rather slowly at 232°. It gives a bright red color with acids and is soluble with a yellow color in aqueous sodium hydroxide.

Calculated for $((CH_3O)C_6H_2Br(OH)CH:)_2C_{12}H_8N_2$: Br, 26.23. Found, 25.91, 26.10.

Bis-nitropiperonylenebenzidine, $(CH_2O_2C_6H_2NO_2CH:)_2C_{12}H_8N_2$.—This derivative was made by mixing hot alcoholic solutions of 6-nitropiperonal[1] (m. p. 97°) and benzidine, made up as follows: 5 grams nitropiperonal in 100 cc. alcohol and 2.4 grams benzidine in 50 cc. alcohol. The reddish yellow precipitate that appeared in a few minutes was allowed to stand some time before filtering and then crystallized from xylene. It decomposes when heated to 273° and when pure is of a dark yellow color, which changes rather rapidly to dark brown on exposure to sunlight.

Calculated for $(CH_2O_2C_6H_2NO_2CH:)_2C_{12}H_8N_2$: N, 10.41. Found, 10.10, 10.25.

Bis-mono-brompiperonylenebenzidine, $(CH_2O_2C_6H_2BrCH:)_2C_{12}H_8N_2$.—When two molecules of brompiperonal[2] (m. p. 129°) were dissolved in hot alcohol and mixed with a hot alcoholic solution of one molecule of benzidine, a yellow substance precipitated almost immediately. The mixture was allowed to stand overnight, and after washing and drying, the compound was crystallized from benzene. M. p. 257° with decomposition. Analysis shows that both amino groups have reacted with the brompiperonal.

Calculated for $(CH_2O_2C_6H_2BrCH:)_2C_{12}H_8N_2$: Br, 26.40. Found, 26.84, 26.44, 26.18.

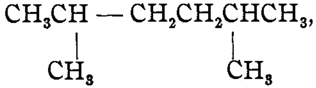
[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

DI-ISOBUTYL OR 2,5-DIMETHYL-HEXANE.

BY LATHAM CLARKE.

Received March 22, 1909.

Although di-isobutyl or 2-5 dimethylhexane,



$$\underset{\displaystyle CH_3}{CH_3\underset{|}{C}H} — CH_2CH_2\underset{\underset{\displaystyle CH_3}{|}}{C}HCH_3,$$

has been known for many years, a new synthesis of it has been considered necessary in the research on the octanes now in progress in this laboratory. The value of this research depends to a great extent on the accuracy of the physical constants, and the data in regard to di-isobutyl vary considerably according to the observations of different investigators, so that they do not appear to have the desired accuracy.

Di-isobutyl was first made by Kolbe[3] in 1849, by the electrolysis of potassium isovalerianate. Kolbe published the boiling point 108°, and the specific gravity, 0.694 at 18°. According to Kopp,[4] to whom

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[1] Fittig, Remsen, *Ann.*, **159**, 134. F. Haber, *Ber.*, **24**, 624.

[2] Oelker, *Ber.*, **24**, 2593.

[3] *Ann.*, **69**, 261.

[4] *Ibid.*, **95**, 335.

Kolbe gave a sample of his hydrocarbon, the boiling point is 108.5° (corrected) at 747.5 millimeters pressure, and the specific gravity at 16.4° is 0.7001 and at 0°, 0.7135.

Wurtz[1] obtained di-isobutyl by treating isobutyl iodide with sodium, and gave the boiling point as 106°.

Schorlemmer[2] synthesized di-isobutyl by the use of isoamyl iodide, isopropyl iodide and sodium, and he gives the boiling point as 109° to 110°.

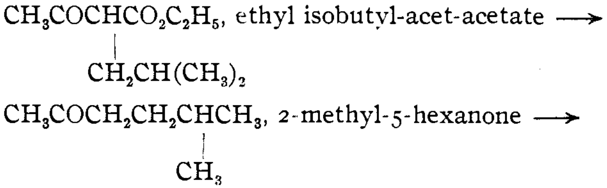
Williams[3] prepared di-isobutyl by the Wurtz reaction, and it is probable that his hydrocarbon was essentially pure. His di-isobutyl boiled at 108–108.3° at 745 millimeters pressure, and had at 0° the specific gravity 0.7090; at 10°, 0.7015, and at 20°, 0.6931.

In this laboratory, the hydrocarbon was prepared by two methods, and the results agree closely with those of Williams. The octane of this research prepared by method I boiled at 108–108.3°, and had at 15° the specific gravity 0.6989 compared to water at 15°. The octane obtained by method II boiled at 108.3–108.5° and had at 15° the specific gravity 0.6993 compared to water at 15°.

The first method was that of Wurtz, in which isobutyl iodide and sodium were used. The isobutyl iodide was fractionated and was easily purified thereby—for its possible impurities of primary alkyl iodides boil high enough to be separated by distillation, while its impurities of tertiary alkyl iodides are decomposed into olefins and hydriodic acid. The hydrocarbon itself was purified by treatment with concentrated sulphuric acid, boiling over sodium, shaking with potassium permanganate solution, and boiling over sodium again.

The second method consisted in preparing ethyl isobutyl-aceto-acetate and saponifying it, forming methyl isoamyl ketone, or 2-methyl-5-hexanone. This was made to react with methyl magnesium iodide, the product being 2,5-dimethyl-2-hexanol, and the hydrocarbon was produced by converting this into the corresponding iodide and reducing.

Summarizing these reactions:



$$CH_3CO\underset{\substack{|\\ CH_2CH(CH_3)_2}}{CH}CO_2C_2H_5\text{, ethyl isobutyl-acet-acetate} \longrightarrow$$

$$CH_3COCH_2CH_2\underset{\substack{|\\ CH_3}}{CH}CH_3\text{, 2-methyl-5-hexanone} \longrightarrow$$

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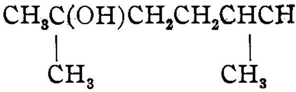
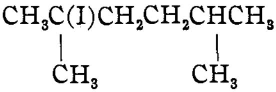
[1] *Ann.*, **96**, 365.

[2] *Ibid.*, **144**, 188.

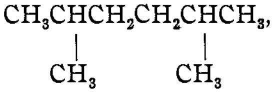
[3] *Soc.*, **31**, 541; also *Soc.*, **35**, 12 .



$CH_3\underset{CH_3}{\underset{|}{C}}(OH)CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$, 2,5-dimethylhexanol ⟶



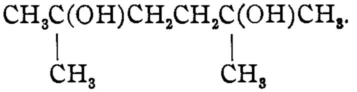
$CH_3\underset{CH_3}{\underset{|}{C}}(I)CH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$, 2,5, dimethyl-2-iodohexane ⟶



$CH_3\underset{CH_3}{\underset{|}{C}}HCH_2CH_2\underset{CH_3}{\underset{|}{C}}HCH_3$, 2,5,-dimethylhexane.

In this method, the isobutyl iodide used in making the ethyl isobutyl-acet-acetate was carefully fractionated as in the first method. The ketone, 2-methyl-5-hexanone, was also carefully distilled. This process together with the customary treatment of the hydrocarbon, insure the purity of the final product.

Still a third method was devised, but was not used on account of its practical difficulties. In this, the plan was to prepare acetonyl acetone, or 2,-5-hexanedione, $CH_3COCH_2CH_2COCH_3$, and treat this with two molecules of methyl magnesium iodide, giving 2,5-dimethyl-2,5-dihydroxy-hexane,



$CH_3\underset{CH_3}{\underset{|}{C}}(OH)CH_2CH_2\underset{CH_3}{\underset{|}{C}}(OH)CH_3$.

This could be converted into the iodo derivative and reduced, forming 2,5-dimethylhexane. Unfortunately, however, no good method exists for the production of acetonyl acetone and so this method, perhaps the best of the three (because isobutyl alcohol is not used), had to be abandoned.

Experimental Part.

First Method.—Isobutyl alcohol was converted into isobutyl iodide by treating 75 grams of the former with 15 grams of red phosphorus and adding in small portions at a time 127 grams of iodine, allowing the mixture to stand overnight and then distilling off the product over the free flame. The isobutyl iodide so prepared was twice fractionated and boiled at 120–1°. The fractionation of the isobutyl iodide gave a very good product and freed it entirely from possible tertiary iodides since the distillation would decompose these into olefins and hydriodic acid.

The isobutyl iodide (120 grams) was treated with sodium (25 grams) by the method already described by Wurtz. When the reaction was completed, the octane was distilled off in an oil bath and boiled over fresh sodium with a return condenser, then treated with concentrated sulphuric acid, and with sodium again, after which it was shaken with a solution of potassium permanganate until no further decoloration took place. One more distillation over sodium completed the purification and the hydrocarbon now contained no unsaturated compound and was without action on metallic mercury.[1] The boiling point was observed to be 108–108.3° at 760 mm. pressure. The yield of the final pure octane was 20 grams.

Calculated for C_8H_{18}:	C, 84.21; H, 15.79
Found:	C, 84.84; H, 15.76

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[1] For the significance of this, see Clarke, THIS JOURNAL, 559.

Properties.—Clear, colorless mobile liquid with a pleasant rather sweetish odor. The boiling point at 760 mm. pressure is 108–108.3°. The specific gravity at 15°, compared to water at 15°, is 0.6989. The index of refraction $n_D^{25} = 1.3926$, determined with a Pulfrich refractometer.

Second Method.—From the sodium salt of acetoacetic ester and isobutyl iodide ethyl isobutylacetoacetate was made by the method of Conrad.[1] Ethyl isobutylacetoacetate has already been made and described by Rohn[2] and others.[3] The boiling point is 216–8° at 760 mm. pressure. In this research it was not redistilled, but in the crude state was converted into the ketone, 2-methyl-5-hexanone.

2-Methyl-5-hexanone, $CH_3COCH_2CH_2CH(CH_3)_2$.—Ethyl isobutyl acetoacetate was transformed into 2-methyl-5-hexanone by boiling for eight hours with four molecules of caustic potash in 15 per cent. solution. The resulting ketone was distilled with steam, and the upper layer of the distillate separated, dried over calcium chloride and distilled. The boiling point of the first fraction was 143–5°, which on a second distillation became constant at 144° at 760 mm. pressure. This is in agreement with the boiling point observed by Rohn,[4] *viz.*, 142–4° and the corrected boiling point cited in Beilstein's Handbuch,[5] *viz.*, 144°. The purity of the octane to be obtained later in this research depended on the purity of this ketone, and great pains were therefore taken to insure its complete purification.

2,5-Dimethyl-2-hexanol, $(CH_3)_2C(OH)CH_2CH_2CH(CH_3)_2$.—This was prepared from 2-methyl-5-hexanone and methyl magnesium iodide by the Grignard reaction. In a typical experiment 50 grams of methyl iodide mixed with an equal volume of dry ethyl ether were poured over 8 grams of magnesium turnings and after solution of the latter had taken place, 40 grams of 2-methyl-5-hexanone dissolved in 40 grams of dry ether were added in small portions at a time with careful cooling by immersion in a bath of ice water. After standing about half an hour, the reaction mixture was allowed to reach room temperature when the carbinol was set free by the usual procedure of treatment with water and hydrochloric acid. The ether solution of the carbinol was separated from the reaction mixture, dried with potassium carbonate and distilled off, after which the residue was fractionated. Practically all the liquid passed over between 145° and 155° and this portion on two rectifications, boiled at 152–4°, the pressure being 760 mm. This, by its properties and an analysis, was proved to be 2,5-dimethyl-2-hexanol. The yield was essentially quantitative, that is, 44 grams were obtained instead of the 45.6 grams of the theoretical. The boiling point of the carbinol was not as sharp as was desired, but it seems to be characteristic of carbinols to have their boiling point much affected by slight impurities.

Calculated for $C_8H_{18}O$:	C, 73.85; H, 13.85
Found:	C, 73.99; H, 14.05

Properties.—2,5-Dimethyl-2-hexanol is a colorless liquid with an odor like other similar tertiary alcohols of this series, but not otherwise characteristic. It is miscible with the common organic solvents but immiscible with water. The boiling point is 152–4° at 760 mm.

2,5-Dimethyl-2-iodohexane, $(CH_3)_2C(I)CH_2CH_2CH(CH_3)_2$.—Sixty-five grams of 2,5-dimethyl-2-hexanol were mixed with 10 grams of red phosphorus and 64 grams of iodine were added in small quantities at a time, the temperature being maintained below 20°

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

[2] *Ann. Liebig*, **90**, 306.

[3] Mixter, *Ber*, **7**, 501.

[4] *Ann.*, **190**, 308.

[5] Beilstein, Handbuch, 3d Auflage, Bd. I, Seite 1001.

by immersion of the flask in tap water. At the end of an hour the temperature was raised gradually to 80° and kept there four hours. After cooling, the alkyl iodide was washed with water, filtered to remove the excess of red phosphorus and dried over calcium chloride.

Reduction of 2,5-*Dimethyl*-2-*iodohexane.*—The reduction of 2,5-dimethyl-2-iodohexane was attempted by two methods only one of which was successful.

The first procedure was to dissolve magnesium turnings in the octyl iodide in the presence of anhydrous ether and decompose the resulting organomagnesium compound with water. The magnesium dissolved without difficulty in the alkyl iodide and the decomposition with water yielded several products, but no appreciable quantity of octane. Lack of time has so far prevented the careful study of these products, but it is hoped that a study of them may be made in the near future.

The second, and successful, method of reduction was as follows: Fifty grams of the alkyl iodide were poured over 100 grams of finely granulated zinc which had previously been treated with a few cubic centimeters of copper sulphate solution. The flask containing the mixture was connected to a long reflux condenser, through the inner tube of which concentrated (38 per cent.) hydrochloric acid was poured in small quantities at a time, the flask at the same time being gently heated. The reaction evolved considerable heat and the reduction took place rapidly, as shown by a thin floating layer which soon appeared and which grew in thickness until it had finally reached a maximum. This floating layer was principally octane, but a considerable quantity of unchanged octyl iodide was still admixed. To reduce this, small pieces of scrap magnesium were dropped through the condenser tube and since these are light and react very actively they float on the plane of contact of the two layers and reduce the unchanged iodide in the upper layer very effectively. When the chemical action had ceased, the octane was distilled off with steam and the upper layer of the distillate separated, washed with concentrated sulphuric acid, boiled over sodium with a reflux condenser, shaken with potassium permanganate solution, until no decoloration took place, and distilled over sodium again. Two fractionations yielded 11 grams of 2,5-dimethylhexane, boiling at 108.3–108.5° at 760 mm. pressure. The yield was therefore about 45 per cent. of the theoretical.

Calculated for C_8H_{18}:	C, 84.21; H, 15.79
Found:	C, 84.53; H, 15.88

Properties.—This octane is a clear, mobile liquid with a pleasant "rather sweetish" odor and boils at 108.3–108.5°. Its specific gravity at 15°, compared to water at 15°, is 0.6993. Its index of refraction, n_D^{25} = 1.3935.

A comparison of the properties of 2,5-dimethylhexane made by the two methods is given herewith.

	Boiling point (760 mm.).	Density, 15°/15°.	Index of refraction, n_D^{25}.
Method I	108.0–108.3°	0.6989	1.3926
Method II	108.3–108.5°	0.6993	1.3935

It will be seen that these properties are nearly identical. Theoretically, the second method seems to be the better for producing a pure product, and the data therefore, of the hydrocarbon made in that way, are probably more correct. For the production of octane of inferior purity, the Wurtz method is much quicker and simpler.

I am much indebted to Mr. F. A. Barry, who very kindly assisted me in determining the indices of refraction.

I wish also to express my indebtedness to the C. M. Warren Fund, by the aid of which much material was procured for this research.

CAMBRIDGE, MASSACHUSETTS.

[CONTRIBUTIONS FROM THE SHEFFIELD LABORATORY OF YALE UNIVERSITY.]

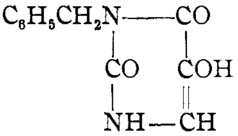
RESEARCHES ON PYRIMIDINES: SYNTHESIS OF 1-METHYL-5-HYDROXYURACIL.

[FORTY-SECOND PAPER.]

BY TREAT B. JOHNSON AND D. BREESE JONES.

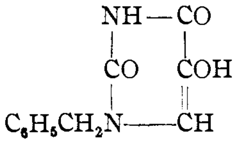
Received March 19, 1909.

In a previous paper from this laboratory, Johnson and McCollum[1] described a new synthesis of 5-hydroxyuracil (isobarbituric acid). They showed that this pyrimidine is formed quantitatively by hydrolysis of 2-ethylmercapto-5-ethoxy-6-oxypyrimidine with hydrochloric acid. In a recent paper, Johnson and Jones[2] have shown that nitrogen-alkyl derivatives of this mercaptopyrimidine can be obtained easily and also undergo hydrolysis, giving nitrogen-alkyl derivatives of 5-hydroxyuracil. They prepared by this method 1- and 3-benzyl-5-hydroxyuracils, I., and II.



$$\begin{array}{rcl} C_6H_5CH_2N & — & CO \\ | & & | \\ CO & & COH \\ | & & \| \\ NH & — & CH \end{array}$$

I.



$$\begin{array}{rcl} NH & — & CO \\ | & & | \\ CO & & COH \\ | & & \| \\ C_6H_5CH_2N & — & CH \end{array}$$

II.

The object of the work described in this paper was to prepare the nitrogen-methyl derivatives of 2-ethylmercapto-5-ethoxy-6-oxypyrimidine[3] and study their behavior on hydrolysis.

5-Hydroxyuracil and nitrogen-alkyl derivatives of this pyrimidine are prepared, according to Behrend's[4] synthesis, by the reduction of 5-nitrouracil and its alkyl derivatives with tin and hydrochloric acid. The only nitrogen-alkyl derivatives of 5-hydroxyuracil that have been synthesized by this method, are methyl-5-hydroxyuracil (methylisobarbituric acid) and ethyl-5-hydroxyuracil (ethylisobarbituric acid). These pyrimidines are incorrectly represented in Beilstein's Handbuch[5] as 1-alkyl pyrimidines III, and IV, and were prepared by Lehmann[6] by reducing methyl- and ethylnitrouracils, to which he assigned, without proof, formulas V, and VI.

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[1] *J. Biol. Chem.*, 1, 437.

[2] *Am. Chem. J.*, 40, 538.

[3] *Loc. cit.*

[4] *Ann.*, 249, 39; *Ibid.*, 251, 239.

[5] Vol. I, 1347, 1348.

[6] *Ann.*, 253, 77.