane, sixty-one grams of 2,5-dimethyl-5-heptanol were mixed with eight grams of red phosphorus and fifty-four grams of iodine and allowed to stand for one hour, after which the mixture was heated on a steam bath for ten hours. The resulting iodide was washed with water and filtered from the unchanged phosphorus but was not distilled.

It was converted into the nonylene without further purification as follows: seventy grams of caustic potash were dissolved in one hundred and five grams ethyl alcohol and seventy grams of the iodide carefully added to the warm mixture. It was then heated on a sand bath for two hours using a reflux condenser. The alcohol and nonylene were next distilled off, the greater part coming over at 80°. By diluting this distillate with water, the nonylene was separated, washed with water and dried over calcium chloride. On boiling the nonylene with sodium there was no tarnishing of the metal, showing that the iodine had been completely removed. On fractionating the liquid, nineteen grams were obtained boiling at 139–140°.

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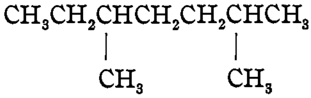
[1] See Beilstein, *Handbuch*, III Aufl., Bd. I, 1000.

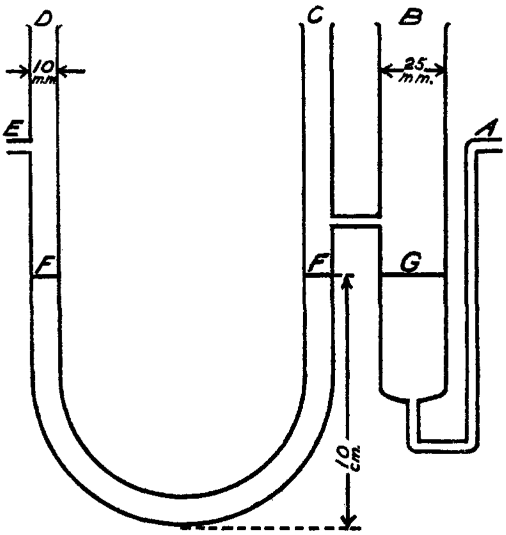
Calculated for C_9H_{18}: C, 85.71; H, 14.29
Found: C, 86.09; H, 13.91

Properties: Colorless liquid with a sweet petroleum-like odor, boiling at 139–140°. Decolorizes bromine in chloroform solution. Miscible with the common organic solvents not miscible with water.

2,5-Dimethyl heptane,  $CH_3CH_2\underset{CH_3}{\underset{|}{CH}}CH_2CH_2\underset{CH_3}{\underset{|}{CH}}CH_3$, was prepared from the nonylene by reducing it by Sabatier and Senderens' method of passing the unsaturated hydrocarbon with an excess of hydrogen over freshly reduced nickel at a temperature of 160–180°. The apparatus used is shown in the accompanying diagram and was a modification by Bedford[1] of that used by Sabatier and Senderens. The original article of Bedford is inaccessible to most readers so a description of our apparatus is herewith included.

The apparatus is of glass and is filled to G and F with nickel oxide, deposited on pumice, which was prepared as follows:

Twenty grams of purest nickel nitrate were heated in a nickel crucible over a blast flame for two hours. Pieces of pumice stone cut up to fit into the apparatus were also heated in the blast lamp in a nickel crucible for one hour. After the nickel oxide which was formed had cooled, it was made into a paste by mixing it with a little distilled water free from chlorine. The pieces of pumice were stirred into this until thoroughly coated and then removed with steel forceps, placed on a large watch glass and dried in an air bath at 95° for two hours.



The nickel prepared pumice was then put in the apparatus and C and D were stoppered with cork stoppers. B was stoppered with a cork having one hole through which a small dropping funnel was inserted. A current of hydrogen was then passed through the apparatus from A to E and the apparatus was heated in an air bath at 300° for eight hours. The hydrogen used was made by the action of hydrochloric acid on zinc

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[1] "Ueber die ungesättigten Säuren des Leinöls, und ihre quantitative Reduktion zu Stearin säure." Inaugural Dissertation zur Erlangung der Doktor, Halle a.S.

and was purified by passing through a solution of caustic potash, over hot copper gauze and finally over solid caustic potash.

After the nickel had been once reduced by heating at 300° for eight hours in a current of hydrogen, it was necessary to heat again to 300° for one hour each time it was used. The apparatus was then placed in an oil bath at 160–180° and the nonylene allowed to drop very slowly (about 6 drops a minute) through the dropping funnel on to G. The nonylene was vaporized and carried by the current of hydrogen entering at A over the nickel in F and out at E where it was condensed by an air condenser.

The nonylene was completely saturated by running it once through the apparatus. The nickel was found to work better if after running a few drops of liquid through the apparatus the first time the nickel was used, the process was stopped, heated up to 300° for an hour and then continued again at 160°. It was also found that the same nickel could not be used for two different substances.

Ten grams of the nonylene gave nine grams of the 2,5-dimethylheptane boiling within one degree. It gave no test for unsaturation. This 2,5-dimethylheptane was fractionated until 4 grams were obtained boiling at 135.6–135.9° under 760 mm. pressure.

Calculated for C_9H_{20}: C, 84.37; H, 15.63
Found: C, 84.12; H, 16.14

Properties: Colorless liquid with a petroleum-like odor, boiling at 135.6–135.9° under 760 mm. pressure. The specific gravity at 15° is 0.7190 referred to water at 15°. The index of refraction was determined with a fine Pulfrich refractometer, N_D (25°) = 1.4020. The hydrocarbon is fairly miscible with the common organic solvents.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

2,4-DIMETHYLHEPTANE.

BY LATHAM CLARKE AND SYDNEY A. BEGGS.

Received November 6, 1911.

This nonane has been synthesized and studied in connection with the researches in this laboratory on the paraffin hydrocarbons.

In the synthesis of 2,4-dimethylheptane, the starting point was ethyl isopropylacetoacetate, which was saponified giving methyl isobutylketone or 2-methyl-4-pentanone. The plan then was to treat the ketone with normal propyl magnesium iodide, which was expected to give an alcohol containing nine atoms of carbon, 2,4-dimethyl-4-heptanol, $CH_3CH_2CH_2C(OH)(CH_3)CH_2CH(CH_3)_2$; the last we intended to convert into the corresponding carbinol iodide, and by then splitting off hydriodic acid by the action of alcoholic potash, the nonylene would be formed