with potassium hydroxide. It was purified by crystallization from 95% alcohol and melted at 108–109° to a clear oil.

Calculated for $C_{15}H_{14}N_3$: N, 17.56. Found, 17.71.

1,3-Di-p-tolyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_6H_4CH_3)_2$.—From *p*-toluidine and benzoylisocyanchloride. It crystallized from benzene in rhombic prisms, which melted at 190°.

Calculated for $C_{22}H_{21}ON_3$: N, 12.24. Found, 12.40.

Hydrochloride, $C_{22}H_{21}ON_3.2HCl$.—This salt is very soluble in alcohol and crystallizes from benzene in prisms, which melt at 190–191° with decomposition.

Calculated for $C_{22}H_{21}ON_3.2HCl$: N, 10.09. Found, 10.01.

Benzoyltetraphenylguanidine, $C_6H_5CON : C[N(C_6H_5)_2]_2$.—From diphenylamine and benzoylisocyanchloride. This was obtained as a colorless solid which crystallized from 95% alcohol in prismatic crystals. It melted at 142–144°.

Calculated for $C_{32}H_{25}ON_3$: N, 8.99. Found, 8.66.

1,3-Dimethyl-1,3-diphenyl-2-benzoylguanidine, $C_6H_5CON : C[N(CH_3)C_6H_5]_2$.—From monomethylaniline and benzoylisocyanchloride. It crystallized from 95% alcohol in well-developed rhombic prisms, which melted at 135°.

Calculated for $C_{22}H_{21}ON_3$: N, 12.24. Found, 12.00.

1,3-Di-p-anisyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_6H_4OCH_3)_2$.—From paraanisidine and benzoylisocyanchloride. It crystallized from alcohol in needles, which melted at 128° to an oil.

Calculated for $C_{22}H_{21}O_3N_3$: N, 11.20. Found, 11.09.

Di-p-anisylguanidine, $HN : C(NHC_6H_4OCH_3)_2$.—Separated from hot alcohol in flakes, which melted at 153°.

Calculated for $C_{15}H_{17}O_2N_3$: N, 14.91. Found, 14.87.

1,3-Di-β-naphthyl-2-benzoylguanidine, $C_6H_5CON : C(NHC_{10}H_7)_2$.—From β-naphthylamine and benzoylisocyanchloride. This base crystallized from alcohol in prisms, which melted at 162°.

Calculated for $C_{28}H_{21}ON_3$: N, 10.07. Found, 10.04.

Di-β-naphthylguanidine, $HN : C(NHC_{10}H_7)_2$.—A quantitative yield of this guanidine is obtained by hydrolysis of the above benzoyl compound. It melted at 197°, with slight effervescence.

Calculated for $C_{21}H_{17}N_3$: N, 13.50. Found, 13.61.

NEW HAVEN, CONN., Nov. 28, 1911.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

2,2,3-TRIMETHYLPENTANE.

BY LATHAM CLARKE AND WEBSTER NEWTON JONES.

Received December 2, 1911.

The hydrocarbons of the formula C_8H_{18} have been a subject of study in this laboratory for some years,[1] and in furtherance of this study, the synthesis and determination of the properties of 2,2,3-trimethylpentane, $(CH_3)_3CCH(CH_3)CH_2CH_3$, have been taken up. This octane is the first to be made in this laboratory, containing a quaternary carbon atom. But one other octane containing a quaternary carbon atom has hitherto been synthesized and that is 2,2,3,3-tetramethylbutane, or hexamethyl ethane, which contains two quaternary carbon atoms and was prepared by Henry.[2]

The literature records but three other paraffin hydrocarbons, with similar quaternary arrangements, *viz.*, 2,2-dimethylpropane,[3] 3,3-dimethylbutane[4] and 3,3-dimethyl pentane.[5]

Like all the other octanes as yet synthesized in this laboratory, 2,2,3-trimethylpentane is a liquid. It boils at 110.5–110.8° at 760 mm. pressure, and has at 15° the specific gravity 0.7219, compared to water at 15°. Henry's 2,2,3,3-tetramethylbutane was a solid, melting at 103–104° and boiling at 106–107° at 765 mm.

Special Theoretical.

The procedure which seemed most promising for the synthesis of 2,2,3-trimethylpentane and which was successfully carried out was as follows:

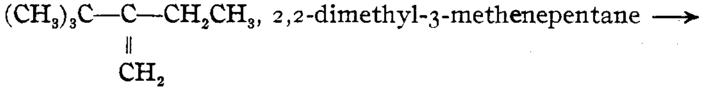
From acetone by reduction, pinacone was formed, and this by boiling with dilute sulfuric acid was rearranged to pinacoline. Since pinacoline is a ketone, it could be made to react with ethyl magnesium bromide producing a tertiary alcohol, 2,2,3-trimethylpentanol-3, which was converted into the corresponding carbinol iodide by means of red phosphorus and iodine. This carbinol iodide readily lost the elements of hydriodic acid on treatment with alcoholic potash, thereby producing 2,2-dimethyl-3-methene pentane, which by passing over finely divided nickel at 160°, in a current of hydrogen, was reduced to the desired octane, 2,2,3-trimethylpentane. These reactions may be summarized as follows:

CH_3COCH_3, acetone $\longrightarrow$ $(CH_3)_2C(OH)C(OH)(CH_3)_2$, pinacone,

$\longrightarrow$ $(CH_3)_3CCOCH_3$, pinacoline $\longrightarrow$

$(CH_3)_3CC(OH)(CH_3)CH_2CH_3$, 2,2,3-trimethylpentanol-3 $\longrightarrow$

$(CH_3)_3CC(I)(CH)CH_2CH_3$, 2,2,3-trimethyl-3-iodopentane $\longrightarrow$



$(CH_3)_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}CH_2CH_3$, 2,2-dimethyl-3-methenepentane $\longrightarrow$

$(CH_3)_3C{-}CH(CH_3)CH_2CH_3$, 2,2,3-trimethylpentane.

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[1] A résumé of the properties of normal octane, the three methylheptanes and the four dimethylhexanes is given in THIS JOURNAL, **33**, 520, *et seq.* The description of another octane, 2-methyl-3-ethylpentane (or the old name, diethylisopropylmethane), not included in the list referred to, may be found as follows: *Am. Chem. J.*, **39**, 574.

[2] *Compt. rend.*, **142**, 1075 (1906).

[3] Lewow, *Z.*, **1870**, 520; **1871**, 257.

[4] Gorianow, *Ann.*, **165**, 107.

[5] Friedel, Ladenburg, *Ann.*, **142**, 310.

Experimental Part.

In this research, acetone was reduced to pinacone by three methods: The first was the old procedure of Friedel and Silva,[1] using sodium in the presence of a strong solution of potassium carbonate, but this is applicable only on a small scale, and gives a small yield, about 10% of the theoretical. The second method was Richard and Langlais' Modification of Couturier and Meunier's process,[2] who employed magnesium amalgam as the reducing agent. This did not prove satisfactory on account of the difficulty of extracting the pinacone at the end of the process, so we took up the method of Holleman,[3] and reduced the acetone with magnesium turnings in the presence of mercuric chloride. The last method was very satisfactory and with certain modifications which we introduced was carried on in the following manner:

One hundred and fifty grams of dry acetone containing 25 grams of mercuric chloride were gradually added to 25 grams of magnesium turnings contained in a liter flask, fitted with a return condenser. After the active reaction which began at first had apparently ceased, the mixture was heated for two hours on the steam bath. The quantitative amount of water (37.5 grams) was then introduced and the heating continued for an hour. An excess of water had to be carefully guarded against, as it formed a sort of emulsion which later prevented the extraction of the pinacone. Next the mixture was treated with 50 cc. of acetone and heated a few moments, then allowed to stand until the precipitate settled, when the supernatant acetone solution of pinacone was decanted, while to the residue fresh acetone was added, heated as before, settled, and the acetone extract once more poured off. This process of extraction was repeated several times or until the acetone extract was no longer colored red.

All the acetone solutions were placed together and fractionally distilled. The portion boiling between 150° and 180° was mixed with water and boiled, then cooled, whereby pinacone hydrate, $C_6H_{14}O_2.6H_2O$, separated out and was recrystallized again from water. Thus the other substances formed in the reduction of the acetone were eliminated by the processes of distillation and crystallization and the pinacone hydrate was obtained in a pure state. The yield of the hydrate was usually 83 grams or 35% of the theoretical figures on the basis of the magnesium.

Pinacoline.—Although various acids may be used for the conversion of pinacone into pinacoline, we found that the most satisfactory was sulfuric acid of a strength of 5%. In a typical experiment, 200 grams of pinacone hydrate were mixed with 350 grams of 5% sulfuric acid and

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[1] *Jarhesb.*, **1873**, 340. Thiele, *Ber.*, **27**, 455, suggests the use of caustic potash in place of potassium carbonate.

[2] *Bull. soc. chim.*, [4] **7**, 454 (1910).

[3] *Rec. trav. chim. Pays-Bas.*, **25**, 206–7.

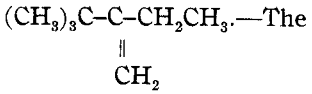
slowly distilled. The pinacoline collected in the receiver as a floating oily layer on the water, and was separated, dried with fused calcium chloride and distilled. The fraction taken for the next reaction boiled at 103–107°. The yield was 84 grams crude pinacoline, corresponding to 95% of the theoretical.

2,2,3-Trimethylpentanol-3, $(CH_3)_3CC(OH)(CH_3)CH_2CH_3$.—This carbinol containing eight atoms of carbon was prepared from pinacoline, by the Barbier-Grignard reaction, using ethyl magnesium bromide. In a typical experiment, 18 grams of magnesium turnings were dissolved in 82 grams of ethyl bromide which had previously been diluted with an equal volume of anhydrous ether. To the solution, 50 grams of pinacoline, diluted with one volume of ether, were added and the mixture was allowed to stand two hours before decomposing in the usual manner with water and hydrochloric acid. The ether layer was removed and dried over potassium carbonate, after which the ether was distilled off, and the residue subjected to fractional distillation. After four fractionations, 34 grams of a liquid were obtained, boiling at 149–152° at 760 mm. pressure. This was 2,2,3-trimethylpentanol-3.

Calculated for $C_8H_{18}O$: C, 73.85; H, 13.60.
Found: C, 74.14; H, 13.85.

Properties: Colorless liquid boiling at 149–152° at 760 mm. pressure. It has an odor quite like that of camphor. It is immiscible with water but miscible with the common organic solvents.

2,2,3-Trimethyl-3-iodopentane, $(CH_3)_3C(I)(CH_3)CH_2CH_3$.—In each experiment, 50 grams of 2,2,3-trimethyl-3-pentanol were mixed with 8 grams of red phosphorus and treated with 60 grams of iodine in small portions at a time, the temperature being maintained below 20°. At the end of an hour, the temperature was raised to 70°, at which point it was held 4 hours. After cooling, the mixture was filtered through glass wool to remove red phosphorus, washed with cold water and converted without further purification into the octylene.



2,2-Dimethyl-3-methenepentane, $(CH_3)_3C{-}\underset{\underset{CH_2}{\|}}{C}{-}CH_2CH_3$.—The octyl iodide of the preceding paragraph was converted into 2,2-dimethyl-3-methenepentane by the following procedure: One hundred and seventy-three grams of octyl iodide were treated on a sand bath for four hours with a solution of 120 grams of potassium hydroxide in 600 cc. of alcohol. By replacing the return condenser with an ordinary condenser, the alcohol was distilled off and carried with it the octylene. Although the octylene boils slightly above 110°, with alcohol it forms a soluble binary mixture boiling at about 80°. By dilution of the alcohol with water, the octylene separated as a floating layer, which was removed and dried over calcium chloride. The yield of crude octylene was 67 grams. This was fractionally distilled and finally yielded 25 grams of octylene boiling at 110.4–110.8° at 760 mm. pressure.

Calculated for C_8H_{16}: C, 85.71; H, 14.29.
Found: C, 85.49; 85.00; 84.72; H, 13.27; 13.50; 14.40.

Properties: Colorless, mobile liquid with a faint musty odor. Boiling point, 110.4–110.8° at 760 mm. pressure. It is not miscible with water, but mixes fairly readily with the common organic solvents.

2,2,3-Trimethylpentane, $(CH_3)_3CH(CH_2)CH_2CH_3$. — The octylene was reduced to the octane by Bedford's modification of Sabatier and Senderens' method,[1] by the action of hydrogen and pure nickel at 160–180°. From 12 grams of octylene, 8 grams of octane were obtained, boiling at 110.5–110.8° at 760 mm. pressure.

Calculated for C_8H_{18}: C, 84.21; H, 15.79.
Found: C, 84.56; 84.63; 83.64; H, 15.69; 15.60; 15.88.

Properties: Colorless, very mobile liquid, with a very faint odor. Boiling point, 110.5–110.8° at 760 mm. pressure. The specific gravity at 15° compared to water at 15° is 0.7219. The index of refraction was determined with a fine Pulfrich refractometer. N_D (25°) = 1.4164.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

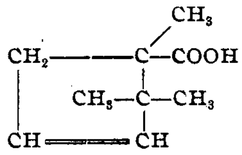
MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. IX. LAURONOLIC ACID AND CAMPHOLACTONE.[2]

BY WILLIAM A. NOYES AND CHARLES E. BURKE.

Received June 26, 1911.

Two unsaturated acids derived from camphor, having the formula $C_8H_{13}COOH$, and having the carboxyl group in the tertiary position are known.

One of these has been isolated by Bredt[3] and since on oxidation it gives camphoronic acid he has given to it the structure



The other acid was first studied by Fittig and Woringer.[4] It has been obtained in two ways: first, by the decomposition of bromo-camphoric acid anhydride by boiling with water or with dilute alkali; second, by the

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[1] The exact process is described by Clarke and Beggs in THIS JOURNAL, 34, 59.

[2] Abstract of a thesis presented by Charles E. Burke in partial fulfilment of the requirement for the degree of Doctor of Philosophy at the University of Illinois.

[3] *Ber.*, **35**, 1286.

[4] *Ann.*, **227**, 6.