

tributed therefore to factors such as the strengthening of the O-C linkage when it becomes oxygen-phenyl. This conclusion<sup>4</sup> is supported by the following observations.

The hydrolyzable O-C link in benzyl-glycosides is quantitatively cleaved to toluene and reducing sugar by hydrogenation with palladium as catalyst under very mild conditions<sup>10</sup> which produce no detectable cleavage of the phenylglucosides. Also, hydriodic acid quantitatively cleaves phenyl-alkyl-ethers into *alkyl* iodide and phenol through scission of the oxygen-*alkyl* rather than the oxygen-phenyl link. The relative strengths of the oxygen-alkyl and oxygen-phenyl links in glycosides is probably of the same order of magnitude as in phenyl-alkyl ethers and may be responsible also for the unusual alkaline cleavage of phenyl-glycosides to glycosans.<sup>11</sup>

### Summary

1. The copper reduction method of Shaffer, Hartman and Somogyi was used to follow the hydrolyses by aqueous hydrochloric acid of initially 0.01 molar solutions of the glycosides identified in the title. The fructosides were hydrolyzed in 0.01 *N* HCl at 15 to 60° and the glucosides in 0.1 *N* HCl at 45 to 96°.

2. The dependences of the first order rate constants,  $k^* = k_{\text{obs}}/(\text{HCl})$ , upon temperature are given within the limits of error by the equation  $\log k^* = \log a^* - b/T$  where  $a^*$  and  $b$  are con-

(10) N. K. Richtmyer, *THIS JOURNAL*, **56**, 1633 (1934).

(11) E. M. Montgomery, N. K. Richtmyer and C. S. Hudson, *ibid.*, **55**, 1848 (1943).

stants. The activation energies are greatest for the glycosides which hydrolyze slowest.

3. A constant difference of  $5.8 \pm 0.5$  kcal./mole exists between the activation energies of gluco- and fructo-pyranosides of *opposite* glycosidic configuration whereas no obvious relationship exists between pairs of the same configuration. The significance of this fact is discussed.

4. Among methyl- and benzyl-glucopyranosides, the activation energy required is greater for  $\alpha$  than  $\beta$  forms, but the reverse is the case among phenyl-glucopyranosides and methyl-fructopyranosides.

5. The activation energies in both the  $\alpha$  and  $\beta$  series of gluco- and fructo-pyranosides decrease in the order methyl, benzyl, phenyl and the same order represents the increase in the rates of hydrolyses.

6. The ratio,  $2.3b/\log a^*$ , equals  $934 \pm 5$  for methyl- and benzyl-, and  $879 \pm 11$  for phenyl-glucopyranosides,  $758 \pm 8$  for methyl- and benzyl-fructopyranosides, and 734 for a methyl-fructofuranoside. The constancy of this ratio within a group enables one to calculate the activation energy and the rate of hydrolysis at any reasonable temperature of a glycoside whose rate of hydrolysis has been determined at but a single temperature provided that the value of  $2.3b/\log a^*$  is known for some glycoside in its group.

7. The activation energies, the ratios,  $2.3b/\log a^*$ , and the relative rates of hydrolyses depend primarily upon the structure of the sugar residue rather than, as in the photochemical hydrolyses, upon the structure of the aglycone

CAMBRIDGE, MASS.

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[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE ETHYL CORPORATION]

## Hexamethylethane<sup>1</sup>

BY GEORGE CALINGAERT, HAROLD SOROOS, VINCENT HNIZDA AND HYMIN SHAPIRO

Hexamethylethane has long attracted the attention of chemists and physicists because of its unusually branched and symmetrical structure, and the effect of this structure on its physical properties. This branched octane melts above 100°, or 157° above the normal isomer, and as high as hexacantane (C<sub>60</sub>H<sub>122</sub>), while retaining the volatility to be expected of its low molecular weight.

While there have been a number of publications of its preparation<sup>2</sup> and properties,<sup>3</sup> only one of

(1) Presented before the Organic Division of the American Chemical Society at Cleveland, Ohio, April 6, 1944.

(2) (a) Krakau (report of Chrapowicki's work), *Bull. soc. chim.*, **35**, 165 (1881); (b) Henry, *Comp. rend.*, **142**, 1075 (1906), *Bull. Acad. roy. Belg.*, Cl. sci., 256 (1906); 352 (1906); *Rec. trav. chim.*, **26**, 84 (1907); **26**, 106 (1907); (c) Richards, *Ann. chim. phys.*, **21**, 323 (1910); (d) Whitmore, Stehman and Herndon, *THIS JOURNAL*, **55**, 3807 (1933); (e) Flood and Calingaert, *ibid.*, **56**, 1211 (1934); (f) Marker and Oakwood, *ibid.*, **60**, 2598 (1938); (g) Greenwood, Whitmore and Crooks, *ibid.*, **60**, 2028 (1938); (h) Whitmore and Wheeler, *ibid.*, **60**, 2899 (1938).

(3) (a) Brackett, *Proc. Natl. Acad. Sci.*, **14**, 857 (1928); (b) Parks

these<sup>4</sup> has reported data on samples of known high purity. This leaves considerable doubt as to its exact physical properties, especially since the melting point reported by Henry,<sup>2b</sup> 103-104°,

and Todd, *Ind. Eng. Chem.*, **21**, 1235 (1929); (c) Parks, Huffman and Thomas, *THIS JOURNAL*, **52**, 1032 (1930); (d) Linder, *J. Phys. Chem.*, **35**, 532 (1931); (e) Lovell, Campbell and Boyd, *Ind. Eng. Chem.*, **23**, 26 (1931); (f) West, *Z. Krist.*, **88**, 195 (1934); (g) Hoog, Smittenberg and Visser, *Congrès Mondial du Pétrol*, Paris, June (1937); (h) Calingaert and Soroos, *J. Org. Chem.*, **2**, 535 (1938); (i) Maman, *Comp. rend.*, **207**, 1401 (1938); (j) Smittenberg, Hoog and Henkes, *THIS JOURNAL*, **60**, 17 (1938); (k) Lambert and Lecomte, *Ann. phys.*, **10**, 503 (1938); (l) Smittenberg, Hoog, Moerbeek and Zijden, *J. Inst. Pet.*, **26**, 294 (1940); (m) Maman, *Chimie et industrie*, **44**, 299 (1940); (n) Whitmore, Marker and Plambeck, *THIS JOURNAL*, **63**, 1626 (1941); (o) Day and Pease, *ibid.*, **63**, 912 (1941); (p) Bauer and Beach, *ibid.*, **64**, 1142 (1942).

(4) Whitmore, Marker and Plambeck<sup>2a</sup> report the melting point and boiling point of material which they estimated had a purity of above 99.4 mole per cent., based upon the melting point range of 250 to 300 milligram samples of every fourth sample of fifty fractions obtained by fractional distillation.

has never been observed by others.<sup>6</sup> The melting point values were also, with one possible exception,<sup>6</sup> as far as could be ascertained, based on observations in capillary tubes, and not on freezing curves, and therefore gave little or no indication of the purity of the samples.

This Laboratory has made several attempts in recent years to prepare a sample of hexamethylethane of known high purity. In a first attempt, the material prepared by condensation of *t*-butyl chloride with *t*-butylmagnesium chloride,<sup>2c</sup> and which was found to contain as an impurity 2,2,4-trimethylpentane, was recrystallized both from its melt and from solvents; the products obtained still failed to melt higher than 101.4°, as against Henry's 103–104°, and did not, in capillary tubes, melt over less than a one-half degree range. It was thought that the hydrocarbon impurity could not be removed satisfactorily by crystallization, and a new batch of hexamethylethane was prepared by the condensation of methylmagnesium chloride with 2,3,3-trimethyl-2-chlorobutane, which method would not be expected to give any hydrocarbon boiling within 20° of hexamethylethane. After chemical treatment for removal of alkyl halides and alcohols, followed by distillation, a product was obtained which did not differ significantly from that prepared by the previous method.

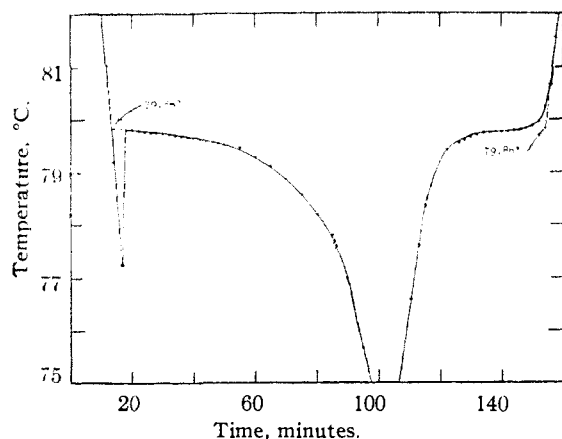


Fig. 1.—Time-temperature freezing and melting curves for naphthalene.

It was then decided to subject the latter material to fractional distillation. Because the boiling point of the compound is only a few degrees above its melting point, this could not be accomplished efficiently in stills of the conventional types. A

(5) The value of 104° reported by Parks, Huffman and Thomas<sup>1c</sup> was not a determination, but a quotation of Henry's value (private communication).

(6) Smittenberg, Hoog and Henkes<sup>1d</sup> describe the method of obtaining freezing and melting curves on a large number of hydrocarbons which included hexamethylethane, but do not show curves for the latter. They report for the compound a melting point of 101.2° and a freezing point of 101.5°, and state that the hydrocarbon froze without supercooling but did not give a horizontal freezing plateau under the conditions employed.

still was therefore designed which could be operated at 900 mm. pressure, at which pressure hexamethylethane boils at 113°. In order to avoid the elaborate equipment which would be necessary to withdraw the distillate as a liquid, the principle used was that of total reflux-intermittent take-off, in which a receiver of the size of the desired fraction overflows continuously into the column. When equilibrium has been reached, the fraction is removed, and distillation is continued in the same manner. In the case of hexamethylethane it was necessary to cool the sample before removing it. Consequently, it was possible to obtain a freezing curve on each fraction as it cooled in the receiver.

More precise freezing curves were then obtained for two of the best cuts. Here also it was necessary to design special equipment because of the high vapor pressure of hexamethylethane at its melting point. The samples were contained in sealed glass ampoules with a thin thermocouple well, and agitation during freezing or melting was obtained by vigorous up and down shaking of the ampoules in the cooling medium. The adequacy of the method was tested by determining the freezing point of a sample of naphthalene as shown in Fig. 1. Cooling and melting curves on the best samples of hexamethylethane were then obtained, as shown in Fig. 2. The best sample showed a

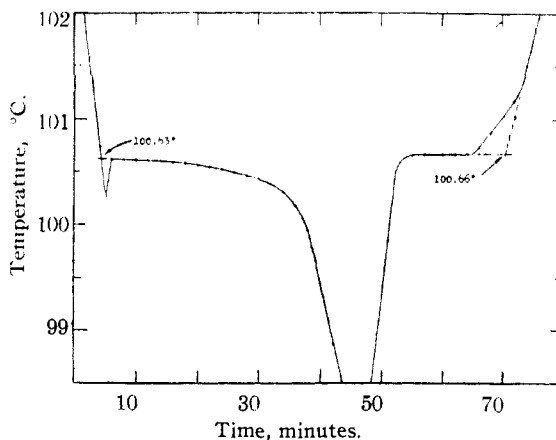


Fig. 2.—Time-temperature freezing and melting curves for hexamethylethane (Fraction 5).

freezing point of 100.63° and a freezing point lowering when one-half frozen of 0.06°. With the usual reservation of the impurity being liquid-soluble and solid-insoluble, this gave a freezing point for pure hexamethylethane of 100.69°. From these data and the heat of fusion determined by Parks and Todd,<sup>3b</sup> the purity of the sample was calculated to be 99.96 ± 0.04%.

The vapor pressure of the purified hydrocarbon over the temperature range 0 to 110° was determined by measuring the difference in pressure exerted by the hydrocarbon and water in a Bremer-Frowein tensimeter.<sup>7</sup> From the data ob-

(7) Frowein, *Z. physik. Chem.*, 1, 5 (1887).

tained, given in Table I, were derived (by methods to be published) the following expressions for the vapor pressure of liquid and solid hexamethylethane.

$$\begin{aligned} \text{Solid: } \log P(\text{mm.}) &= 7.78882 - 1625.7/(t + 226) \\ \text{Liquid: } \log P(\text{mm.}) &= 6.87665 - 1327.8/(t + 226) \end{aligned}$$

Intersection of the solid and liquid range equations gave  $100.58^\circ$  for the melting point, in excellent agreement with the experimentally measured value,  $100.60^\circ$ , for the same material. The calculated boiling point is  $106.30 \pm 0.02^\circ$ . The heats of fusion, vaporization, and sublimation, computed at the melting point using the Clausius-

Clapeyron equation and reasonable  $P$ - $V$ - $T$  estimations, are 1700, 7550 and 9250 cal./g. mole, respectively. The calculated heat of vaporization at the boiling point is 7530 cal./g. mole, and the calculated heat of sublimation at  $25^\circ$  is 10,470 cal./g. mole. The accuracy of these five figures is estimated to be about  $\pm 2\%$ . The calculated heat of fusion is in excellent agreement with the calorimetric measurements of Parks and Todd,<sup>3b</sup>  $1700 \pm 2\%$ , and the heat of sublimation at  $25^\circ$  is also in good agreement with the calorimetric measurements of Osborne and Ginnings,<sup>8</sup>  $10,239 \pm 2\%$ .

Determinations of the density and refractive index of solid hexamethylethane gave the values:  $d^{25}_4$  0.823 g./ml., and  $n^{20}_D$  1.4695.

TABLE I  
VAPOR PRESSURE OF HEXAMETHYLETHANE

	Temp., °C.	Vapor pressure, mm.		Devn. <sup>c</sup>
		Obsd. <sup>a</sup>	Calcd. <sup>b</sup>	
Solid	3.30	6.3	4.9	+0.1
	4.89	7.0	5.6	0.0
	5.88	7.4	6.0	0.0
	9.87	9.2	7.8	+0.1
	10.87	9.8	8.4	0.0
	14.88	12.3	10.9	+0.1
	15.89	13.0	11.6	+0.1
	19.90	16.4	14.9	+0.1
	20.90	17.4	15.9	+0.1
	24.91	21.9	20.4	0.0
	25.91	23.2	21.7	-0.1
	30.02	29.3	27.8	-0.3
	34.90	37.7	36.2	-0.1
	39.98	49.1	47.5	0.0
	44.88	62.9	61.3	0.0
	49.99	81.0	79.4	-0.2
	54.88	102.0	100.3	-0.1
	59.97	128.8	127.1	-0.1
	59.97	128.7	127.0	0.0
	64.87	160.1	158.4	0.0
69.98	199.5	197.6	+0.2	
79.96	300.6	298.8	0.0	
90.03	443.1	441.3	0.0	
95.00	531.9	530.1	0.0	
97.99	591.8	589.9	+0.4	
98.98	613.2	611.3	+0.1	
98.98	613.2	611.3	+0.1	
98.98	613.4	611.5	-0.1	
99.48	623.9	622.0	+0.3	
99.78	631.0	629.1	-0.1	
100.00	635.6	633.7	+0.2	
100.02	636.2	634.3	0.0	
100.03	636.5	634.6	0.0	
Solid	100.03	636.5	634.6	0.0
	101.05	657.4	655.5	+0.2
Liquid	102.03	676.4	674.5	-0.2
	104.03	715.2	713.3	+0.2
	106.07	757.2	755.3	0.0
	106.07	757.2	755.3	0.0
	108.08	799.8	797.9	+0.4
	109.57	833.7	831.8	-0.4

<sup>a</sup> Corrected for inert gas by subtracting 0.0050  $T$  mm. from observed pressures. <sup>b</sup> Calculated using the Antoine equations given in the text. <sup>c</sup> Deviation of calculated values from corrected pressures

## Discussion

The value obtained for the freezing point of hexamethylethane in the present work is slightly lower than the best values reported by others.<sup>2e,3j,3n</sup> This is probably attributable to the difference in methods used. Melting point values for this hydrocarbon obtained by determinations in capillary tubes without stirring are likely to be high and show a melting range, unless the temperature of the bath is raised at a very slow rate. Thus it was found that in order to obtain by the capillary tube method the value observed by the freezing curve method, it was necessary to increase the temperature of the bath at a rate not greater than  $0.1^\circ$  per four minutes. Such variations in the melting point of other hydrocarbons by the capillary tube method, depending on the rate of heating and the personal equation, have also been observed by others.<sup>9</sup>

**Acknowledgment.**—The authors wish to acknowledge the assistance of Mr. George W. Thomson in the calculations of the vapor pressure equations and the thermal properties of hexamethylethane.

## Experimental

### Preparation of Hexamethylethane

**2,3,3-Trimethylbutanol-2.**<sup>10</sup>—In a typical preparation of this alcohol, an ether solution of *t*-butylmagnesium chloride prepared from 97 g. (4.0 g. atoms) of magnesium turnings, 380 g. (4.1 moles) of redistilled *t*-butyl chloride, and 1000 ml. of anhydrous ether, in accordance with the procedure of Whitmore and Badertscher,<sup>11</sup> and contained in a 5-liter 3-neck flask fitted with a reflux condenser and vapor-proof mechanical stirrer,<sup>12</sup> was carbonated by the method of Gilman, St. John and Schulze.<sup>13</sup> To the reaction mixture, after it had stood overnight and the excess carbon dioxide had been distilled by heating and stirring, was added over a period of one to two hours an ether solution of methylmagnesium chloride prepared from 195

(8) Private communication.

(9) Piper, *et al.*, *Biochem. J.*, **25**, 2072 (1931); Seyer, Patterson and Keays, *THIS JOURNAL*, **66**, 179 (1944).

(10) The method used for the preparation of this alcohol was suggested by Dr. A. L. Henne.

(11) Whitmore and Badertscher, *THIS JOURNAL*, **55**, 1559 (1933).

(12) Calingaert, *Ind. Eng. Chem., Anal. Ed.*, **12**, 51 (1940).

(13) "Organic Syntheses," Vol. XI, John Wiley and Sons, Inc., New York, N. Y., 1931, p. 81.

g. (8.0 g. atoms) of magnesium turnings, an excess of methyl chloride, and 2000 ml. of anhydrous ether. The heat generated during the addition was dissipated by the application of a cold water-bath. When the addition was completed, the mixture was stirred and refluxed for two hours, and then allowed to stand at room temperature overnight. The reaction mixture was hydrolyzed by the addition of 6 *N* hydrochloric acid, the ether layer was separated, and the aqueous layer was extracted three times with small portions of ether. The ether solutions were combined and dried over anhydrous sodium carbonate. After filtration, the solvent was removed by distillation, and the residue of crude 2,3,3-trimethylbutanol-2, without further purification, was converted to the corresponding alkyl chloride as described below.

**2,3,3-Trimethyl-2-chlorobutane.**—The crude alcohol from each of four preparations was shaken with 400 ml. of concentrated hydrochloric acid, fortified after reaction had ceased by the addition of hydrogen chloride gas. Some additional alkyl chloride was thus precipitated. After the reaction was over, the precipitated alkyl chloride was taken up in ether, shaken with 5% sodium carbonate solution, and dried over anhydrous sodium carbonate. The ether was then removed by distillation at room temperature, and the residue of crude alkyl chloride was dried by pumping with a vacuum pump. In the latter operation a wide-bore dry-ice trap was inserted between the product flask and pump to condense the portion of the highly volatile product which would otherwise be lost. The yield of crude 2,3,3-trimethyl-2-chlorobutane from four 4-mole preparations was 1012 g., or 47% based on the magnesium used in the preparation of the *t*-butylmagnesium chloride for preparation of the alcohol.

The crude product was purified by recrystallization from

methyl alcohol. In a typical experiment, 255 g. of the crude alkyl chloride was dissolved in 1000 ml. of redistilled methyl alcohol at 55°, and the solution was filtered hot and cooled to -25°. The solid was filtered on a cold Büchner funnel and dried by pumping with a vacuum pump as described above. The yield of recrystallized alkyl chloride was 198 g., or 78%. The chloride was found to sublime between 128 and 134° in a capillary tube.

**Interaction of 2,3,3-Trimethyl-2-chlorobutane with Methylmagnesium Chloride.**—To each of two preparations of methylmagnesium chloride from 85 g. (3.5 g. atoms) of magnesium, excess methyl chloride, and 875 ml. of anhydrous ether, contained in a 5-liter 3-neck flask fitted with a reflux condenser, vapor-proof mechanical stirrer, and dropping funnel, was added 269 g. (2.0 moles) of recrystallized 2,3,3-trimethyl-2-chlorobutane dissolved in enough ether to make 865 ml. of solution. After starting the reaction at room temperature with only a small amount of the halide solution, a cold water-bath at 20° was placed around the flask, and the remainder of the halide solution was added slowly over a period of four hours. The reaction mixtures were allowed to stand at room temperature for one week, during which time slow evolution of gas occurred and two immiscible layers formed. After the standing period, the reaction mixtures were hydrolyzed by the addition of 6 *N* hydrochloric acid, the ether layers were separated, and the aqueous layers were extracted twice with small portions of ether. The ether solutions from the two runs were combined, dried over anhydrous sodium carbonate and filtered. After removal of the ether by distillation through an 80-cm. column, the residue was distilled through a 30-cm. column, the delivery tube of which was heated electrically by a nichrome wire winding. The yield of crude hexamethylethane, b. p. 95-107°, was 221 g., or 48%<sup>14</sup> based on the 2,3,3-trimethyl-2-chlorobutane.

To the crude product was added 48 g. of material from previous preparations by the same method, and the combined material was dissolved in 1250 ml. of redistilled *n*-pentane. This solution was refluxed with 5% potassium hydroxide solution, shaken four times with concentrated sulfuric acid, washed with 5% sodium bicarbonate solution and dried over anhydrous sodium carbonate. After distillation of most of the solvent and refluxing over sodium-potassium alloy, the residue was distilled from fresh sodium-potassium alloy through the 30-cm. column described above. This yielded 212 g. of material distilling at 92 to 107° (mainly at 102 to 104°), or 79% of the crude product. The distilled product was subjected to fractional distillation as described below.

**Fractional Distillation of Hexamethylethane.**—The pressure still used for the fractional distillation of hexamethylethane is illustrated in Fig. 3.

The still pot consisted of a 500-ml. Pyrex flask A, to the bottom of which was sealed a mercury manometer tube C. Tungsten wire contacts B in the manometer tube, the upper one of which could be adjusted to the desired height, were connected to an electrical circuit consisting of a mercury relay, an electrical resistance, and the heater on the still pot. The heater consisted of electrical resistance wire imbedded in a spherical shell of Hytempite which fitted around the bottom half of the still pot. The manometer arrangement not only served to maintain the heat input and the pressure in the still within narrow limits, but also acted as a safety valve in the event the pressure within the still rose to an unsafe value.

The column itself was a 36-inch section of 5/8-inch Ewell-Lecky column,<sup>15</sup> sealed directly to the still pot. The column was surrounded by a heating jacket of 1-inch glass tubing wound with nichrome resistance wire, and an outer jacket of 1.5-inch glass tubing. Thermocouple leads placed at various points within the heating jacket were used for measuring the temperature of the column. Elec-

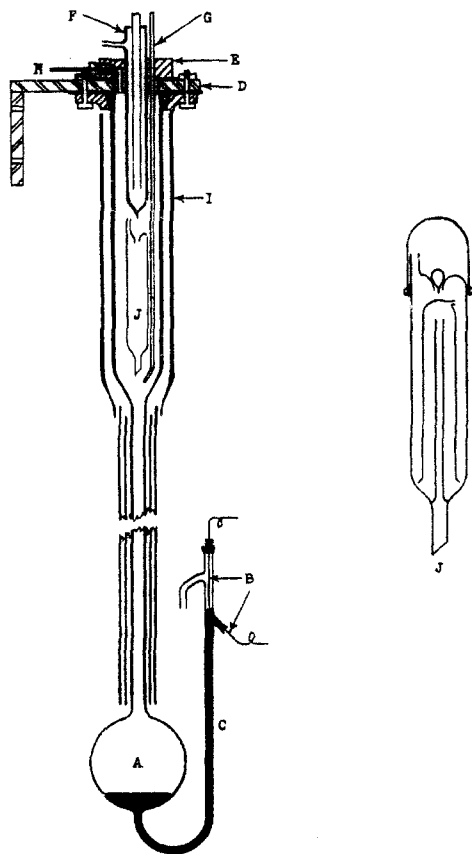


Fig. 3.—Pressure still for fractional distillation of hexamethylethane.

(14) This yield is to be compared with a yield of 3% reported by Whitmore, Stehman and Herndon.<sup>14</sup>

(15) Lecky and Ewell, *Ind. Eng. Chem., Anal. Ed.*, **12**, 544 (1940).

tric current, controlled by a Variac, was supplied to the heating jacket from a 110-volt source.

The still head, which was sealed directly to the column, was a 2 X 14-inch section of standard Pyrex glass pipe, the upper end of which was flared and fitted into a standard iron flange for glass pipe. The flange was secured by means of a Koroseal gasket, and the blind flange steel plate D served as a support for the entire still. The steel plate D had a 2-inch hole, threaded to receive the screw plug E bearing the steel condenser F, thermocouple well G, and the vent tube H. The still head itself was wound with nichrome resistance wire, and was enclosed by the jacket I of 3-inch glass tubing. In operation, ethylene glycol at 101–103° was circulated through the condenser by means of a small centrifugal pump.

The receiver J for collecting the hydrocarbon fraction was hung from a hook in the bottom of the condenser by a wire handle. The receiver was of glass, had a capacity of about 35 ml., and, as illustrated, was designed to overflow liquid drawn from the bottom, thus insuring that the contents always represented the last material condensed. Its top was funnel shaped, and was fitted with a glass ball float which allowed condensed liquid to flow into the receiver but minimized loss of material by evaporation when the sample was later cooled. An Anschütz thermometer was inserted in the opening in the top.

Approximately 200 g. of hexamethylethane was charged into the still head while maintaining an atmosphere of nitrogen in the still, and, after closing the opening, was melted into the still pot. The screw plug bearing the condenser and receiver was screwed into the opening, and heat was applied to the still pot, column jacket, and still head. As the pressure approached 140 mm. above atmospheric pressure, the nitrogen was vented through a dry-ice trap until the vapors of hexamethylethane reached the condenser, at which time the vent was closed and the still was allowed to operate automatically under total reflux. After approximately six hours of operation the heating elements were shut off, and the still was allowed to cool to room temperature. Temperature readings were taken of the product in the receiver as it cooled and solidified, and from the plot of these against time the freezing point of each fraction was determined.

After the still had cooled to room temperature (usually by standing overnight), the plug was removed from the still head, the receiver was removed and replaced by a duplicate receiver, the plug assembly was replaced, and the operations described above were repeated until the entire charge had been distilled. The distillation data are listed in Table II.

TABLE II

## FRACTIONAL DISTILLATION OF HEXAMETHYLETHANE

Fraction	Wt., g.	B. p., °C. (900 mm.)	F. p., °C.
0 <sup>a</sup>	13		
1	22	112.3	99.4
2	22	112.6	100.5
3	19	112.7	100.7
4	22	112.7	100.7
5	21.5	112.7	100.7
6	22	112.9	100.7
7	22	112.8	100.7
8	16	112.9	100.6
Residue	12.5		

<sup>a</sup> Collected in a trap attached to the vent line of the still.

**Determination of the Freezing Point of Hexamethylethane.**—The apparatus used in obtaining freezing and melting curves on two of the purified fractions of hexamethylethane consisted of a mechanical shaker for agitating a sealed ampoule of the sample, an electrically-heated air-bath for heating or cooling the sample, and a thermocouple, potentiometer and galvanometer for measuring temperatures.

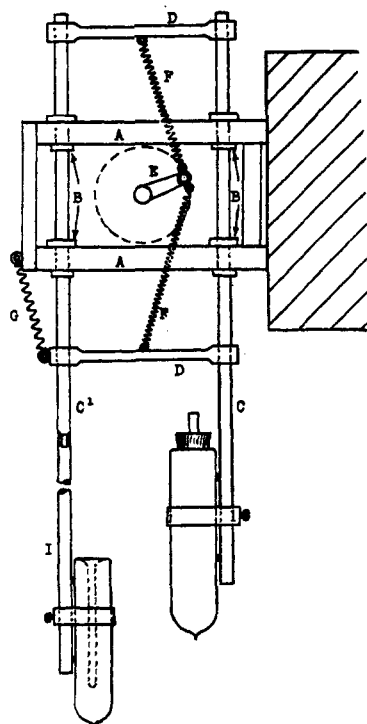


Fig. 4.—Mechanical reciprocating shaker.

The mechanical reciprocating shaker, illustrated in Fig. 4, consisted of the support A fitted with Oilite bushings B through which passed the two steel rods C. The latter were coupled together by the tie rods D which in turn were connected to the crank E by the springs F. The third spring G served to counterbalance the weight of a 75-ml. silvered Dewar containing shaved ice for the reference junction of the thermocouple clamped to C, and the glass ampoule with the thermocouple well containing the hydrocarbon clamped to the steel tube I. The tube I was brazed to C', and was slotted to take the thermocouple lead from the hydrocarbon ampoule. The shaker was operated through the crank E by a 1/8-horsepower electric motor equipped with a reducing gear. The speed of the motor was controlled by a variable resistance in the electrical circuit.

The air-bath consisted of a 1-quart unsilvered Dewar, the outside of which was wound with a heating element of nichrome resistance wire. Within the Dewar was a grid heater of nichrome resistance wire which covered the lower half of the flask. The Dewar was stoppered with a split-cork stopper bearing a hole through which the rod of the shaker bearing the hydrocarbon ampoule traveled, and two thermometers for measuring the temperature of the lower and upper portions of the bath.

Temperature measurements were made by means of a three-junction iron-constantan thermocouple in conjunction with a Leeds and Northrup type K potentiometer and a desk-type galvanometer, sensitive to changes of one microvolt, or 0.01°. The thermocouple was calibrated in the range 20–100° against boiling water and a calibrated (by Natl. Bur. Stds.) 24-inch mercury thermometer graduated from 0 to 100° in divisions of 0.1°.

The procedure for the melting point and freezing point determinations was as follows: The sealed ampoule containing about 20 g. of hydrocarbon was clamped to the lower end of the shaker rod I, and the 75-ml. Dewar filled with 50 g. of shaved ice was clamped to C. One and one-half-inch cardboard discs were attached to the shaker rod I at the top and bottom of the ampoule for stirring the air in the bath. With the thermocouple junctions in place, and the air-bath placed about the hydrocarbon ampoule,

the external heaters of the air-bath were turned on and the shaker was started (180–200 oscillations per minute). When the temperature of the bath was within 5–10° of the melting point of the hydrocarbon, the internal grid heater was used to raise the temperature of the bath several degrees above the melting point of the hydrocarbon, and temperature measurements were made as the sample melted. When the sample had completely melted, the current in the grid heater was reduced, and temperature measurements were taken as the sample cooled. During this time the temperature of the bath was maintained about 4° below that of the sample.

The method of determining from the time-temperature cooling curves the freezing point of the sample and extrapolating the freezing point to perfect purity was that of Mair, Glasgow and Rossini.<sup>16</sup>

Figure 1 shows the time-temperature freezing and melting curves obtained on a sample of technical naphthalene purified by a single sublimation. The freezing curve gave an initial freezing point of 79.86 ± 0.02° and a freezing point lowering of 0.26° when one-half frozen. From these data, the amount of impurity in the sample was estimated to be 0.005 ± 0.001 mole fraction, and the freezing point of pure naphthalene was estimated to be 80.12°. Mair and Streiff<sup>17</sup> report 80.27 ± 0.02° for the freezing point of pure naphthalene.

The time-temperature freezing and melting curves obtained on hexamethylethane fraction 5 are shown in Fig. 2. The freezing curve gave an initial freezing point of 100.63° and a freezing point depression of 0.06° when the sample was one-half frozen.

Hexamethylethane fraction 6 gave an initial freezing point of 100.60° and a freezing point lowering when one-half frozen of 0.10°.

**Determination of the Vapor Pressure of Hexamethylethane.**—The vapor pressure of hexamethylethane (fract. 6) over the temperature range 0 to 110° was determined by measuring the difference in pressure exerted by the hydrocarbon and water in a Bremer-Frowein tensimeter.<sup>7</sup> The tensimeter was immersed in a bath of ethylene glycol, fitted with heating elements for raising its temperature, and an electric stirrer. Vapor pressure measurements were made by recording the difference in mercury levels in the manometer at temperature intervals varying from 1 to 10° in the range 0 to 110°. The bath was maintained at constant temperature for at least fifteen minutes before readings were taken, by control of the current into the heaters. The difference in mercury levels was read to an accuracy of ±0.1 mm. from a steel scale immersed in the bath, by means of a telescope, and the readings were corrected for expansion of the steel scale and the change in density of the mercury with temperature. Temperatures were measured to ±0.01° by the 24-inch calibrated thermometer previously described, and also by the thermocouple used in the freezing point determinations.

From the data obtained, the vapor pressure of hexamethylethane was calculated by subtracting the difference in pressure readings from the vapor pressure of water, using for the latter the data of Osborne, Stinson and Ginnings.<sup>18</sup>

Several attempts were made to fit various standard empirical equations to the original vapor pressure-temperature data for the solid. All gave unreasonable results and indicated that the calculated logarithms of the pressures at the lower temperatures were too low. This suggested the presence of a systematic error in the pressure

measurements which would be masked at the higher pressures, but be more noticeable at the lower pressures. Accordingly, realizing that no special precautions had been taken to rigorously exclude water vapor in the arm of the tensimeter containing the hexamethylethane, the vapor pressure of the hydrocarbon was remeasured at two points, 0 and 22°, in a vacuum manometer, after the hydrocarbon had been dried over phosphorus pentoxide and water vapor had rigorously been excluded from the system. This gave values about 1.4 mm. lower than those obtained in the tensimeter. Accordingly, 0.005 *T* mm. (corresponding to 1.4 mm. at the lower temperatures) was subtracted from the observed values obtained in the tensimeter, giving the corrected values shown in Table I.

**Density and Refractive Index of Solid Hexamethylethane.**—To determine the density of solid hexamethylethane, approximately 20 g. of the hydrocarbon (fract. 7) was melted in a glass ampoule of known volume (24.30 ml.) and weight, and was frozen to a clear glass. After weighing the ampoule and its contents, mercury was added to fill the free space, and the tube and its contents were again weighed. From the data obtained, the density of solid hexamethylethane was calculated to be 0.823 g./ml. at 23°.

The refractive index of hexamethylethane (fract. 6), determined with an Abbe refractometer, was found to be  $n_D^{20}$  1.4695.

### Summary

Hexamethylethane, prepared by the condensation of 2,3,3-trimethyl-2-chlorobutane with methylmagnesium chloride, was purified by fractional distillation in a specially-designed pressure still.

Freezing and melting curves were obtained on the two best fractions. The best fraction gave a freezing point of 100.63° and a freezing point lowering when one-half frozen of 0.06°. From these data the purity of the sample was calculated to be 99.96 ± 0.04 mole per cent. and the freezing point of pure hexamethylethane was estimated to be 100.69°.

The vapor pressure of the purified hydrocarbon was measured over the temperature range 0 to 110° in a Bremer-Frowein tensimeter, and from the data obtained were derived the following expressions for the vapor pressure of hexamethylethane.

$$\begin{aligned} \text{Solid: } \log P(\text{mm.}) &= 7.78882 - 1625.7/(t + 226) \\ \text{Liquid: } \log P(\text{mm.}) &= 6.87665 - 1327.8/(t + 226) \end{aligned}$$

Computations from the vapor pressure data of the heats of fusion, vaporization, and sublimation at the melting point, using the Clausius-Clapeyron equation, gave the values 1700, 7550 and 9250 cal./g. mole, respectively. The calculated boiling point is 106.30 ± 0.02°, and the calculated heat of vaporization at the boiling point is 7530 cal./g. mole.

Determinations of the density and refractive index of solid hexamethylethane gave the values:  $d_{23}^{23}$  0.823 g./ml., and  $n_D^{20}$  1.4695.

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(16) Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

(17) Mair and Streiff, *ibid.*, **24**, 395 (1940).

(18) Osborne, Stinson and Ginnings, *ibid.*, **23**, 261 (1939).