NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL NOTE

No. 1019

THE SYNTHESIS AND PURIFICATION OF AROMATIC HYDROCARBONS

I - BUTYLBENZENE

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SUMMARY

A 13-gallon quantity of butylbenzene was synthesized and purified by large-scale preparation of 4-phenyl-1-butene from benzylmagnesium chloride and allyl chloride with subsequent hydrogenation of the olefin. The physical constants for pure samples of 4-phenyl-1-butene and butylbenzene were determined and the position of the double bond in the olefin was established.

INTRODUCTION

The synthesis and purification of aromatic hydrocarbons is part of a general investigation being conducted at the NACA Cleveland laboratory on the evaluation of such compounds as antiknock blending agents for current aviation fuels. The investigation includes the aromatics from benzene through all of the possible structures with 9 carbon atoms and some with 10 carbon atoms. Several of the aromatic hydrocarbons were obtained from commercial sources and were purified by fractional distillation, fractional crystallization, or by chemical means. The compounds that could not be commercially obtained were synthesized by the Organic Synthesis Section of the Fuels and Lubricants Division.

The present report, which is the first of a series dealing with the preparation of hydrocarbons for use in engine tests at the Cleveland laboratory, describes the synthesis and purification of a 13-gallon quantity of pure butylbenzene and presents physical properties of butylbenzene and 4-phenyl-1-butene. Because there is considerable discrepancy in the literature as to the correct physical properties for the olefin, the position of the double bond was determined by ozonolysis. The synthesis described herein involves the

preparation of 4-phenyl-1-butene and subsequent hydrogenation of the olefin to butylbenzene. A number of methods of synthesizing these hydrocarbons are given in the literature, but only the relatively recent papers will be cited.

The olefin 4-phenyl-1-butene was prepared by condensation of benzylmagnesium chloride with allyl chloride in reference 1 and from the same Grignard reagent with allyl-p-toluenesulfonate in reference 2. The olefin has also been prepared by the condensation of benzylmagnesium bromide with allyl chloride (reference 3), by the condensation of allylmagnesium chloride with benzyl chloride (reference 4), and by treatment of 4-phenyl-1-bromobutane with alkali (reference 5). A Wurtz-Fittig synthesis with bromobenzene and butyl bromide is reported in reference 6 for the preparation of butylbenzene in excellent yield. The Friedel-Crafts reaction of butyryl chloride with benzene and subsequent reduction of the reaction product by the Wolff-Kishner method were utilized in reference 7. The condensation of phenylmagnesium bromide and butyraldehyde is reported by A.P.I. hydrocarbon research project 45 to give 1-phenyl-1-butanol, which was dehydrated to the olefin and hydrogenated to yield butylbenzene.

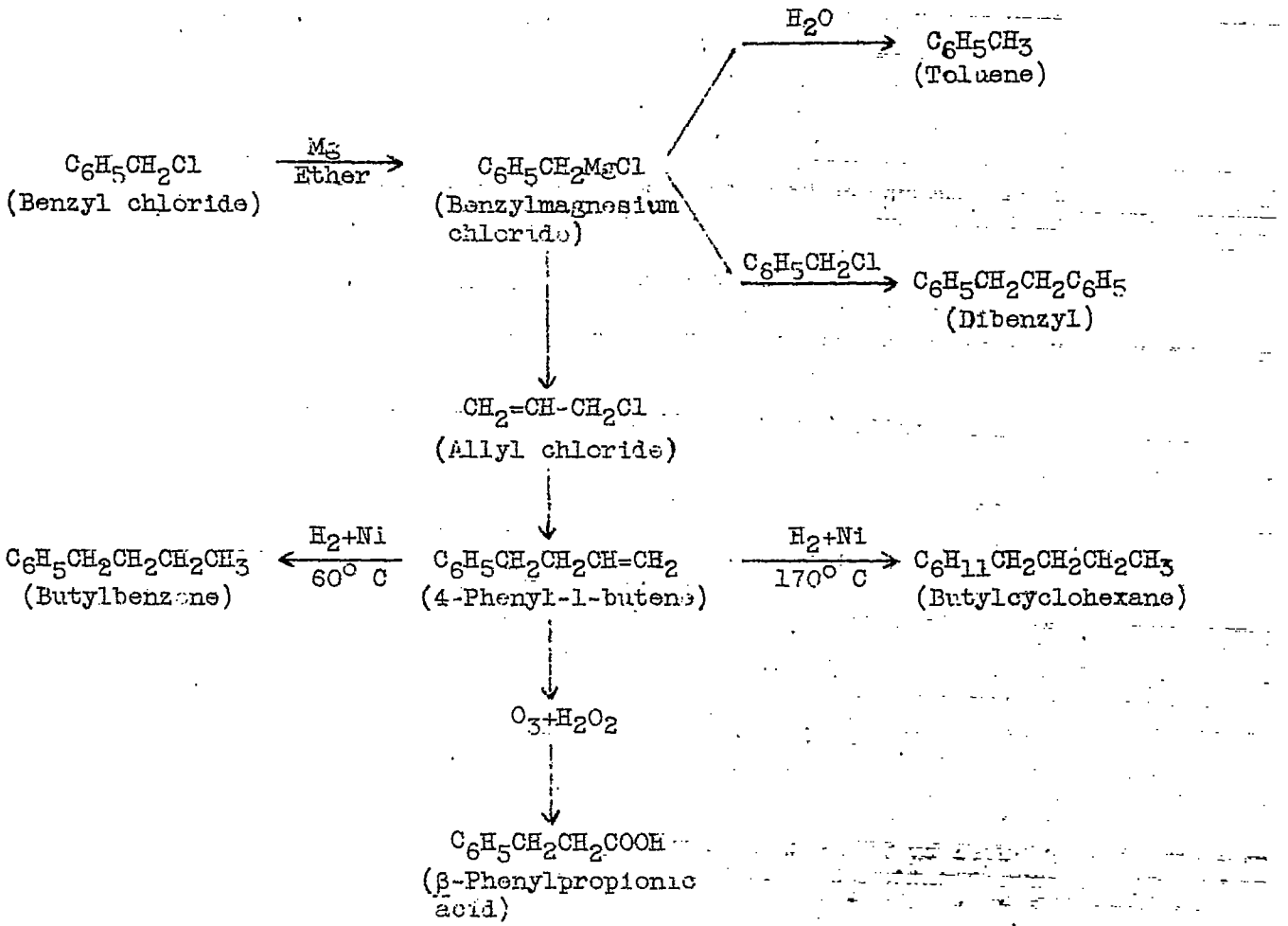
The preparation described herein, which was begun in April 1944, is presented in two main sections: (a) a general discussion of the method and presentation of the yields and the physical constants of the hydrocarbons and (b) the experimental details.

DISCUSSION OF SYNTHESIS

The method used at the Cleveland laboratory for the synthesis of butylbenzene consists in the condensation of benzylmagnesium chloride with allyl chloride to give 4-phenyl-1-butene followed by hydrogenation of this olefin. The preparation of the olefin was accompanied by a large yield of dibenzyl and a small amount of toluene. Dibenzyl is apparently formed by the condensation of benzylmagnesium chloride with benzyl chloride, and toluene is formed by hydrolysis of the Grignard reagent. Both impurities are easily separated from the desired olefin. The yields of the three products obtained from a typical run of 395 moles of benzyl chloride were as follows:

Product	Yield	
	(kg)	(percent)
Toluene	0.7	1.9
Dibenzyl	17.0	47.3
4-Phenyl-1-butene	18.8	36.0
Total ----------	----	85.2

The position of the double bond in 4-phenyl-1-butene was determined by ozonization followed by oxidation. The isolation of β-phenylpropionic acid confirmed the structure of this olefin. The hydrogenation of the double bond in 4-phenyl-1-butene was carried out with extreme ease and gave a quantitative yield of butylbenzene. When the hydrogenation was conducted at elevated temperatures, the resulting product was butylcyclohexane. The reactions are illustrated as follows:



Both 4-phenyl-1-butene and butylbenzene were obtained in a high state of purity, as shown by the freezing curves in figures 1 and 2. A freezing curve for the engine sample of butylbenzene is also included (fig. 3). Temperatures were measured with a platinum

resistance thermometer. Physical constants of butylbenzene and 4-phenyl-1-butene determined at the Cleveland laboratory are recorded in table I as well as values from a number of references.

EXPERIMENTAL DETAILS

Preparation of 4-phenyl-1-butene. - A glass-lined reactor with a 100-gallon capacity was used for the synthesis. The reactor was jacketed for steam and hot or cold water and was equipped with a power stirrer, an efficient reflux condenser, and a copper tank for the addition of liquids. In the reactor 9.6 kilograms (395 moles) of magnesium turnings was covered with 10 gallons of ether, which was previously dried by passing it through a 2-inch by 10-foot column of Florite. An ether solution containing 2 moles of benzylmagnesium chloride and 1.8 kilograms of benzyl chloride was added to the mixture. After the initial reaction had subsided, reflux was maintained by the continuous addition of 48.1 kilograms of benzyl chloride dissolved in 10 gallons of ether. The preparation of the Grignard reagent required 2 days. Titration of a sample with acid indicated the presence of approximately 350 moles of Grignard reagent.

A 30.3-kilogram quantity (394 moles) of allyl chloride dissolved in 10 gallons of ether was added to the Grignard reagent at such a rate that rapid reflux was maintained. The condensation required 2 days after which the reaction mixture no longer showed evidence of the presence of Grignard reagent when tested with Michler's ketone. The reaction mixture was then hydrolyzed by the addition of 35 gallons of 5-percent hydrochloric acid. The acid layer was drawn off and the ether-hydrocarbon layer was washed successively in the reactor with 25-gallon portions of water, 5-percent sodium bicarbonate solution, and water. Ether, unreacted allyl chloride, and possibly 1,5 hexadiene were then distilled from the reaction mixture. The residue consisted of 43.1 kilograms of a yellow fluorescent hydrocarbon mixture that gave a slightly positive Beilstein test. This mixture was stirred in a 12-gallon bottle with 0.2 kilogram of sliced sodium metal for several days after which the solid material was removed by filtration. The halogen-free filtrate was then distilled in a fractionating column of 20-gallon capacity with a 2-inch by 12-foot packed column. The products and yields are listed in the preceding section and the physical constants of 4-phenyl-1-butene are listed in table I.

Ozonolysis of 4-phenyl-1-butene. - In order to determine the position of the double bond in 4-phenyl-1-butene, the olefin was ozonized and the ozonide decomposed with hydrogen peroxide. A cooled solution containing 13.2 grams of 4-phenyl-1-butene in 90 cc of

absolute ethyl acetate was saturated with ozone. The solvent was evaporated in a stream of air at room temperature and was replaced by 50 cc of glacial acetic acid. This solution was placed in a three-necked flask and a mixture consisting of 50 cc of water, 1 cc of concentrated sulfuric acid, and 35 grams of hydrogen peroxide (30-percent solution) was added dropwise.

The resulting mixture was refluxed for 2 hours, cooled in an ice bath, and extracted with ether. The ether layer was dried and the solvent removed leaving a yellow oil that crystallized from a large volume of water. β-Phenylpropionic acid (8.0 grams of needles) was obtained on one recrystallization: melting point, 46° to 47.5° C; neutral equivalent, 150; p-bromophenacyl ester: melting point, 103° to 104° C. These constants agree well with the following values given in reference 8 — β-phenylpropionic acid: melting point, 48° C; neutral equivalent, 150; p-bromophenacyl ester: melting point, 104° C.

Preparation of butylbenzene. - Butylbenzene was prepared from 7.5 kilograms (55.8 moles) of 4-phenyl-1-butene in which was suspended 2 percent of U.O.P. Hydrogenation Catalyst (nickel on kieselguhr). The reaction was carried out in a steel autoclave of 20-liter capacity, fitted with a rocker-type shaker. Hydrogen gas was added and heat applied. At 60° C and a pressure of 1000 pounds per square inch, the reaction proceeded easily and the theoretical quantity of hydrogen was consumed. The reaction was quite exothermic. After cooling, the contents were removed and filtered, and the colorless butylbenzene was subjected to fractional distillation in a 100-theoretical-plate column of 20-gallon capacity. The yield of butylbenzene was quantitative and about 13 gallons was produced by this method. The physical constants are listed in table I.

Butylcyclohexane was obtained when the olefin was hydrogenated at higher temperatures. A 60-percent yield was obtained at 170° C

and a pressure of 1000 pounds per square inch. The physical constants of the butylcyclohexane agreed favorably with the values in reference 12.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, August 23, 1945.

REFERENCES

1. Levina, R. Ya., and Petrov, D. A.: Catalytic Isomerization of Unsaturated Hydrocarbons with a Double Bond in the α,β-Position. Chem. Abs., vol. 31, no. 16, Aug. 20, 1937, p. 5772. (Original article in Jour. Gen. Chem. (U.S.S.R.), vol. 7, 1937, pp. 747-749.)

2. Gilman, Henry, and Beaber, Nathaniel J.: The Preparation of Hydrocarbons by the Reaction between Alkyl Sulfonates and Organomagnesium Halides. Jour. Am. Chem. Soc., vol. 47, no. 2, Feb. 1925, pp. 518-525.

3. Kozacik, A. P., and Reid, E. Emmet: Lengthening Carbon Chains by Three Units: Assay of Primary Bromides from the Addition of Hydrogen Bromide. Jour. Am. Chem. Soc., vol. 60, no. 10, Oct. 1938, pp. 2436-2438.

4. Gilman, Henry, and Mc Glumphy, J. H.: La Préparation Indépendante du Bromure d'Allylmagnésium. Bull. Soc. Chim. France, Mémoires, t. XLIII, sér. 4, art. 136, 1928, pp. 1322-1328.

5. Lagerev, S. P.: The Effect of Radicals on the Direction of the Addition of the Components of Hydrogen Halide Acids. Chem. Abs., vol. 35, no. 7, April 10, 1941, p. 2119. (Original article in Trudy Uzbekskogo Gosudarst Univ., vol. 6, 1936, pp. 71-88.)

6. Read, R. R., and Foster, L. S.: Normal Butylbenzene. Jour. Am. Chem. Soc., vol. 48, no. 6, June 1926, pp. 1606-1607.

7. Schmidt, Albert Wolfgang, Hopp, Gerhard, und Schoeller, Viktor: Darstellungsweise und Physikalische Daten von Monoalkylbenzolen. Berichte d. D. Chem. Gesellschaft, Abteilung B (Abh.), Jahrg. 72, Nr. 11, Art. 319, Nov. 8, 1939, pp. 1893-1897.

8. Shriner, Ralph L., and Fuson, Reynold C.: The Systematic Identification of Organic Compounds. John Wiley & Sons, Inc., 2d ed., 1940, p. 98.

9. Hurd, Charles D., and Bollman, Harry T.: The Pyrolysis of Alpha Unsaturated Hydrocarbons. Jour. Am. Chem. Soc., vol. 55, no. 2, Feb. 1933, pp. 699-702.

10. Evans, E. B.: The Viscosities of Hydrocarbons. Parts VII and VIII. Jour. Inst. Petroleum Technologists, vol. 24, 1938, pp. 537-553.

11. Parks, G. S., and Huffman, H. M.: Some Fusion and Transition Data for Hydrocarbons. Ind. and Eng. Chem., vol. 23, no. 10, Oct. 1, 1931, pp. 1138-1139.

12. Doss, M. P.: Physical Constants of the Principal Hydrocarbons. The Texas Co. (New York), 4th ed., 1943, p. 100.

TABLE I - PHYSICAL CONSTANTS OF BUTYLBENZENE AND 4-PHENYL-1-BUTENE

Compound	Source of constants	Boiling point		Refractive index n_D^{20}	Density at 20° C (grams/ml)	Freezing point (°C)
		Temperature (°C)	Pressure (mm)			
4-Phenyl-1-butene	NACA Cleveland laboratory	181.5	760	1.5074	0.8822	-69.95
	Reference 1	62.5	13	1.5064	.8915	------
	Reference 2	175-177	-----	-------	.906	------
	Reference 3	181-182	-----	-------	--------	------
	Reference 5	75.0	15	1.520	.890	------
	Reference 8	175.0	-----	1.5090	--------	------
	Reference 9	177-178	754	1.5059	.8831	------
Butylbenzene	NACA Cleveland laboratory[a]	183.3	760	1.4899	0.8601	-87.97
	NACA Cleveland laboratory[b]	183.2	760	1.4898	.8601	-88.19
	Reference 6	181-184	-----	-------	--------	------
	Reference 7	----------	-----	1.4899	.8613	------
	Reference 10	182.1-183.1	760	1.4880	.8668	------
	Reference 11	----------	-----	-------	--------	-88.5

[a]"Best" sample.

[b]Engine sample.

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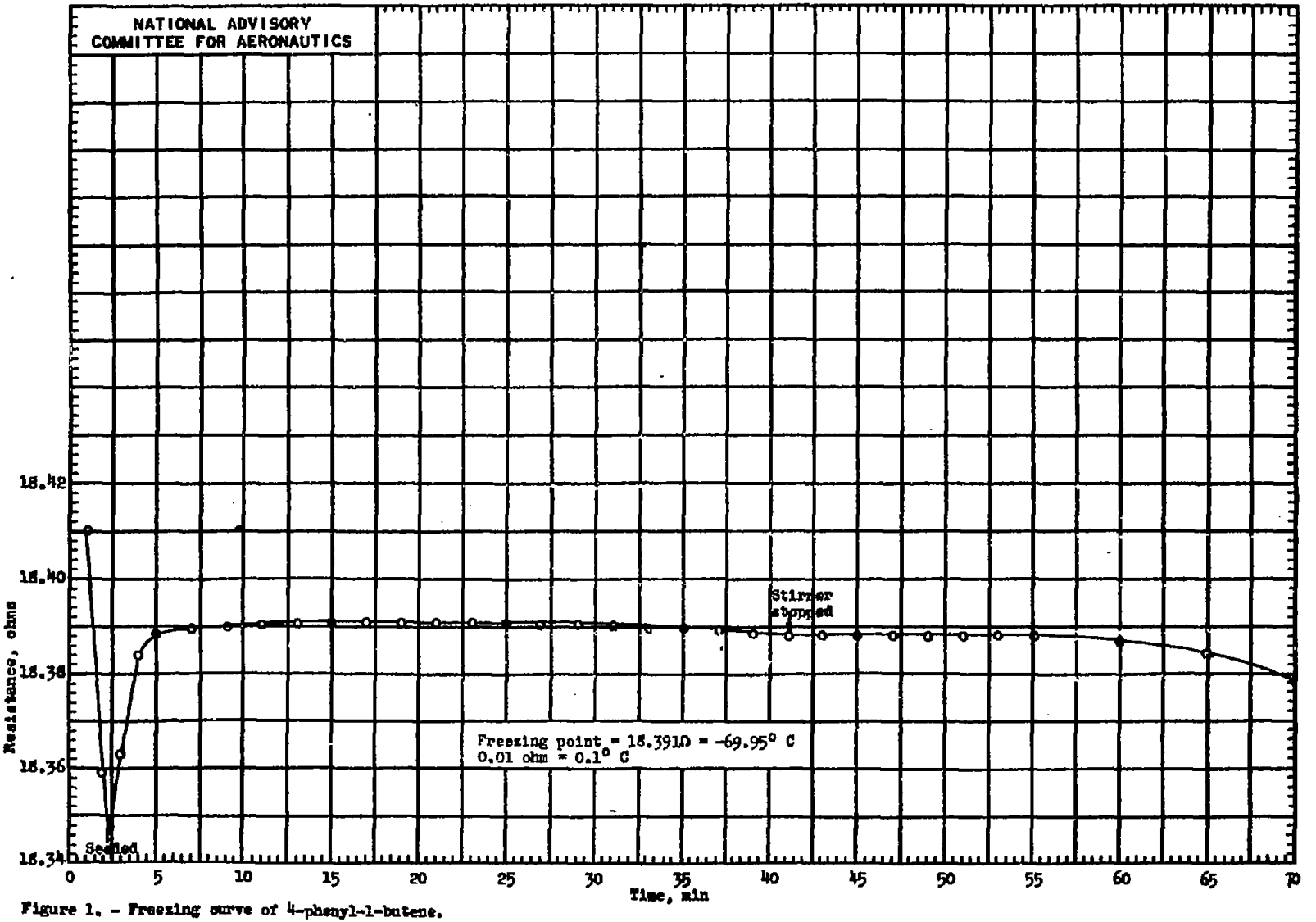

Figure 1. - Freezing curve of 4-phenyl-1-butene.

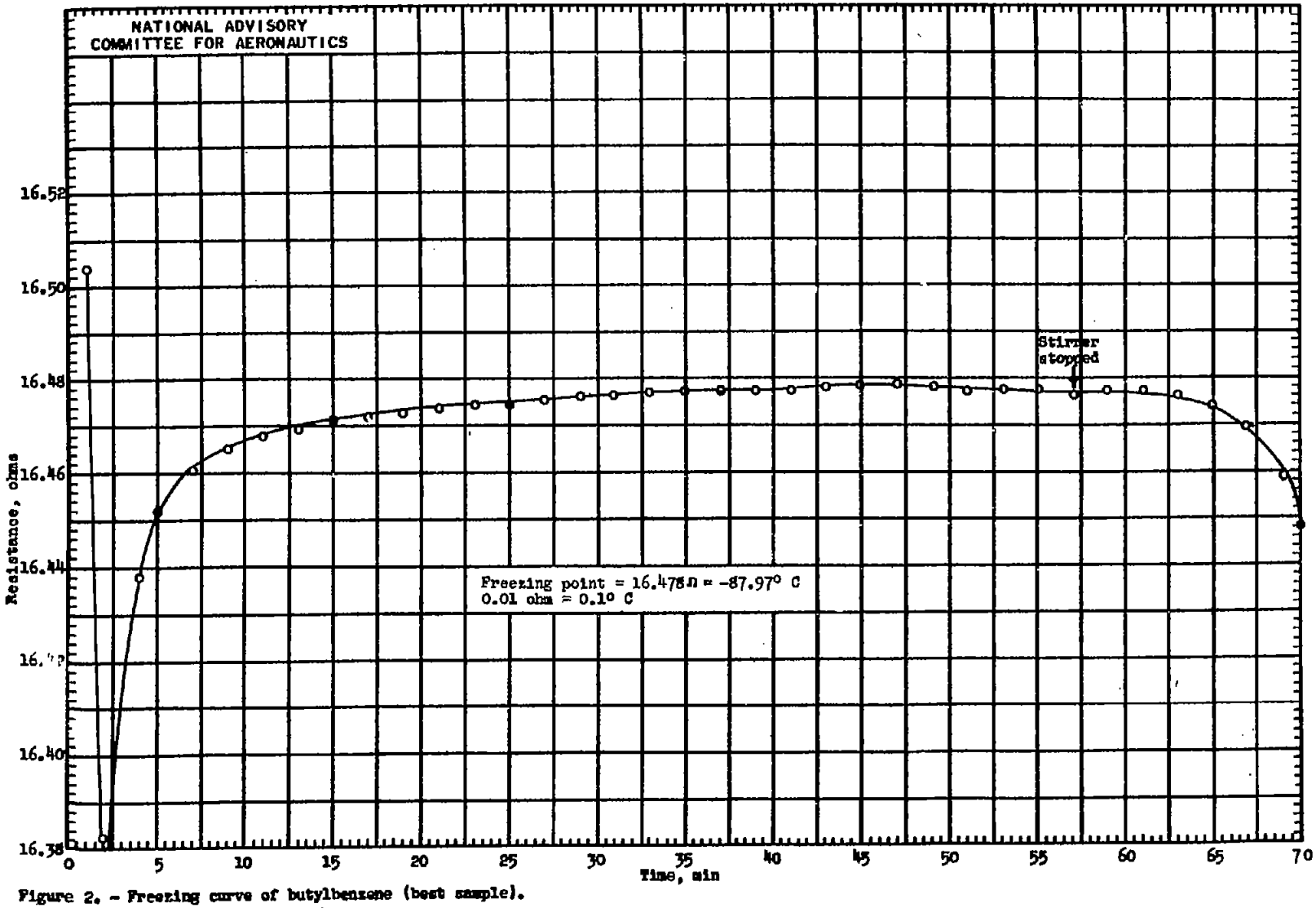

Figure 2. - Freezing curve of butylbenzene (best sample).

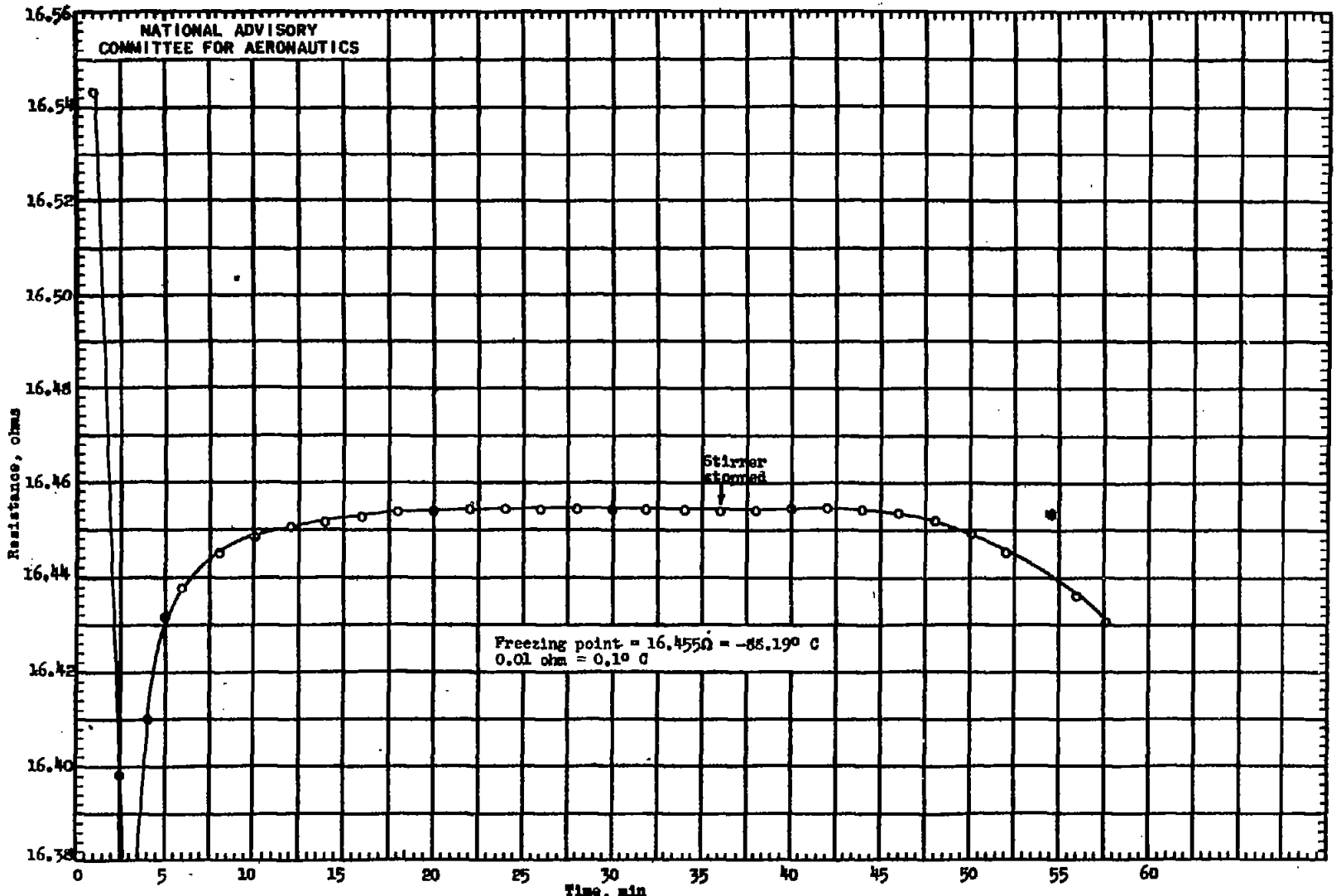

Figure 3. - Freezing curve of butylbenzene (engine material).

Fig. 3