

	Average values for original primary active amyl alcohol to make the		Average values for regenerated primary active amyl alcohol obtained from the	
	Chloride	Bromide	Chloride	Bromide
B. p., °C. (20 mm.)	50.1	50.1	50.1	50.1
$n_D^{20}$	1.4109	1.4109	1.4109	1.4109
$d_4^{20}$	0.81876	0.81846	0.81842	0.81829
$d_4$	0.813 <sup>27.5</sup>	0.813 <sup>27.5</sup>	0.796 <sup>26</sup>	0.795 <sup>27</sup>
$\alpha_D$	-4.8 <sup>27.5</sup>	-4.8 <sup>27.5</sup>	-4.28 <sup>26</sup>	-4.48 <sup>27</sup>
$[\alpha]_D$	-5.9 <sup>27.5</sup>	-5.9 <sup>27.5</sup>	-5.38 <sup>26</sup>	-5.63 <sup>27</sup>

magnesium iodide and one mole of the ester in 500 cc. of ether for two weeks gave 126.5 g. of crude iodide and much resin formation. Fractionation of the crude product gave 17.5% of primary active amyl iodide, b. p. (Cottrell) 47.1° (20 mm.),  $n_D^{20}$  1.4969,  $d_4^{20}$  1.5227,  $[\alpha]_D^{20}$  +4.84°.

**Regeneration of Primary Active Amyl Alcohol from the Corresponding Chloride and Bromide.**—The primary active amyl chloride and bromide were converted into the Grignard compounds in 83 and 76% yields, respectively. Treatment of the Grignard compounds with oxygen at 0° and decomposition of the complex with water regenerated the primary active amyl alcohol. A comparison of the constants for the regenerated alcohol with those of the original alcohol is given.

A similar attempt to regenerate the active alcohol from primary active amyl iodide failed.

### Summary

1. The preparation and physical constants of the primary active amyl chloride, bromide and iodide are reported.

2. Primary active amyl alcohol can be regenerated from the corresponding chloride or bromide by conversion to the Grignard compound and treatment with oxygen. The iodide cannot be used for the conversion.

3. The total racemization in the steps alcohol → bromide or chloride → Grignard reagent → alcohol is not over 10%.

STATE COLLEGE, PENNA.

RECEIVED JULY 11, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

## The Nonanes. 2-Methyloctane, 3-Ethylheptane, 2,3-Dimethylheptane and 2,2,4,4-Tetramethylpentane<sup>1</sup>

BY FRANK C. WHITMORE AND HARRIET A. SOUTHGATE

The present work was undertaken because of the interest in this Laboratory in petroleum hydrocarbons, in rearrangements in the aliphatic series, in the limitations of typical aliphatic reactions and in the relation of structure to physical properties of aliphatic compounds.

Theoretically, thirty-five structurally isomeric nonanes are possible. Twelve were known when the present work was started, namely, *n*-nonane, the three monomethyloctanes, 2,4-, 2,5-, 2,6- and 3,3-dimethylheptanes, 4-ethylheptane, 2,3,5- and 2,2,5-trimethylhexanes, and 3,3-diethylpentane. The scattered and incomplete data on the physical properties of these eleven nonanes indicate that regularities exist similar to those found in the hexanes, heptanes and octanes.

Three new nonanes, 3-ethylheptane, 2,3-dimethylheptane and the most highly branched nonane, 2,2,4,4-tetramethylpentane, have been synthesized in the present study. Since the data

on 2-methyloctane are meager,<sup>2</sup> this compound also was prepared.

The 2,2,4,4-tetramethylpentane was obtained in poor yield from 2,2,4-trimethyl-4-bromopentane or the corresponding chloride with dimethylzinc. The main course of the latter reaction involved the removal of halogen acid to form the known diisobutylenes. This agrees with results obtained by S. N. Wrenn of this Laboratory on the action of a variety of alkaline agents with these halides. The other three nonanes were obtained by dehydration of the tertiary alcohols, 2-methyl-2-octanol, 3-ethyl-3-heptanol, and 2,3-dimethyl-3-heptanol by Hibbert's<sup>3</sup> iodine method and hydrogenating the olefin mixtures at high pressure using a nickel catalyst supported on alumina.

The reactions involved in these syntheses are not ones which are accompanied by rearrange-

(2) Späth, *Monatsh.*, **34**, 1965 (1913); Richards and Shipley, *This Journal*, **41**, 2002 (1919); Dobjranski and Chessin, *Chem. Zentr.*, **101**, I, 2662 (1930).

(3) Hibbert, *This Journal*, **37**, 1748 (1915).

(1) Original manuscript received April 23, 1934.

ments. The physical constants recorded for the four nonanes indicate a high degree of purity. It is interesting that the most highly branched nonane boils lower than *n*-octane.

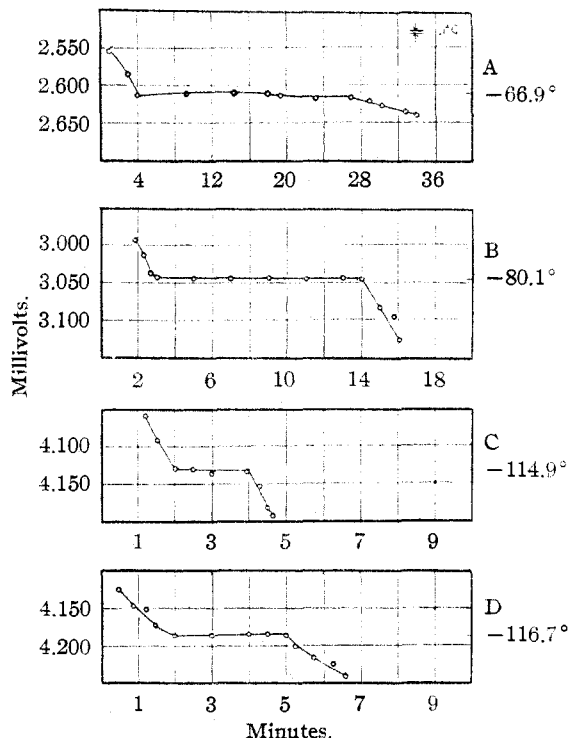


Fig. 1.—A. Freezing curve of 2,2,4,4-tetramethylpentane: cooling medium, carbon dioxide + acetone; B, C, D. Freezing curves of 2-methyloctane, 3-methylheptane, and 2,3-dimethylheptane: cooling medium, liquid air.

### Experimental

**Dimethylhexylcarbinol.**—Methyl hexyl ketone, b. p. 169.9–171.5° (735 mm.),  $n_D^{20}$  1.4150, was prepared in 26–32% yield by dehydrogenation with a copper catalyst of capryl alcohol supplied by the Röhm and Haas Company of Philadelphia. It was treated in 2-mole lots with methylmagnesium chloride solution in the usual way. The product was fractionated under reduced pressure through a 43 × 1.4 cm. column of the usual type used in this Laboratory. The dimethylhexylcarbinol, b. p. 82–85° (20 mm.),  $n_D^{20}$  1.427, was obtained in 85% yield.

**Methylisopropyl-*n*-butylcarbinol.**—Methyl isopropyl ketone, b. p. 93–95° (732 mm.), prepared from *t*-amyl alcohol<sup>4</sup> supplied by the Sharples Solvents Corporation of Philadelphia was treated in 3-mole lots with *n*-butylmagnesium bromide as usual. The methylisopropyl-*n*-butylcarbinol, b. p. 75–78° (16 mm.),  $n_D^{20}$  1.4355, was obtained in 65% yield.

**Diethyl-*n*-butylcarbinol.**—Diethylcarbinol, b. p. 113–118° (732 mm.), was oxidized by chromic acid mixture to diethyl ketone, b. p. 102–105°, in 65% yield. Diethyl ketone in a 4-mole lot was treated as usual with *n*-butyl-

magnesium bromide. The yield of diethyl-*n*-butylcarbinol, b. p. 95–97° (36 mm.), was 67%.

**Dehydration of the Carbinols.**—This was done by refluxing with a trace of iodine. The olefins were dried with anhydrous copper sulfate, refluxed over sodium and fractionated. Dehydration of 260 g. of 2-methyl-2-octanol gave 165 g. of olefins, b. p. 144.5–146° (722 mm.),  $n_D^{20}$  1.4223; 360 g. of 3-ethyl-3-heptanol gave 242 g. of olefins b. p. 137.5° (734 mm.), 1.4261; 319 g. of 2,3-dimethyl-3-heptanol gave 181 g., b. p. 135–140° (735 mm.), 1.4237–1.4252. Hydrogenation using a nickel catalyst on activated alumina and hydrogen under pressure gave the corresponding hydrocarbons in 98–100% yield.

**2,2,4,4-Tetramethylpentane.**—Dimethylzinc was prepared in 82–100% yields in lots up to 4 moles.<sup>5</sup> 2,2,4-Trimethyl-4-bromopentane, b. p. 75° (36 mm.),  $n_D^{20}$  1.455, was prepared by saturating a diisobutylene fraction of  $n_D^{20}$  1.4085 with dry hydrogen bromide at 15°.<sup>6</sup> Removal of excess hydrogen bromide was found to be essential. This was done by cooling the mixture and applying reduced pressure and by passing carbon dioxide through the mixture. The corresponding chloride has been obtained by heating diisobutylene with fuming hydrochloric acid in sealed tubes at 105°<sup>7</sup> and by simply saturating diisobutylene with hydrogen chloride at 15°. The 2,2,4-trimethyl-4-chloropentane, b. p. 53° (29 mm.),  $n_D^{20}$  1.431 was obtained in 75% yield.

Dimethylzinc was treated in an atmosphere of carbon dioxide with 2,2,4-trimethyl-4-chloropentane or the corresponding bromide. The chloro compound gave better results. During ten hours 408 g. (2.8 moles) of the chloride was added to a stirred solution of 147 g. (1.55 moles titrated) of dimethylzinc in 150 cc. of dry tetralin in a 3-necked flask provided with a dropping funnel, condenser, and mercury-seal stirrer. The temperature was maintained at 40°. Precipitation started almost immediately and rendered stirring difficult. After standing overnight the mixture was acidified with hydrochloric acid. The organic layer was washed with sodium bicarbonate solution and dried with 10 g. of calcium chloride. Fractionation through the 43 × 1.4 cm. column yielded mainly diisobutylenes formed by the removal of hydrochloric acid from the chloride, a small amount of higher polyisobutylenes and a yield of 18% (average of many runs) of the crude 2,2,4,4-tetramethylpentane, b. p. 120–125° (730 mm.),  $n_D^{20}$  1.408.

**Purification of the Nonanes.**—Each of the four nonanes was shaken with successive one-tenth volume portions of concentrated sulfuric acid until a fresh portion showed no color. All acid was removed by washing with sodium bicarbonate solution and then with water. After drying over calcium chloride the product was fractionated.

**Measurement of Physical Properties.**—A Valentine No. 451 refractometer was used for determining the refractive indices. The temperature was controlled to 0.1°.

Boiling points were measured with a Cottrell type boiling point apparatus. The temperature was read by means of a copper-copel thermocouple checked against a

(5) Lachman, *Am. Chem. J.*, **19**, 410 (1897); Noller, *This Journal*, **51**, 494 (1929); Renshaw, *ibid.*, **42**, 1472 (1920).

(6) Tongberg, *et al.*, *ibid.* **54**, 3708 (1932).

(7) Butlerow, *Ann.*, **189**, 44 (1877); Kondakow, *J. prakt. Chem.*, [2] **54**, 449 (1897).

(4) Whitmore, Evers and Rothrock, *Org. Syntheses*, **13**, 68 (1933).

TABLE I  
 SUMMARY OF PHYSICAL PROPERTIES

Nonane	F. p., °C.	B. p. (760 m.) °C.	B. p. °C.	Mm.	$n_{20}^D$	$d_{20}^{25}$	Viscosity	
							37.8° poises	100° × 10
2-Methyloctane	-80.1	142.80	141.65	727.5	1.40285	0.7107	5.25	2.79
2,3-Dimethylheptane	(-116.7)	140.65	139.05	728.0	1.40850	.7235	5.21	3.30
	glass	initial	initial					
3-Ethylheptane	glass (-114.9)	143.10	142.10	738.5	1.40900	.7260	4.90	2.61
2,2,4,4-Tetramethylpentane	-66.9	122.30	121.30	738.5	1.40695	.7185	6.80	3.39
	to -67.1							

Bureau of Standards couple and also checked at the boiling points of *n*-hexane, *n*-heptane, water, 2,2,4-trimethylpentane, naphthalene and toluene. Boiling points recorded represent the boiling point when 50% of the sample had been removed.

The freezing points were determined with samples of about 20 cc. of the nonane placed in a glass-jacketed test-tube which was lowered into a Dewar flask containing a mixture of carbon dioxide snow and acetone or liquid air. The sample was stirred vigorously and the temperature determined every twenty to thirty seconds by means of a chromel-copel thermocouple<sup>8</sup> and a Leeds Northrup Port-

(8) Tongberg, Pickens, Fenske and Whitmore, *THIS JOURNAL*, **54**, 3706 (1932).

able, Double Range Potentiometer. The cooling curves are given in Fig. 1.

Densities and viscosities were determined by W. A. Herbst of this Laboratory.

### Summary

2-Methyloctane and three new nonanes, 2,3-dimethylheptane, 3-ethyloctane and 2,2,4,4-tetramethylpentane have been prepared.

Boiling point, index of refraction, density, freezing curves and viscosity have been determined for the four nonanes.

STATE COLLEGE, PENNA. RECEIVED AUGUST 15, 1938

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

## A New Synthesis of Tertiary Hydrocarbons

BY FRANK C. WHITMORE AND H. PHILIP OREM

The general method of preparation of saturated aliphatic hydrocarbons involves the hydrogenation of an olefin formed by dehydration of the corresponding alcohol or by removal of halogen acid from the alkyl halide.<sup>1</sup> Other methods, such as the hydrolysis of the Grignard reagent and the reduction of the halide with "nascent" hydrogen<sup>2</sup> have been used.

Levene<sup>3</sup> prepared hexadecane from cetyl iodide by adding zinc dust to the iodide and passing in dry hydrogen chloride with heating for several hours. In the present study, a modification of this method has been applied to tertiary iodides. Five tertiary aliphatic hydrocarbons have been prepared from their corresponding tertiary alcohols by the modified method. This offers a new and simple method of preparing branched-chain hydrocarbons from tertiary alcohols.

(1) Edgar, Calingaert and Marker, *THIS JOURNAL*, **51**, 1483 (1929); Calingaert and Soroos, *ibid.*, **58**, 635 (1936).

(2) Clarke, *ibid.*, **30**, 1147 (1908); **31**, 589 (1909).

(3) Levene and West, *J. Biol. Chem.*, **20**, 523 (1915).

### Experimental

**Preparation of the Alcohols.**—Four of the alcohols were prepared from Grignard reagent and ketone; the other from Grignard reagent and acid chloride.

**Preparation and Purification of the Hydrocarbons.**—The hydrocarbons were prepared by treating the tertiary alcohols with dry hydrogen iodide<sup>4</sup> until one and one-half times the theoretical quantity of hydrogen iodide had been added. Then zinc dust (Baker c. p. 95%) was added in small quantities until reaction ceased. The mixture was then stirred and dry hydrogen chloride was passed in with the addition of more zinc until four times the theoretical quantity was added. The flask was heated to 70–80° with stirring and the addition of hydrogen chloride for approximately ten hours for each half mole of alcohol used. Water was then added slowly to give equal volumes of water and reaction product in the flask. The hydrocarbon was steam distilled and separated from the water layer.

The hydrocarbon was purified by washing with 70% (by weight) sulfuric acid until only a pale yellow color remained, then with 85% sulfuric acid, and finally with concentrated sulfuric acid until little color appeared upon adding fresh acid. The product was then washed once

(4) Kastle and Bullock, *THIS JOURNAL*, **18**, 109 (1896).