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.

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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 isobutyl-ketone 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

of the formula $CH_3CH_2CH_2C{=}CH_2CH(CH_3)_2$, which is 4-methene-2-methylheptane. By reduction of the nonylene, the saturated octane would be produced. We found, however, that when normal propyl magnesium iodide reacted with the above mentioned ketone, the product was the *desired nonylene*, evidently formed from the carbinol, to be expected, by the elimination of one molecule of water. The actual reactions therefore involved in the synthesis of 2,4-dimethylheptane were those of the following summary:

$CH_3COCH[CH(CH_3)_2]CO_2C_2H_5$, Ethyl isopropylacetoacetate $\longrightarrow$
$CH_3COCH_2CH(CH_3)_2$, 2-Methyl-4-pentanone + $CH_3CH_2CH_2MgI$ $\longrightarrow$
$CH_3CH_2CH_2C{=}CH_2CH(CH_3)_2$, 2-Methene-4-methylheptane $\longrightarrow$
$CH_3CH_2CH_2CH(CH_3)CH_2CH(CH_3)_2$, or 2,4-Dimethylheptane.

The peculiar reaction above noted, where a tertiary alcohol formed in a Barbier-Grignard reaction splits off water to form an unsaturated compound, has not been recorded before in the purely aliphatic series so far as we can find, although cases are known among the aromatic-aliphatic series.[1]

Owing to the lack of time the exact constitution of the nonylene was not determined, but it was almost surely that of the ascribed formula. The only thing in doubt, however, is the position of the double bond and this does not affect the constitution of the nonane, as the double bond is saturated in the next step.

Experimental Part.

Methyl isobutyl ketone, $CH_3COCH_2CH(CH_3)_2$, was obtained from isopropyl acetacetic ester by boiling for eight hours with a 10% solution of caustic potash. The ketone was then distilled off with steam, washed with water, dried over calcium chloride and fractionated. From two hundred grams of ester seventy grams of ketone were obtained, boiling at 114–115°.

The nonylene, 2-methene-4-methylheptane, was made from the ketone by treating with an excess of normal propyl magnesium iodide. Twenty-four grams of magnesium were dissolved in 171 grams of normal propyl iodide which had been mixed with an equal volume of ether and 70 grams of the ketone diluted with an equal volume of ether were then added slowly and the whole warmed on a steam bath for two hours. The reaction product was decomposed in the usual manner with ice water and finally with dilute hydrochloric acid. The ether solution was separated

[1] Grignard and Tissier, *Compt. rend.*, 132, 1182 (1901).

and dried over potassium carbonate, the ether was then distilled off and the residue consisting of the nonylene fractionated. The yield was twenty grams of hydrocarbon boiling at 132–133°.

Calculated for C_9H_{18}: C, 85.71; H, 14.29
Found: C, 85.29; H, 14.22.

Properties: Colorless liquid boiling at 132–133°.

Miscible with all the common organic solvents. Immiscible with water. Decolorizes bromine in chloroform solution. It has an odor like that of petroleum.

2,4-Dimethylheptane, $CH_3CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}HCH\underset{\displaystyle CH_3}{\underset{|}{C}}HCH_3$, was made from the nonylene by reducing it by Sabatier and Senderens' method of passing the vapor of the nonylene with an excess of hydrogen over freshly reduced nickel at 160–180°, after the manner of the reduction of 2-methyl-5-metheneheptane to 2,5-dimethylheptane described in the preceding paper. The nonane was then carefully fractionated with a fifth degree thermometer until five grams were obtained boiling at 132.9–133°.

Calculated for C_9H_{20}: C, 84.37; H, 15.63
Found: C, 84.28; H, 15.92

Properties: Colorless liquid boiling at 132.9–133° at 752 millimeters pressure. It is miscible in the common organic solvents. Does not decolorize bromine in chloroform. Odor of petroleum. Sp. gr. is 0.7206 at 15° compared to water at 15°. The index of refraction was determined with a Pulfrich refractometer N_D (25°) = 1.4014.

CAMBRIDGE, MASS.,
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS.]

MOLECULAR REARRANGEMENTS IN THE CAMPHOR SERIES. VIII. CAMPHONOLIC ACID AND CAMPHONOLOLACTONE.

BY WILLIAM A. NOYES, E. E. GORSLINE AND R. S. POTTER.

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Three lactones are known which correspond to three hydroxy acids which retain the tertiary carboxyl of camphoric acid. These are:

1. Campholactone, obtained by Fitting and Woringer[1] in distilling lauronolic acid and formed when lauronolic acid is warmed with dilute acids.

2. Isocampholactone, first obtained in an impure condition by one of us[2] in decomposing aminolauronic acid,

[1] *Ann.*, **227**, 10.
[2] *Am. Chem. J.*, **17**, 432; **32**, 290.