U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1306

Part of Journal of Research of the National Bureau of Standards, Volume 24, June 1940

PREPARATION AND SOME PHYSICAL PROPERTIES OF 2,2,4,4-TETRAMETHYLPENTANE

By Frank L. Howard

ABSTRACT

Over 2 liters of purified 2,2,4,4-tetramethylpentane was prepared synthetically. Physical constants determined on the purest fraction included freezing point, boiling point and its variation with pressure, and refractive index and density and their variations with temperature.

CONTENTS

I. INTRODUCTION

In connection with an investigation of paraffin hydrocarbons being conducted by the National Bureau of Standards for the National Advisory Committee for Aeronautics, the Navy Bureau of Aeronautics, and the Army Air Corps, 2,2,4,4-tetramethylpentane was prepared synthetically, and was purified by fractional distillation in an automatically controlled 6-m helix-packed column.

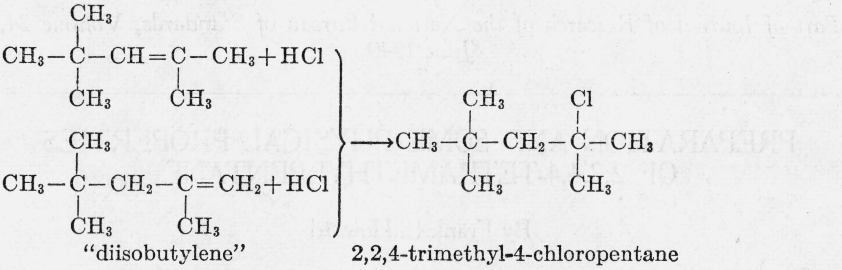
II. PREPARATION OF 2,2,4,4-TETRAMETHYLPENTANE

The method of Whitmore and Southgate [1][1] was used to prepare 2,2,4,4-tetramethylpentane and consists in reacting dimethyl zinc with 2,2,4-trimethyl 4-chloropentane. The yield was increased and the various manipulations were expedited by certain alterations in the procedure, which is therefore given in full.

---

[1] Figures in brackets refer to the literature references at the end of this paper.

The reactions involved are shown in the following diagram:

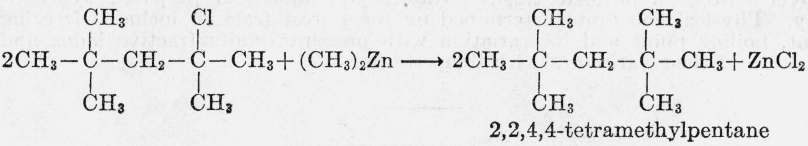


$$\left.\begin{array}{l}\mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH{=}\underset{CH_3}{\underset{|}{C}}{-}CH_3+HCl} \\[2ex] \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_2{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2+HCl}\end{array}\right\}\longrightarrow \mathrm{CH_3{-}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_2{-}\underset{CH_3}{\overset{Cl}{\overset{|}{\underset{|}{C}}}}{-}CH_3}$$

"diisobutylene" 2,2,4-trimethyl-4-chloropentane

$Zn\ (Cu)_x + CH_3I \longrightarrow CH_3ZnI$

$2CH_3ZnI \longrightarrow (CH_3)_2Zn + ZnI_2$



$$\mathrm{2CH_3{-}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_2{-}\underset{CH_3}{\overset{Cl}{\overset{|}{\underset{|}{C}}}}{-}CH_3+(CH_3)_2Zn\longrightarrow 2CH_3{-}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_2{-}\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}{-}CH_3+ZnCl_2}$$

2,2,4,4-tetramethylpentane

1. 2,2,4-TRIMETHYL-4-CHLOROPENTANE

This compound was prepared by the action of hydrogen chloride on "diisobutylene." The apparatus is shown in figure 1. The two tubes (*C* and *D*) were filled with glass helices admixed with fused zinc chloride. Diisobutylene from a 500-ml separatory funnel (*A*) was added to a stream of dry hydrogen chloride, through *B*, which flowed

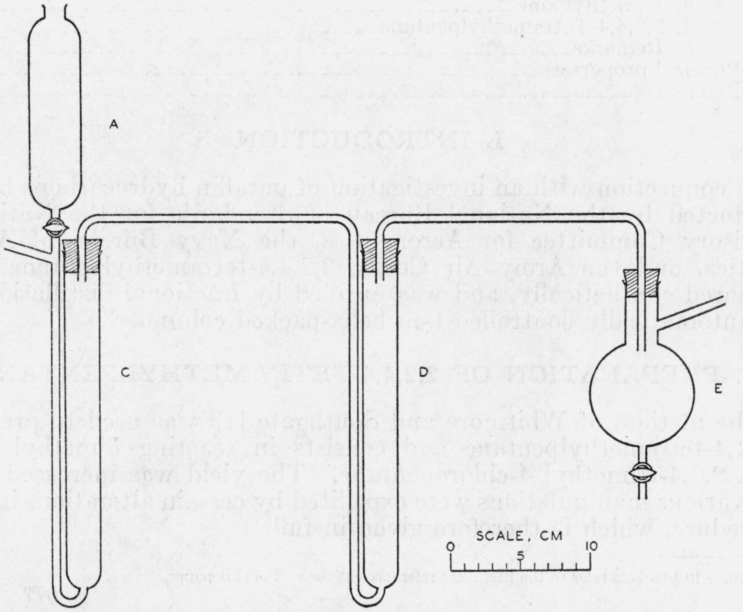


FIGURE 1.—*Apparatus used in the preparation of 2,2,4-trimethyl-4-chloropentane.*

to the bottom of the first test tube. The resulting liquid plus gas was forced from the top of the first test tube into the bottom of the second. The product from this second reaction chamber flowed from the top and collected in a separatory funnel (*E*) from which the slight excess of hydrogen chloride was allowed to flow through *F* to a suitable absorber. The two chambers were immersed in a bath of chloroform-carbon tetrachloride, kept between −20° and −25° C by addition of carbon dioxide.

The product was the same as that formed by saturating diisobutylene with hydrogen chloride at 0° C in the absence of a catalyst, but was formed about 12 to 15 times as fast by the technique described. The absorption of hydrogen chloride was much faster at lower temperatures, but the apparatus became clogged with crystalline product.

The melting point of nearly pure alkyl chloride was found to be −26° C, whereas the product from the reactor melted around −30° C. The melting point was raised when the product was purified by crystallization, and excess hydrogen chloride removed by bubbling carbon dioxide through the liquid at 0° C. It was not distilled (save for a small sample), because of the ease with which it decomposed to hydrogen chloride and the corresponding olefins.

2. ZINC-COPPER COUPLE

An intimate mixture of 480 g of technical zinc dust and 60 g of cupric oxide, reagent quality, was introduced into a 150- by 2.7-cm Pyrex tube placed horizontally and plugged with asbestos 15 cm from one end, and was spread evenly in the bottom half of the tube with a scraper. A loose plug of asbestos was inserted into the tube, and a stream of hydrogen, washed with sulfuric acid, was introduced. After the tube was thoroughly swept with hydrogen, it was placed in a 15-in. tube furnace. Heating was started first at the hydrogen-entrance end of the tube, where, after 5 to 10 min, reduction became apparent. The furnace temperature at this time was in the vicinity of 550° C. The tube was left in its original position until minute shining pellets were imbedded in the metal. Then the tube was moved so that the next section of zinc-copper oxide mixture was heated. At this time a faint red glow was observed to progress along the mixture, leaving in its wake a matrix of pellets of very small size, while the upper part of the tube became clouded with a film of condensed zinc. Overheating, evidenced by a yellow to green color, was avoided by moving the tube steadily through the furnace, so that the glow caused by reduction remained in the forward half of the furnace. Overheating caused the pellets to sinter together and resulted in a less active couple. When all the material was reduced and the water driven from the tube, the latter was allowed to cool. The product was removed and used as soon as possible. The entire process consumed about a half hour. Throughout the reduction, hydrogen was passed through the tube at about 40 to 50 ml/min.

3. DIMETHYL ZINC

Two batches of zinc-copper alloy, together with 500 ml (8 moles) of methyl iodide, were placed in a 2-liter round-bottom flask (fig. 2, *A*). The flask was fitted with a cork, through which a hole was bored at 30°

to the vertical. Through the hole was inserted the end of a 40-cm condenser (*B*) which was bent through 90°. The other end of the condenser was fitted with a 120° bend, on which was placed a No. 14 cork, ready for insertion into a side neck of a 5-liter 3-necked flask. By rotating the 2-liter flask and stopper about the vertical axis, the condenser could be lowered for downward distillation. To the upper end of the condenser was attached, beyond the cork, a short rubber tube carrying a T-tube (*C*). The other two sides of the T were connected to a source of carbon dioxide, and to a mercury trap, through 70 cm of Pyrex tubing. All the corks in this apparatus were select, tight-fitting, and well shellacked.

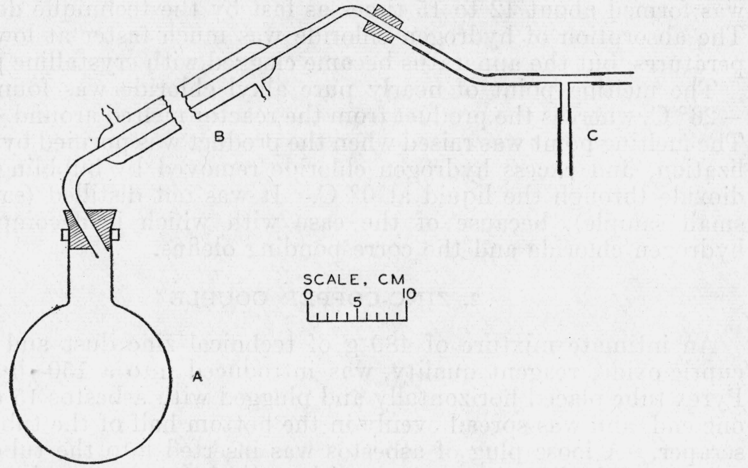


Figure 2.—*Apparatus used in the preparation of dimethyl zinc.*

The rubber tube connecting the T-tube with the carbon dioxide supply was closed with a screw clamp. The flask was warmed in an oil bath at 60° C until reaction started, which was evidenced by an increase in reflux rate, then the flame was removed from the bath. Reflux continued smoothly for 24 to 36 hr, after which the flask was again heated at 60° C until reflux ceased (2 to 7 hr) and then allowed to cool. After the flask had cooled, the screw clamp on the carbon dioxide line was opened and the system was filled with carbon dioxide. Then the rubber connection was removed from the end of the condenser and a small cork placed in the opening. Dimethyl zinc was distilled immediately from this apparatus directly into the vessel used for the next step in this synthesis.

A 5-liter 3-necked flask was fitted with a mercury-sealed stirrer and a reflux condenser. The top of the condenser was fitted with a T-tube, one arm of which was connected to a vent, the other arm to a cylinder of carbon dioxide. A slow stream of carbon dioxide was passed across this T to prevent air being sucked back into the flask. Five-hundred millimeters of dry tetrahydronaphthalene (tetralin) was placed in the flask, after which it was swept thoroughly with carbon dioxide.

The condenser on the dimethyl zinc apparatus was lowered, the small cork in the end of the condenser quickly removed, and the end of the condenser inserted into the free neck of the 5-liter flask.

The oil bath was heated to about 90° C, which caused a steady distillation of dimethyl zinc. The temperature was then gradually raised to 200° C and held there as long as distillation took place. When all the dimethyl zinc was distilled, the oil bath was removed, the flask allowed to cool, and the condenser raised. A cork carrying a separatory funnel was quickly placed in the small neck which held the condenser. This operation of removing the condenser and inserting the separatory funnel was carried out while a steady stream of carbon dioxide was played on the apparatus.

4. 2,2,4,4-TETRAMETHYLPENTANE

The 5-liter flask assembly was placed in a small galvanized tub. Water was added until the flask was half immersed. Cooling was effected by conducting water at 5° C through 25 feet of 5/16-inch copper tubing made into a coil around the flask.

The stirrer was started and a mixture of 1,500 ml of tetralin and 1,190 g (8 moles) of 2,2,4-trimethyl-4-chloropentane added to the dimethyl zinc already in the flask, during 6 to 8 hours, with the bath temperature kept below 7° C. After about one-fourth of the alkyl chloride was added, crystals of zinc chloride began to form. As addition was continued, the reaction mixture attained the appearance of a creamy sludge. No difficulty was encountered in stirring, unless the alkyl chloride was added too fast, which caused the formation of curds. When all the alkyl chloride had been added, the mixture was allowed to stand overnight in the cold bath. Then 500 ml of water was added, followed by 500 ml of 15-percent hydrochloric acid. A very clean, uncolored organic layer was thereby obtained.

This layer was separated, washed with water, then with 5-percent aqueous sodium bicarbonate, followed by three more washings with water. It was then dried over calcium chloride and distilled through a 150-by 2-cm helix-packed column [2]. After a forerun of diisobutylene (150 to 450 ml), there was obtained 595 to 687 ml of crude 2,2,4,4-tetramethylpentane (boiling range 119° to 124° C). This is equivalent to a yield of 42 to 48 percent, based on the amount of methyl iodide. Whitmore and Southgate [1] reported a yield of 18 percent.

Twenty-eight hundred milliliters of crude 2,2,4,4-tetramethylpentane prepared as described above was purified by subjecting it to the following treatment: Ten washings with concentrated sulfuric acid; two washings with water; one washing with 5-percent aqueous sodium bicarbonate; one washing with water, drying with calcium chloride, refluxing over sodium, distillation, passing through a column (100 by 2 cm) of silica gel; five washings with sulfuric acid; one washing with water; one washing of bicarbonate; one washing with water, drying with calcium chloride, refluxing over sodium, and distillation through a 150-by 2-cm column [2]. The fraction which boiled at 122° to 123° C was collected, and amounted to 2,210 ml. This purified material was distilled in an automatically controlled helix-packed column in the manner briefly described earlier [3]. The data on the distillation are given in table 1.

TABLE 1.—*Data on distillation of 2,2,4,4-tetramethylpentane*

Fraction number	Reflux time	n_D^{20} (uncorrected)
	hr.	
1	19.0	1.4067
2	21.5	1.4068
3	33.5	1.4067
4	11.5	1.4068
5	26.0	1.4068
6	24.0	1.4066
7	6.0	1.4066
8	6.0	1.4065
9	6.0	1.4067
10	6.0	1.4067
11	12.0	1.4067
12	12.0	1.4067
13	6.0	1.4067
14	6.0	1.4068
15	4.0	1.4067
16	4.0	1.4069
17	4.0	1.4068
18	12.0	1.4069
19	0.3	1.4067
20	.3	1.4069
21	.3	1.4069
22	.2	1.4068
23	.2	1.4066
24	.1	1.4069
25	.1	1.4069
26	.1	1.4069
27	.1	1.4070
28	.1	1.4071
29	.1	1.4085

5. REMARKS

An attempt was made to prepare dimethyl zinc by conducting methyl chloride over the zinc-copper alloy in the same tube in which the alloy was made. Some dimethyl zinc formed, but the reaction was slow and difficulty was experienced in getting reaction below the surface of the metal. It is the opinion of the author that a satisfactory method could be devised to carry out this reaction.

An attempt was made to prepare 2,2,4,4-tetramethylpentane by the action of 2,2,4-trimethyl-4-chloropentane on the mixture of methyl aluminum chlorides obtained by the action of methyl chloride on duralumin turnings. The addition was carried out at a bath temperature of −40° C, with carbon bisulfide as a solvent. The mixture was decomposed by adding dilute hydrochloric acid at −30° C, and worked up in the usual manner.

The product was distilled in a 10- by 900-mm column packed with glass helices [2]. The temperature steadily rose during distillation, and four fractions were obtained. the data being given in table 2. All the fractions had the very disagreeable odor of sulfur-containing compounds. The results indicate that there was probably considerable rearrangement and polymerization, due to the aluminum chloride by-product of the reaction, along with interaction with the solvent.

TABLE 2.—*Distillation data on products from methyl aluminum chlorides and 2, 2, 4-trimethyl 4-chloropentane*

Fraction	Boiling range	n_D^{20}	Volume
	°*C*		*ml*
1	up to 82	1. 55351	70
2	82 to 120	1. 40407	10
3	120 to 136	1. 40835	10
4	136 to 161	1. 41880	15
5 res			90

Only one trial was made; but the reaction may be worth while, if the proper choice of solvent, time of reaction, temperature, and concentrations are found.

III. PHYSICAL PROPERTIES

Fractions 12, 13, and 14 were combined, and physical properties were determined on this material by the methods described in previous papers [3 and 4]. The distillation curve, figure 3, shows the material to be of high purity. The data plotted in figure 4 were obtained by slowly cooling the solution until crystallization occurred, then slowly warming it until liquefaction was complete. The average of the temperatures at *A* and *B* is taken as the initial freezing point ("liquidus temperature"). The difference between *A* or *B* and the liquidus temperature, amounting to a few thousandths of a degree, is believed to result from the influence of external environment on the reading of the thermometer.

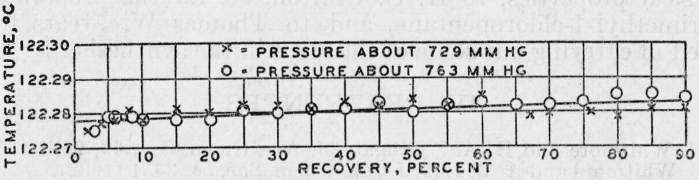


FIGURE 3.—*Distillation curve of 2,2,4,4-tetramethylpentane.*

Points represent values measured at the pressures indicated, and corrected to 760 mm Hg.

Table 3 shows the data obtained on all the physical constants determined, together with those obtained by Whitmore and Southgate [1]

TABLE 3.—*Properties of 2,2,4,4-tetramethylpentane*

Reference	Freezing point	Boiling point at 760 mm Hg	$\frac{dT}{dP}$	Refractive index		$\frac{dn}{dt}$	Density		$\frac{d\rho}{dT}$
				n_D^{20}	n_D^{25}		ρ^{20}	ρ^{25}	
	°*C*	°*C*	*deg/mm* Hg			*per deg*	*g/ml*	*g/ml*	*g/ml deg*
Whitmore and Southgate [1]	−66.9 to −67.1	122. 30		1. 40695			0. 7185		
Present work [a]	−66. 600	122. 281	0. 0492	1. 40677	1. 40451	−0. 000453	. 71957	0. 71566	−0. 000782

[a] The uncertainty of each value is believed not to exceed a few units in the last decimal place given.

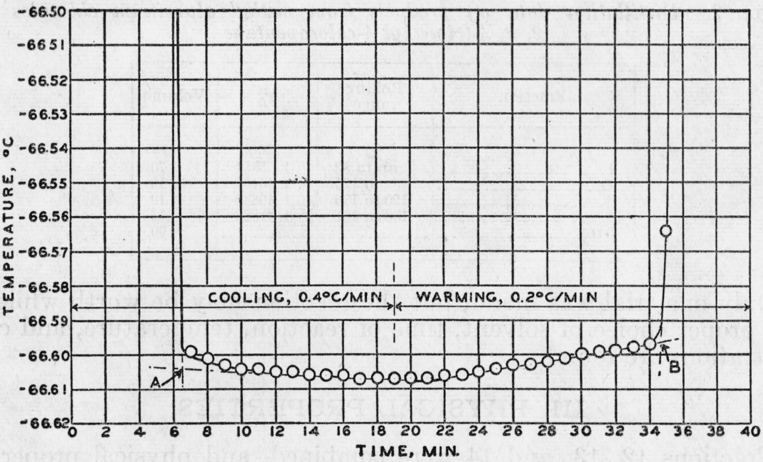


FIGURE 4.—*Freezing and melting curves of 2,2,4,4-tetramethylpentane.*

The author is indebted to Donald B. Brooks for the determination of physical properties, to H. C. Crafton, Jr. for the preparation of 2,2,4-trimethyl-4-chloropentane, and to Thomas W. Mears for aid rendered in carrying out some of the steps in the synthesis.

IV. REFERENCES

[1] F. C. Whitmore and H. A. Southgate, J. Am. Chem. Soc. **60**, 2571 (1938).
[2] F. C. Whitmore and A. R. Lux, J. Am. Chem. Soc. **54**, 3451 (1932).
[3] Donald B. Brooks, Frank L. Howard, and Hugh C. Crafton, Jr., J. Research NBS **23**, 637 (1939) RP1259.
[4] Donald B. Brooks, Frank L. Howard, and Hugh C. Crafton, Jr., J. Research NBS **24**, 33 (1940) RP1271.

WASHINGTON, March 29, 1940.