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2,6-DIMETHYLHEPTANE: ITS SYNTHESIS, PROPERTIES, AND COMPARISON WITH AN ISONONANE FROM PETRO- LEUM¹

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ABSTRACT

An isononane boiling at 135.2° C was tentatively identified as 2,6-dimethylheptane at the time of its isolation from a midcontinent petroleum. 2,6-Dimethylheptane has been synthesized by means of the Grignard reaction and the properties of a purified fraction compared with those of the isononane from petroleum. The properties of the isononane from petroleum are in good accord with those of 2,6-dimethylheptane. The properties of 2,6-dimethylheptane (extrapolated to a purity of 100.0 mole percent from measurements actually made on material of purity 99.6 mole percent) are as follows: Boiling point at 760 mm Hg, 135.21° ± 0.02° C; freezing point in air, -102.95 ± 0.10° C; density at 20° C, 0.70891 ± 0.00003 g/ml; refractive index, n_D^{20} 1.40073 ± 0.00005; critical solution temperature in aniline, 80.0° ± 0.3° C.

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I. INTRODUCTION

The isolation from a midcontinent petroleum of an isomeric nonane boiling at 135.2° C has been described in an earlier paper by White and Rose [1].⁵ The identification of the compound was attempted at the time, by comparing the physical constants of the hydrocarbon from petroleum with those reported for the few nonanes known to boil near 135° C. The compound had properties most nearly like those reported for 2,6-dimethylheptane [2, 3], but the agreement was not sufficient, in the absence of knowledge concerning 19 of the 35 structurally possible isomers of C₉H₂₀, to make the identification complete.

The indication from the correlation of physical properties that the compound might be 2,6-dimethylheptane was in keeping with a suspected dimethylheptane structure, a supposition based on the fact that all of the isoparaffinic hydrocarbons previously isolated from the

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⁵ Figures in brackets indicate the literature references at the end of this paper.

petroleum have been mono- or dimethyl derivatives and on the further fact that the isomeric nonane in question boiled at a much lower temperature than any of the monomethyloctanes. This view was supported by a study of the diagrams, prepared by Calingaert and Hladky, correlating the physical properties of the alkanes with their molecular structure [4].⁶

Moreover, a study of the near infrared absorption spectra in the region 5,400 to 8,900 cm^{-1} (1.82 to 1.12 μ) showed the absorption characteristic of isoparaffins. For this region, the salient features of the absorption of branched or methylated paraffins have been discussed by Liddel and Kasper [5] and later by Rose [6]. A mathematical analysis of the molal absorption index, according to the method recently described by one of the authors [7], yielded the following values for the number of component structural groups in the molecule: $-\text{CH}_3$, 4 ± 0.4 ; $-\text{CH}_2$, 3 ± 0.4 ; $-\text{CH}$, 2 ± 0.6 . This indicated that the isononane was a dimethylheptane or a methylethylhexane in which the branches are not attached to the same carbon atom.⁷

II. SYNTHESIS OF 2,6-DIMETHYLHEPTANE

Synthetic 2,6-dimethylheptane was prepared and purified by the general method described earlier by Calingaert and Soroos [8]. In this case, isobutyl magnesium bromide was coupled with ethyl formate, producing 2,6-dimethylheptanol-4 (bp/18 mm, 80.0 to 81.50° C; d_4^{20} , 0.810; n_D^{20} , 1.4232) in a 74-percent yield. This carbinol was hydrogenated in three steps, giving a 90-percent yield of crude alkane, which was then treated with 98-percent sulfuric acid, washed, dried, refluxed over sodium-potassium alloy, and finally fractionated carefully in a column packed with crushed carborundum.

III. PHYSICAL PROPERTIES OF SYNTHETIC 2,6-DIMETHYLHEPTANE AND ITS COMPARISON WITH AN ISONONANE OBTAINED FROM PETROLEUM

The physical properties of the synthetic material purified by distillation were determined. The values obtained are listed in table 1 under the designation "best by distillation."

⁶ These diagrams indicate the boiling points and molecular volumes (densities) of not only the known members of groups of isomeric paraffins but also of several of the unknown members by interpolation and extrapolation of curves for homologous series.

⁷ The details and experimental data for this analysis are given in the paper cited [7].

TABLE 1.—Physical properties of two preparations of synthetic 2,6-dimethylheptane and of the isononane from petroleum

Physical property	Isononane from petroleum	Synthetic 2,6-dimethylheptane	
		"Best by distillation"	"Best by distillation and crystallization"
Normal boiling point, °C	* 135.208 ± 0.003	* 135.210 ± 0.003	(b)
Pressure coefficient, dt/dp °C/mm Hg		0.0490	
Initial freezing point in air, °C	* -103.24 ± 0.02	-104.1 ± 0.03	* -103.04 ± 0.02
Density at 20° C, g/ml	d 0.70963 ± 0.00002	d 0.70949 ± 0.00002	d 0.70894 ± 0.00002
Temperature coefficient, dD/dt , per degree			* -0.00079
Refractive index, n_D^{20}	f 1.40115 ± 0.00005	f 1.40095 ± 0.00005	f 1.40075 ± 0.00005
Temperature coefficient, dn/dt , per degree			* -0.00049
Critical solution temperature in aniline, °C	* b 79.9 ± 0.2	* 80.3 ± 0.2	* 80.0 ± 0.2
Purity, mole percent		j 98.8	j 99.6

* Determined by E. R. Smith of the Physical Chemistry Section of this Bureau in a standard Swietoslowski ebullimeter [1].

† Difference in boiling and condensation points: Petroleum sample, 0.033° C; synthetic ("best by distillation"), 0.008° C. It should be noted that these results are misleading if used as a criterion of purity, because the synthetic preparation before crystallization contained four times the amount of the impurity in the isononane from petroleum.

b Not measured, assumed to be the same as for the preparation before crystallization.

c Initial freezing point. Data obtained with a platinum resistance thermometer of 25 ohms.

d Determined by the Division of Weights and Measures of this Bureau.

e From measurements at 20° and 25° C.

f Determined on a calibrated Abbe refractometer (Valentine design).

g Comparative values. At this temperature the mixture contained 37 mole percent of the hydrocarbon.

h The previously reported [1] value, 81.2 ± 0.5° C, is considered to be in error because of lack of stirring during the observation.

i Calculated from the slope of the freezing curve (see text).

In figure 1, curve III (broken) is the time-temperature freezing curve for the synthetic 2,6-dimethylheptane, "best by distillation."

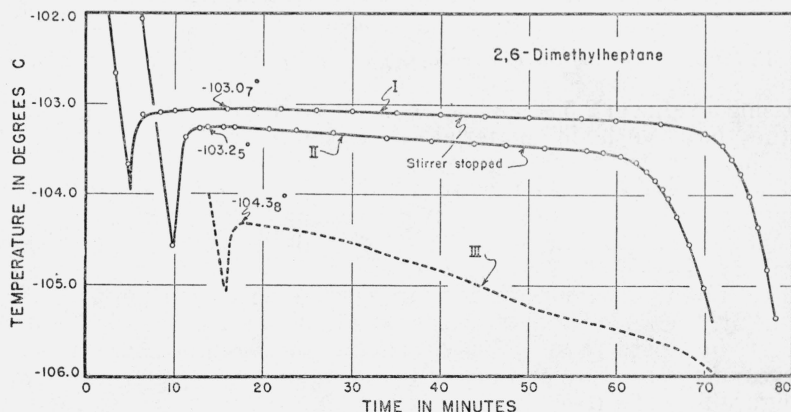


FIGURE 1.—Cooling curves of 2,6-dimethylheptane.

Curve I, synthetic, purified by distillation and crystallization; curve II, from petroleum; curve III, synthetic, purified by distillation alone. Curves II and III are the same, respectively, as curves I and II in figure 2. The time scale for curves II and III is twice the actual scale.

The slope of the curve during the freezing interval indicated that the material was not of the highest purity, and consequently the distilled synthetic material was further purified by crystallization. A 200-ml portion was twice crystallized from its solution in dichlorodifluoro-

methane, the crystals being separated from the liquid phase by centrifuging. There was obtained a 50-ml fraction which was degassed and filtered through silica gel to remove the last traces of solvent. The values of the properties of the highly purified synthetic 2,6-dimethylheptane are listed in table 1 under the heading, "best by distillation and crystallization." Hereafter, this preparation is referred to as the "best" synthetic material.

The behavior during freezing of the "best" synthetic material is shown in curve *I* of figure 1. The highest observed point on curve *I* is -103.07°C , and the initial freezing point is -103.06°C . From the initial freezing point and the slope of the curve, the freezing point of the substance 100.0 percent pure is estimated⁸ to be -102.95°C .

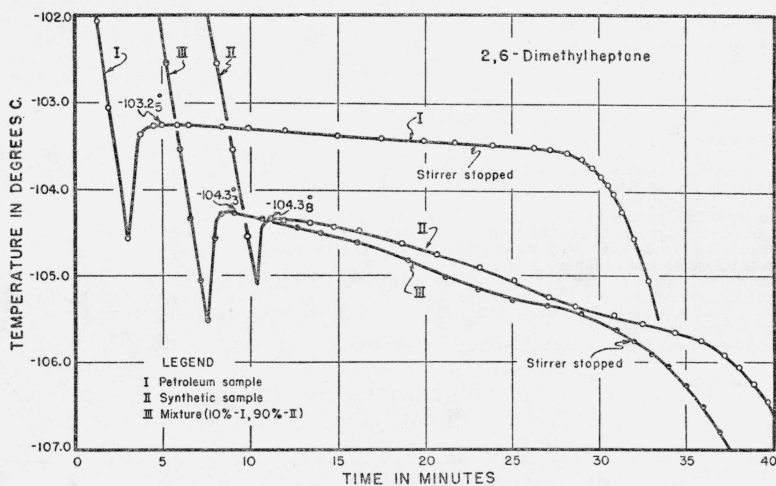


FIGURE 2.—Cooling curves of various preparations of 2,6-dimethylheptane.

Using a value of 2.5 ± 0.2 kcal/mole for its heat of fusion,⁹ the purity of the "best synthetic" material was calculated to be 99.6 ± 0.1 mole percent.

The properties previously reported for the isononane from petroleum [1] are listed in table 1. A calculation of the purity, made in a manner similar to that for the synthetic 2,6-dimethylheptane, yielded a value of 98.8 ± 0.2 mole percent.

The cooling behavior of a mixture containing 10 parts of the petroleum hydrocarbon and 90 parts of synthetic 2,6-dimethylheptane ("best by distillation") was studied. Time-temperature freezing curves of the mixture and of the two component materials are shown in figure 2. The freezing point of the mixture, as indicated in curve *III*, lay between that of the hydrocarbon from petroleum and that of the synthetic preparation (curves *I* and *II*, respectively), and was proportionately nearer to the freezing point of the latter.

⁸ The computations are based on the assumptions that the midpoint of the freezing interval indicates the point at which the material is half frozen [9], that at the midpoint where the mixture is half frozen the concentration of impurity in the liquid has doubled, and that the impurity is soluble in the liquid phase but not in the solid phase.

⁹ From data on the heats of fusion of other paraffin hydrocarbons, the heat of fusion of 2,6-dimethylheptane was estimated to be 2.7 ± 0.4 kcal/mole. In connection with another investigation [12], the heat of fusion of the isononane from petroleum was calculated to be 2.5 ± 0.2 kcal/mole, from values of the molecular depression of the freezing point produced by the addition, to the isononane, of known quantities of ethylcyclohexane.

TABLE 2.—Values of the properties ^a of the hydrocarbon, 100.0 mole percent pure, obtained by extrapolation of measurements actually made on synthetic 2,6-dimethylheptane, 99.6 mole percent pure, and on the isononane from petroleum, 98.8 mole percent pure

Physical property	Synthetic	Petroleum
Normal boiling point, °C.....	135.21 ± 0.02	135.21 ± 0.02
Freezing point in air, °C.....	^b -102.95 ± 0.03	^b -103.04 ± 0.06
Density at 20° C, g/ml.....	0.70891 ± 0.00003	0.70876 ± 0.00010
Refractive index, n_D^{20}	1.40073 ± 0.00005	1.40079 ± 0.00010

^a For values of the coefficients of these properties with temperature or pressure see table 1.

^b These uncertainties are relative. It is estimated that the values are good to ±0.10° C (including uncertainties in the method and in thermometry).

Table 2 gives values of the properties of the hydrocarbon, 100.0 mole percent pure, obtained by extrapolation of measurements actually made on synthetic 2,6-dimethylheptane, 99.6 mole percent pure, and on the isononane from petroleum, 98.8 mole percent pure. The extrapolations were made on the assumptions that the impurity in the synthetic material was normal nonane and that in the isononane from petroleum was a nonanaphthene [1, 10, 12], and that, within the small range involved, the values of density and refractive index are linear functions of the mole fractions of the components. The freezing point was calculated according to the procedure previously mentioned. The nature of the impurities was deduced from the manner of preparation and purification of the respective materials. Conservative estimates of the uncertainties have been assigned to the values, there being included in the uncertainty one-third of the amount of extrapolation of the freezing point and one-tenth of the amount of the extrapolation of the density and refractive index. The values from the two preparations are substantially in agreement within the assigned limits of uncertainty.

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