TABLE I

SUMMARY OF PHYSICAL PROPERTIES

Nonane	F. p., °C.	B. p. (760 mm.) °C.	B. p. °C.	Mm.	$n^{20°}D$	$d^{20}{}_4$	Viscosity 37.8° poises × 10	100°
2-Methyloctane	−80.1	142.80	141.65	727.5	1.40285	0.7107	5.25	2.79
2,3-Dimethylheptane	(−116.7) glass	140.65 initial	139.05 initial	728.0	1.40850	.7235	5.21	3.30
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 to −67.1	122.30	121.30	738.5	1.40695	.7185	6.80	3.39

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[8] and a Leeds Northrup Portable, 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

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

[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.[1] Other methods, such as the hydrolysis of the Grignard reagent and the reduction of the halide with "nascent" hydrogen[2] have been used.

Levene[3] 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.

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[4] 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

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[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).

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

Carbinols	$n^{20}D$	d^{20}_4	Reaction		Yield, %
2-Methylhexanol-2	1.4186	0.8146	BuMgBr	Me_2CO[a]	80
2-Methyloctanol-2	1.4280	.8210	MeMgCl	Me-*n*-hexyl ketone	74
3-Ethylheptanol-3	1.4360	.8429	EtMgBr	*n*-Valeryl chloride[b]	66
3-Methylnonanol-3	1.4358	.8311	EtMgBr	Me-*n*-hexyl ketone	76
4-Methyldecanol-4	1.4375	.8296	PrMgBr	Me-*n*-hexyl ketone	56

[a] Acetone was purified by fractional distillation from solid potassium permanganate and freshly prepared calcium oxide.

[b] *n*-Valeryl chloride (b. p. 126° (730 mm.); $n^{20}D$ 1.4200) was prepared from the acid by treatment with thionyl chloride in 84% yield. The valeric acid (b. p. 86° (18 mm.), $n^{20}D$ 1.4080) was prepared in 81% yield by treating *n*-butylmagnesium bromide with carbon dioxide. The flask containing the Grignard reagent was cooled to 0°, solid lumps of carbon dioxide were dropped into the solution and the material allowed to stand overnight. Secondary and tertiary alcohols may be formed if the addition of carbon dioxide gas is slow. Gilman, *Rec. trav. chim.*, **49**, 1172 (1930).

PROPERTIES OF THE HYDROCARBONS

Hydrocarbons	B. p. °C.	Mm.	B. p. °C.[a]	Mm.	d^{20}_4	$n^{20}D$	F. p., °C.	Yield, %
2-Methylhexane	89.1	735	90.3	760	0.6794	1.3851	−120.3	23.7
2-Methyloctane	141.6	736	142.8	760	.7132	1.4030	[b]	48.8
3-Ethylheptane	141.9	736	143.1	760	.7272	1.4090	[b]	38.3
3-Methylnonane	166.3	732	167.6	760	.7319	1.4123	−90.0	30.1
4-Methyldecane	186.8	739	188.1	760	.7422	1.4177	−92.9	27.8

[a] The boiling points were taken at 760 mm. with a Cottrell b. p. apparatus and a barostat.

[b] Refer to Frank C. Whitmore and H. A. Southgate, THIS JOURNAL, **60**, 2571 (1938).

with water, twice with 25% sodium hydroxide solution, and dried over sodium. It was carefully fractionated[5] from sodium–potassium alloy, washed with concentrated sulfuric acid, water, 25% sodium hydroxide, dried over sodium, and refractionated from sodium–potassium alloy to give a constant index material that gave no halide test with copper wire and no olefin test with bromine in carbon tetrachloride.

Summary

A new synthesis of tertiary hydrocarbons has been described, and applied to five aliphatic hydro carbons.

STATE COLLEGE, PENNA. RECEIVED AUGUST 16, 1938

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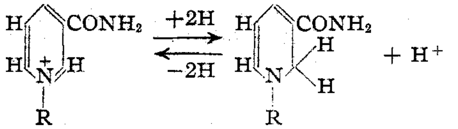
(5) Whitmore and Lux, THIS JOURNAL, **54**, 3451 (1932).

[CONTRIBUTION FROM THE BIOLOGICAL INSTITUTE OF THE CARLSBERG FOUNDATION, COPENHAGEN]

Hydrogenation of Vitamin B_1 and Other Quaternary Thiazoles[1]

BY FRITZ LIPMANN AND GERTY PERLMANN

Dehydrogenation of various substrates in the cell is effected by quaternary pyridine compounds—nicotinic acid derivatives[2,3]—acting as hydrogen-transporting systems between the respective substrates and other hydrogen carriers.[2,4] The catalytic action of these pyridinium compounds is due to alternate hydrogenation and dehydrogenation at the double bond adjoining the quaternary nitrogen.



(1)

The action of vitamin B_1 (which hereafter in this paper will be referred to as "thiamin") as codehydrase for pyruvic acid dehydrogenation was made highly probable by the work of Peters and co-workers[5] with avitaminotic tissues (see also Lipmann[6]). Using the pyruvic acid dehydrogenase of *Bacterium Delbrückii*, the codehydrase function of thiamin—as thiamin pyrophosphate, Lohmann's cocarboxylase[7]—could be shown definitely.[8]

The presence of a quaternary thiazole in thiamin,[9] the well-known similarity between thiazoles and pyridines together with the codehydrase function of thiamin suggested a similar mode of action for the pyridine and thiazole codehydrases.

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(1) This investigation was supported by a grant from the Ella Sachs Plotz Foundation.

(2) (a) O. Warburg and W. Christian, *Biochem. Z.*, **287**, 291 (1936); (b) O. Warburg, *Ergebnisse Enzymforschung.*, **7**, 210 (1938).

(3) P. Karrer, G. Schwarzenbach, F. Benz and U. Solmsson, *Helv. Chim. Acta*, **19**, 811 (1936).

(4) H. v. Euler, *Ergebnisse Physiol.*, **38**, 1 (1936).

(5) R. A. Peters, *Biochem. J.*, **31**, 2240 (1937).

(6) F. Lipmann, *Skand. Arch. Physiol.*, **76**, 255 (1937).

(7) K. Lohmann and P. Schuster, *Biochem. Z.*, **294**, 188 (1937).

(8) F. Lipmann, *Enzymologia*, **4**, 65 (1937).

(9) R. R. Williams and A. E. Ruehle, THIS JOURNAL, **57**, 1856 (1935).