teristic odor of benzonitrile. The solid was purified by crystallization from 95 per cent. alcohol and melted, after the third crystallization, constant at 192°. It was identified as diphenyldiacetamide. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.53; Found, 5.59.

Action of Phenylacetonitrile on Benzoic Acid.—Ten grams of the nitrile and 10.4 grams of benzoic acid were heated for 5 hours at 240° and finally for 2 hours at 260°. On opening the tube we obtained a crystallin substance and an oil having the odor of benzonitrile. The solid was triturated with a little cold 95 per cent. alcohol to remove the oil, and melted without further purification at about 166–172° to a turbid liquid. It behaved in every way like a mixture, and after two recrystallizations from alcohol the melting point was raised to 192° indicating the presence of diphenyldiacetamide. A mixture of the compound and some diphenyldiacetamide from the previous experiment melted at exactly the same temperature. The alcoholic filtrates, after crystallization of the diacidamide, were combined and concentrated. On cooling, colorless prisms finally separated, which melted, not sharply, at 145–147°. Not enough of this material was obtained sufficiently pure for analyses, but its melting point, and the fact that it was decomposed by alkali giving only benzoic acid, indicated that it was dibenzamide.

Action of Benzoylisocyanate on β-Phenylpropionic Acid. Formation of β-Phenylpropionylbenzamide,[1] $C_6H_5CONH.CO.CH_2CH_2C_6H_5$.—Benzoylisocyanate and the above acid reacted almost immediately, on mixing, with evolution of heat and carbon dioxide. After heating at 100° for a few minutes the reaction was complete and the diacidamide was obtained in a crystallin condition. The yield was practically quantitative. It crystallized from alcohol and melted at 104–105° to a clear oil. Analysis (Kjeldahl):

Calculated for $C_{16}H_{15}O_2N$: N, 5.35; Found, 5.14.

NEW HAVEN, CONN.,
January 21, 1911.

2,3-DIMETHYLHEXANE.

BY LATHAM CLARKE.

Received February 8, 1911.

This paper ccntains first an account of the preparation and properties of 2,3-dimethylhexane, $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, the study of which has been taken up in continuation of a research on the octanes begun some time ago in the laboratory;[2] and second, a comparison of eight octanes, *viz.*, normal octane, the three methylheptanes, and the

[1] Colby and Dodge, *Loc. cit.*
[2] Preliminary Notice, *Ber.*, 40, 352.

four dimethylhexanes, which last series, the synthesis of 2,3-dimethyl-hexane now completes.

The graphical formulas of the above-mentioned octanes are as follows:

1. $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$, Normal.[1]
2. $CH_3CH(CH_3)CH_2CH_2CH_2CH_2CH_3$, 2–Methylheptane.[2]
3. $CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_3$, 3–Methylheptane.[3]
4. $CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$, 4–Methylheptane.[4]
5. $CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3–Dimethylhexane.[5]
6. $CH_3CH(CH_3)CH_2CH(CH_3)CH_2CH_3$, 2,4–Dimethylhexane.
7. $CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$, 2,5–Dimethylhexane.[6]
8. $CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$, 3,4–Dimethylhexane.[7]

A table of the boiling points, specific gravities and indices of refraction of these hydrocarbons follows:

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

Normal Octane.—The boiling point and other constants given above were determined in this laboratory.[8]

2-Methylheptane.—Data obtained from the hydrocarbon prepared by two methods.[9]

3-Methylheptane.—Data obtained from the hydrocarbon made in this laboratory.[10] Mlle. Welt[11] gives the boiling point 110° to 120° but her compound was evidently not very pure.

4-Methylheptane.—Data obtained from a sample made in this laboratory.[12]

[1] T. Riche, *Ann.*, 117, 265; Schorlemmer, *Ibid.*, 161, 280; 152, 152; 147, 227; Zincke, *Ibid.*, 152, 15; Paterno and Peratoner, *Ber.*, 22, 467.

[2] Clarke, THIS JOURNAL, 31, 107 (1909).

[3] Welt, *Ann. chim. phys.*, [7] 6, 121; Clarke, THIS JOURNAL, 31, 558.

[4] Clarke, *Ber.*, 40, 352; *Amer. Chem. J.*, 39, 87.

[5] Clarke, THIS JOURNAL, 30, 1144.

[6] Wurtz, *Ann.*, 96, 365; Schorlemmer, *Ibid.*, 114, 188; Kolbe, *Ibid.*, 69, 261; Young, *J. Chem. Soc.*, 77, 1136; Clarke, THIS JOURNAL, 31, 585.

[7] Norris and Green, *Am. Chem. J.*, 26, 313. This octane also has been made in this laboratory, but the work is as yet unpublished.

[8] Other authors state the following boiling points: Thorpe, *Soc. Trans.*, 37, 77, 125.46°; Young, *Soc.*, 77, 145, 125.8° at 760 mm. The specific gravity is given by Thorpe as 0.71883 at 0°/4°, and by Young as 0.71850, 0.71817 and 0.71848 at 0°/4°.

[9] Clarke, THIS JOURNAL, 31, 114, 116.

[10] Clarke, *Ibid*, 31, 559.

[11] *Ann. chim. phys.*, [7] 6, 121.

[12] *Am. Chem. J.*, 39, 96.

2,3-Dimethylhexane.—These data are the average of the results obtained when the hydrocarbon was made by two methods as explained later in this paper.

2,4-Dimethylhexane.—Data obtained from the octane made by two methods.[1]   These gave the following results:

	Boiling point.	Specific gravity, 15/15.	Index of refraction, N_D 25°.
First Method..........	109.8°–110° at 762 mm.	0.7083	1.3986
Second Method........	110.0° at 763 mm.	0.7083	1.3986

2,5-Dimethylhexane.—The above data are the average of the results obtained from specimens of the hydrocarbon prepared by two methods.[2]

	Boiling point.	Specific gravity, 15/15.	Index of refraction, N_D 25°.
First Method..........	108. – 108.3° at 760 mm.	0.6989	1.3926
Second Method........	108.3 – 108.5° at 760 mm.	0.6993	1.3935
Average..............	108.25°	0.6991	1.3930

Other observers have published the following data which have been collected by Young and Fortey.[3]

	Boiling point at t°.	Corrected to 760 mm.
Kolbe, *Ann.,* **69,** 259 (1849)............		108°.
Kopp, *Ann.,* **95,** 335 (1855)............	108.5° at 747.5 mm.	109.1°
Thorpe, *J. Chem. Soc.,* **37,** 219 (1880)...	108.2°–108.7° at 748.2 mm.	108.53°
Schiff, *Ann.,* **220,** 88 (1883)............	107.8°–107.9° at 751.4 mm.	108.25°
Williams, *Ann.,* **35,** 125 (1879)........	108.2° at 745. mm.	108.9°
Pawlewski, *Ber.,* **16,** 2634 (1883)		107.5°
Young and Fortey, *Loc. cit*............		109.2°

	Specific gravity at t°.	Calculated at 0°/4°.
Kolbe, *Jahresb.,* **1,** 559 (1848)...............	0.6940 at 18°.	0.7091
Wurtz, *Jahresb.,* **8,** 576 (1855)...............		0.7057
Kopp, *Loc. cit*.............................		0.7135
Williams, *Loc. cit*.........................		{0.7091
		{0.7085
Schorlemmer, *Jahresb.,* **20,** 567 (1867)........	0.698 at 16.5°	0.7119
Thorpe, *Loc. cit*.........................		0.7111
Schiff, *Loc. cit*...........................	0.7001 at 12.1°/4°	0.7103
Young and Fortey, *Loc. cit*................	0.69996 at 11.9°/4°	0.71021

3,4-Dimethylhexane. — Data observed in this laboratory on a sample prepared by the action of sodium on 2-iodobutane following the method described by Norris and Green.[4]

[1] Clarke, THIS JOURNAL, 30, 1148, 1151.

[2] Clarke, *Ibid.,* **31,** 588, 589.

[3] *J. Chem. Soc.,* **77,** 1137.

[4] *Am. Chem. J.,* **26,** 318.

Their data were as follows: Boiling point, 116° to 116.2° at 750 mm. pressure. Specific gravity, 0°/4°, 0.7332, at 25°/4, 0.7165.

A study of the table of physical properties now reveals some interesting relationships.

The octanes here seem to fall into three classes: First, normal octane stands by itself for its boiling point is nearly seven degrees higher than the next lower, whereas its specific gravity is lower than most of the others, in fact, but two of the eight given are higher than it, and it stands in the same position in regard to relative index of refraction. Second, the methylheptanes form a group of three. Between the boiling point of the lowest and the boiling point of the highest boiling there is a difference of but two degrees. 2-Methylheptane boils the lowest; on moving the methyl group to the 3-position, an increase of 1.6° is observed, and on moving the methyl to the 4-position a further increase of 0.4° is brought about. As the boiling point rises, the specific gravity increases but in much greater proportion. We should expect the indices of refraction to follow the specific gravities, and as the latter increases, so should the former. But this does not appear to be so, 4-methylheptane has the greatest specific gravity of the three, but the index of refraction is less than that of 3-methylheptane. Third, the dimethylhexanes form a group of four. The physical constants exhibit a wider range than do those of the methylheptanes. The lowest boiling member of this series is 2,5-dimethylhexane, viz., 108.25°; this has also the lowest specific gravity and lowest index of refraction. Next above 2,5-dimethylhexane in boiling point comes 2,4-dimethylhexane, above this 2,3-dimethylhexane, and highest of all comes 3,4-dimethylhexane. The specific gravities rise with increasing boiling point and the index of refraction follows this order too, with the exception of the 3,4-dimethylhexane, which has an index lower than that shown by the compound when the methyl groups are in the 2,3-position.

These three classes, into which the octanes enumerated thus divide themselves, have the following essential difference in structure. The normal compound contains two methyl groups, the methylheptanes contain three, and the dimethylhexanes four. Increasing the number of methyl groups increases the volatility of the compound and we can now establish a set of comparative data in this subject.

The boiling point of normal octane is 124.7° while that of 2-methylheptane is 116.0°, which shows a lowering of 8.7° in going from a straight chain containing eight carbon atoms with two methyl groups to a chain containing seven members and three methyl groups. This is a greater difference than exists between normal and iso-hexane, and normal and iso-heptane, as shown by the following table:

	Boiling point at 760 mm.	Difference.
Hexane, $CH_3CH_2CH_2CH_2CH_2CH_3$..........	68.8[1]	
Isohexane, $CH_3CH(CH_3)CH_2CH_2CH_3$.......	62.0 [2]	6.8°
Heptane, $CH_3CH_2CH_2CH_2CH_2CH_2CH_3$......	98.2 – 98.5 Ave. 98.35° [3]	
Isoheptane, $CH_3CH(CH_3)CH_2CH_2CH_2CH_3$...	Ave. 90.3	8.0°

The fact is here brought out that with increasing molecular weight and increasing length of carbon chain, the lowering effect of the "iso group" becomes greater and greater.

In considering the dimethyl hexanes, it can now be shown that the boiling point of the 2,5-dimethylhexane is about as much lower than the boiling point of 2-methylheptane as isoheptane is lower than normal heptane.

2-Methylheptane (or iso-octane) has the boiling point 116°. We have now a straight chain *seven* carbon atoms in length, and if we now replace our normal groups at the opposit end of the chain by an iso group, we observe the lowering is the same as that which takes place in going from normal heptane to isoheptane, which is 8°, *viz.*: 116.0 – 8.0° = 108.0°. The actual is 108.25°, which is probably within the limits of experimental error.

	Boiling point.	Difference.
$CH_3CH_2CH_2CH_2CH_2CH_3$......................	98.35°	
$CH_3CH(CH_3)CH_2CH_2CH_2CH_3$....................	90.3°	8.0°
$CH_3CH_2CH_2CH_2CH_2CH(CH_3)CH_3$.................	116.0°	
$CH_3CH(CH_3)CH_2CH_2CH(CH_3)CH_3$...............	108.25°	7.75°

Taking now the case of 2,4-dimethylhexane or calling it 3,5-dimethylhexane for the sake of clearness, we should expect from the above relations that the boiling point would be as much lower than that of 3-methylheptane, as isoheptane is lower than normal heptane, *viz.*, 8.0° lower.

	Boiling point.	Difference.
$CH_3CH_2CH(CH_3)CH_2CH_2CH_2CH_3$, 3-methylheptane.....	117.6°	
$CH_3CH_2CH(CH_3)CH_2CH(CH_3)CH_3$, 2,4-dimethylhexane or 3,5-dimethylhexane...	110° at 763	7.6°

The boiling point of 2,4-dimethylhexane corrected to 760 mm. would be slightly less than 109.9°, making the difference here 7.7°, so that this also is a very fair agreement.

By the same method of calculation, the boiling point of 2,3-dimethylhexane should be the same as that of 3,5-dimethylhexane, *viz.*, 117.6° — 8.0° = 109.6°. But instead of being 109.6°, it is 113.9°, which is 4.3° higher.

[1] Average of Young, 68.95°, *Soc.*, **73**, 906; and Friedel and Gorgen, 68.60°, *Compt. rend.*, **127**, 592.

[2] Observed in this Laboratory in sample made by method described in the *Am. Chem. J.*, **35**, 513.

[3] Young, *Soc.*, **73**, 906.

Boiling point.

$CH_3CH_2CH(CH_3)CH_2CH_2CH_3$, 3-methylheptane   117.6°

$CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3-dimethylhexane   113.9°

The methyl groups no longer act independently of each other as they apparently have in the two previous cases, but here they are attached to adjacent carbon atoms whereas in the other cases the carbon atoms to which they were joined were separated by one or more —CH_2— groups.

In 3,4-dimethylhexane, we have a configuration similar to that of 2,3-dimethylhexane, and here again the observed boiling point is higher than that which may be calculated as follows. The boiling point of 3-methylhexane is 7.3° lower than that of the normal heptane:

Boiling point.

$CH_3CH_2CH_2CH_2CH_2CH_2CH_3$............ 98.35°

$CH_3CH_2CH(CH_3)CH_2CH_2CH_3$........... 91.° [1]

Starting now with 4-methylheptane and replacing the —$CH_2CH_2CH_2CH_3$ group by —$CH(CH_3)CH_2CH_2$, we might expect to get a lowering of 7.3°; since this would be parallel to the foregoing calculations, this would give for 3,4-dimethylhexane, the boiling point 110.7°, but the actual is 116.5°, which is 5.8° higher.

Boiling point.

$CH_3CH_2CH_2CH(CH_3)CH_2CH_2CH_3$....... 118°

$CH_3CH_2CH(CH_3)CH(CH_3)CH_2CH_3$....... 116.5°

These results seem to show that the methyl group tends to produce volatility, for the methylheptanes containing three methyl groups boil several degrees lower than the normal octane, which contains but two. The position of the methyl group makes only a slight difference in the boiling points, since those of the three methyl heptanes are within two degrees of one another. The density of the compounds rises as the methyl group is moved successively from the 2-, to the 3-, or to the 4-position. This may be due to the repellent action of CH_3 groups towards each other, making the compound containing the methyl in the 2-position least compact, producing a liquid of less density than for example, the 4-methylheptane, where the methyl groups are farther removed, and which is a compound of relatively high specific gravity.

In the case of 2,5-dimethylhexane, we have four methyl groups, and each pair of CH_3 groups acts independently of the other, giving a very volatil compound, and as has already been explained, the introduction of the second "iso group" into the iso-octane or methylheptane has produced the lowering of 8° which was characteristic of the heptanes

[1] Just, *Ann.*, 220, 154. This hydrocarbon has also been made by Mlle. Welt, *A. Chem.*, [7] 6, 121, who observed the boiling point, 80–88°, but her compound was evidently not very pure. The physical properties of this hydrocarbon will be determined as soon as possible in this laboratory.

themselves. The compound is the least dense of the series and thus bears out the theory that methyl groups in the "iso" position have a repellent action on one another and produce a compound of relatively low specific gravity and boiling point.
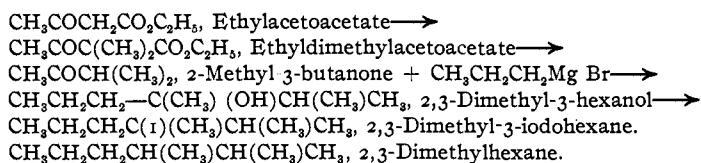
With 2,4-dimethylhexane, the independence of action of the "iso" methyl group and that present on the No. 4 carbon atom is shown and the lowering of boiling point produced by substituting the straight chain in the 4-methylheptane by the "iso" group is that observed in the case of the two corresponding heptanes.

2,3-dimethylhexane has a boiling point higher by practically 4° than 2,4-dimethylhexane, while the two should boil at the same temperature, if the methyl groups were independent of each other. In this case the repellent action of the methyl groups is much more than overbalanced by the spatial configuration which is such that a compact molecule results, and to this may be ascribed the higher boiling point and greater density as compared to the 2,4-dimethyl compound. The same explanation applies to the observation that 3,4-dimethylhexane boils so high, —116.5°, and has the greatest density of any octane as yet obtained, its specific gravity being 0.7270 at 15°, compared to water at 15°.
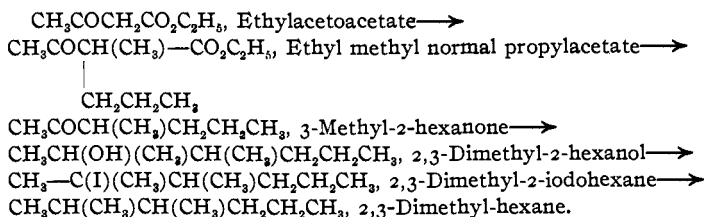
Special Theoretical.

For the synthesis of 2,3-dimethylhexane two methods were employed: The first method consisted of the following steps: Ethyldimethylacetoacetate was prepared from methyl iodide and ethyl sodium acetoacetate, and by saponifying this dimethylacetone, or 2-methyl-3-butanone was obtained. From pure normal propyl alcohol, the corresponding carbinol bromine was made and from this in turn the organo-magnesium derivative. The action of this normal propylmagnesium bromide on 2-methyl-3-butanone produced the carbinol, 2,3-dimethyl-3-hexanol, which was converted into 2,3-dimethyl-3-iodohexane, and reduced, thereby yielding 2,3-dimethylhexane.

SUMMARY.

$CH_3COCH_2CO_2C_2H_5$, Ethylacetoacetate⟶
$CH_3COC(CH_3)_2CO_2C_2H_5$, Ethyldimethylacetoacetate⟶
$CH_3COCH(CH_3)_2$, 2-Methyl-3-butanone + $CH_3CH_2CH_2Mg\ Br$⟶
$CH_3CH_2CH_2—C(CH_3)\ (OH)CH(CH_3)CH_3$, 2,3-Dimethyl-3-hexanol⟶
$CH_3CH_2CH_2C(1)(CH_3)CH(CH_3)CH_3$, 2,3-Dimethyl-3-iodohexane.
$CH_3CH_2CH_2CH(CH_3)CH(CH_3)CH_3$, 2,3-Dimethylhexane.

In synthesizing 2,3-dimethylhexane by the second method, the initial compound was ethylacetoacetate, from which ethyl methyl normal propylacetoacetate was prepared, and then saponified, forming 3-methyl-2-hexanone. This was treated with methyl-magnesium iodide, whereby 2,3-dimethyl-2-hexanol was produced, which was converted into the corresponding iodohexane and reduced, yielding 2,3-dimethylhexane.

SUMMARY

$CH_3COCH_2CO_2C_2H_5$, Ethylacetoacetate—→

$CH_3COCH(CH_3)$—$CO_2C_2H_5$, Ethyl methyl normal propylacetate—→

  |
  $CH_2CH_2CH_3$

$CH_3COCH(CH_3)CH_2CH_2CH_3$, 3-Methyl-2-hexanone—→

$CH_3CH(OH)(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3-Dimethyl-2-hexanol—→

CH_3—$C(I)(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3-Dimethyl-2-iodohexane—→

$CH_3CH(CH_3)CH(CH_3)CH_2CH_2CH_3$, 2,3-Dimethyl-hexane.

Both these methods are quite satisfactory but the second is to be preferred, as in the different steps better yields are obtained.

The hydrocarbons made by both methods were apparently identical. The physical constants were as follows:

	Boiling point.	Specific gravity, 15/15.	Index of refraction, N_D 25°.
Octane by Method No. 1.....	113.8–114 at 760 mm.	0.7241	..
Octane by Method No. 2.....	113.8–114 at 760 mm.	0.7252	1.4075
Average....	113.9° at 760 mm.	0.7246	1.4075

The difference in the above specific gravities is undoubtedly due to an experimental error. The amount of the hydrocarbon made by method No. 1 was barely enough to properly fill the pycnometer, and to this fact the differences in the results is undoubtedly due.

Experimental Part.

First Method.—In the preparation of ethyl dimethylacetoacetate from ethyl sodium acetoacetate and methyl iodide, many difficulties were encountered and good yields could not be obtained. It was found that the most satisfactory procedure was to make and use the ethyl mono-sodium acetoacetate in benzene solution and to allow this solution to stand with excess of methyl iodide for a week or more at room temperature, then to distil off the unchanged methyl iodide, extract the sodium iodide from theethylmethylaceto acetate by shaking out with water, dry the ethylmethylacetoacetate with solid potassium carbonate, and treat with a second molecule of sodium and methyl iodide in the manner just described, again allowing the mixture to stand for a week. In this way fairly good yields could be obtained.

It is best to illustrate this procedure by an experiment. 130 grams of ethylacetoacetate were mixed with 300 grams of dry benzene and to the solution 23 grams of sodium were added, a small piece at a time, with heating on the steam bath. When all the sodium had been dissolved, the solution was cooled and 175 grams of methyl iodide were added and the mixture allowed to stand for a week, best in a warm place. Any unchanged methyl iodide was then distilled off and the residue treated with enough water to remove the sodium iodide, after which the ethylmethylacetoacetate was dried with a small amount of potassium carbon-

ate. To the dried benzene solution, 23 grams of sodium were introduced as before, and after the addition of 175 grams of methyl iodide again allowed to stand for a week. The ethyldimethylacetoacetate was then obtained by the same procedure of distilling off the excess of methyl iodide, treating with water to remove sodium iodide and drying with potassium carbonate, after which the benzene was distilled off on an oil bath. The yield of ethyl dimethylacetoacetate in this crude state was from 60 to 70 per cent. of the theoretical. It was not purified especially but was distilled once and then converted into the ketone $CH_3COCH(CH_3)$ by saponification.

The saponification of ethyl dimethylacetoacetate to 2-methyl 3-butanone was easily accomplished by boiling with 4 molecules of caustic potash in 10 per cent. aqueous solution for six hours, distilling with steam, separating and drying the upper layer of the distillate with calcium chloride, and fractionating with a long Hempel column. The ketone thus obtained boiled at 95–95.3° at 760 millimeters pressure.

2,3-Dimethyl-3-hexanol, $CH_3CH_2CH_2C(CH_3)(OH)CH(CH_3)CH_3$.—This compound was made in the manner of the following experiment: 4 grams of magnesium were dissolved in a mixture of 21 grams of normal propyl bromide and 20 grams of anhydrous ether, and to the cold solution 15 grams of 2-methyl-3-butanone, diluted with an equal volume of ether, were slowly added. After half an hour's standing, the carbinol was freed by the usual procedure of adding water and hydrochloric acid, drying the ether layer with potassium carbonate, and fractionating. Thus, 10 grams of carbinol were obtained, boiling at 158°–158.2°, at 758 millimeters pressure, after three distillations. From the method of formation it was known to be 2,3-dimethyl-3-hexanol, with the following constitution: $CH_3CH(CH_3)C(CH_3)(OH)CH_2CH_2CH_3$. The reaction was accompanied by the formation of two high-boiling liquids neither of which could be fractionated. The analysis was satisfactory.[1]

Properties: Liquid boiling at 158°–158.2° at 758 millimeters pressure and with a strong odor something like eucalyptus oil. It is miscible with the common organic solvents but immiscible with water.

Preparation and Reduction of 2-3-Dimethyl-3-iodohexane, $CH_3CH(CH_3)C(I)(CH_3)CH_2CH_2CH_3$.—Ten grams of 2,3-dimethyl-3-hexanol were mixed with 1.5 grams of red phosphorus and treated with 10 grams of iodine; the reaction flask at first was kept cold by a cold water bath but at the end of an hour was warmed to 60° and allowed to remain at that temperature for three hours. The carbinol iodide was purified, not by distillation, but by shaking out twice with cold water and filtering through glass wool to remove unchanged phosphorus. It·

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[1] During my absence of a year in Europe, the analytical note-book containing this and other numerical data was mislaid, and the figures are, therefore, not accessible.

was then reduced by zinc and hydrochloric acid, and finally by scrap magnesium and hydrochloric acid to remove final traces of halogen. The resulting octane was distilled with steam from the reduction mixture, treated with concentrated sulphuric acid, shaken with dilute potassium permanganate solution until no more discoloration took place, boiled over sodium with a return condenser, and carefully fractionated. About 4 grams of octane were obtained in this way, practically all of which boiled at 113.8° to 114° at 758 millimeters. The liquid was halogen-free and contained no unsaturated hydrocarbon. The analysis was satisfactory.

Properties: Colorless, very mobil liquid, boiling at 113.8° to 114° at 758 millimeters pressure, and with a rather strong odor. It has at 15° the specific gravity 0.7241 compared to water at 15°.

Second Method.—Ethyl methyl normal propyl acetoacetate was made from ethyl acetoacetate, but with some trouble. The best procedure was to first prepare ethyl normal propyl acetoacetate by Conrad's method,[1] using sodium ethylate, ethyl acetoacetate, and ethyl iodide, and to isolate and purify the reaction product. This is dissolved in two parts of benzene, and treated with one molecule of sodium, and when solution of the latter has taken place, with one molecule of methyl iodide at room temperature, the reaction mixture being allowed to stand a week or ten days. The benzene is distilled off, the sodium iodide extracted with water, the residue dried and distilled. At best, the yield is not very good, not over 60 per cent. of the theoretical.

3-Methyl-2-hexanone, $CH_3COCH(CH_3)CH_2CH_2CH_3$.—One molecule of ethyl methyl normal propyl acetoacetate was boiled for ten hours with four molecules of caustic potash in ten per cent. aqueous solution, and the resulting ketone distilled off with steam, the distillate separated, dried with calcium chloride and twice fractionated. The boiling point is 136–137°,[2] at 760 millimeters pressure. 190 grams of the acetoacetic ester derivative usually yielded between 40 and 50 grams of 3-methyl-2-hexanone. The analysis was satisfactory.

2,3-Dimethyl-2-hexanol, $CH_3C(OH)(CH_3)CH(CH_3)CH_2CH_2CH_3$.—A solution of methyl magnesium iodide was prepared by dissolving 12 grams of magnesium turnings in a mixture of 80 grams of methyl iodide and 80 grams of absolute ether. To this solution 57 grams of 3-methyl-2-hexanone mixed with an equal volume of absolute ether were gradually added, and the whole allowed to stand one hour, when the carbinol was set free by the customary treatment with water and hydrochloric acid. The ether layer was separated, dried over potassium carbonate, the ether distilled off, and the residue fractionated, which yielded 54

[1] Conrad and Limpach, *Ann.*, **192**, 557.
[2] Jones, *Ann.*, **226**, 293, gives the boiling point as 142°–147°.

grams of 2,3-dimethyl-2-hexanol boiling at 150°–151° at 756 millimeters pressure. The analysis was satisfactory.

Properties: Colorless liquid, boiling at 150°–151° at 756 mm. pressure, with an odor something like that of musty apples. It is insoluble in water but miscible in all proportions with the common organic solvents.

Preparation and Reduction of 2,3-Dimethyl-2-iodohexane.—33 grams of 2,3-dimethyl-2-hexanol were mixed with 3.5 grams of red phosphorus and 32 grams of iodine were added to the mixture which was allowed to stand over night at room temperature, and then next day was heated for an hour at 80°. The resulting iodide was washed with water, filtered through asbestos to remove unchanged phosphorus and reduced in the following manner:

In a 250 cubic centimeter flask, fitted with a return condenser, about 200 grams of finely divided zinc[1] were placed and the flask was then immersed in a bath of cold water. The octyl iodide was introduced into the flask and was mixed with the zinc by thorough shaking. Concentrated (38 per cent.) hydrochloric acid was poured through the condenser tube until the flask was half full, when the apparatus was set aside and allowed to remain three days. The amount of octyl iodide was such that the zinc was almost covered by it, forming a sort of paste and the acid being cold, acted very slowly and on the zinc which was itself nearly covered by octyl iodide. The result was that the evolution of hydrogen, for the most part, took place at the surface of contact of the acid and octyl iodide, and the result was a very satisfactory reduction of the alkyl iodide to the hydrocarbon. At the end of three days, the layer of octane had collected above the aqueous solution and was separated, dried with calcium chloride and fractionated. The portion boiling at 110–115° was further purified as shown presently, while the residue which did not distil at 115° or above was put back into the reduction flask and the process repeated. The crude octane was purified in the usual manner by treating with concentrated sulfuric acid, shaking with potassium permanganate solution, and distilling over sodium, after which it was carefully fractionated, when about 10 grams of 2,3-dimethylhexane were obtained. The boiling point on the last fractionation was 113.8° to 114° at 760 millimeters pressure, but most of the fraction came over at the latter figure. The analysis was satisfactory.

Properties: Colorless, very mobil liquid, boiling at 113.8° to 114° at 760 millimeters pressure and possessing a characteristic rather strong odor. It has, at 15°, the specific gravity 0.7252 compared to water at 15°. The index of refraction was determined with the kind assistance of Mr. F. W. Barry and was found to be N_D (25°) = 1.4075.

[1] This had previously been treated with a few cubic centimeters of a dilute solution of copper sulfate.

·The above work was done in this laboratory during the year 1908–09. The research on the octanes will be continued and the brief comparison of the first eight given in this paper will be extended from time to time as each new series is completed.

I am deeply indebted to the C. M. Warren Fund for Research for much of the material used in this study.

CAMBRIDGE, MASS.

ON TRIPHENYLMETHYL.

[TWENTIETH PAPER.]

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1. Introduction.

In previous papers bearing on the constitution of triphenylmethyl and its many analogs the following facts of importance, among others, were brought out: (1) The triarylmethyls are capable of existing in two modifications—the colored and the colorless;[2] the colored form is not limited to the solid phase alone, but as has been shown by J. Schmidlin,[3] the two modifications exist in equilibrium with each other even when in solution. (2) In the colored modification one phenyl group has become apparently changed in its function, for in it the para position is extremely reactive and mobil, in strong contrast to the great stability of the three phenyl nuclei in triphenylmethane itself.[4] (3) A similarly striking change in the functions of one phenyl nucleus, simultaneously with the production of color and of salt-like properties in the compound itself, has been shown to take place when the colorless triphenycarbinol halides are dissolved in sulfur dioxide, or when the triphenylcarbinols—always colorless—are changed to the corresponding carbinol sulfates, always colored.[5]

The theoretical explanation which has been advanced in order to account for these newly acquired functions in the phenyl nucleus consists in attrib-

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[1] This investigation was presented by Mr. Van Slyke to the Graduate School of the University of Michigan, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] *Ber.*, 34, 2729 (1901); 35, 2406 (1902); 37, 2036 (1904); 40, 1881 (1907).

[3] *Ibid.*, 41, 2471 (1908).

[4] *Ibid.*, 39, 3274 (1906).

[5] *Ibid.*, 40, 1847 (1907); 42, 406 (1909).