OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-254

COPY NO. - 24

DATE - June 14, 1962

SYNTHESIS OF n-HEXYL- AND n-HEPTYLBENZENE

H. L. Holsopple

ABSTRACT

Two alkylbenzenes, n-hexylbenzene and n-heptylbenzene, were synthesized by reacting bromobenzene and sodium with the appropriate normal alkylbromide (n-hexylbromide and n-heptylbromide respectively). The resulting product was separated by distillation at atmospheric pressure and then purified by distillation over sodium under reduced pressure. Yields were 47 per cent for n-hexylbenzene and 59 per cent for n-heptylbenzene based on alkylbromide as the limiting reactant. Elemental analysis and measurements of physical characteristics were in good agreement with theoretical and literature values.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

Synthesis of n-Hexyl- and n-Heptylbenzene

H. L. Holsopple

The preparation of several normal-alkylbenzenes was required to carry out studies by Chemical Technology Development Section C of the behavior of solvent extraction reagents and diluents. A quantity of pure n-hexylbenzene and n-heptylbenzene was synthesized for this program.

There are several methods of preparing alkylbenzenes. The Fittig and Grignard syntheses are most widely used. These two methods of attaching an aliphatic side chain to an aromatic nucleus were used in the preparation of the C_6 and C_7 alkylbenzenes.

1. Fittig Synthesis. This reaction, in which metallic sodium reacts with organic halides is the classical method for the synthesis of benzene homologs and was the most productive method tried. It can be represented as follows:

$$\text{Aryl-Br} + 2\ \text{Na} \rightarrow \text{Aryl-Na} + \text{NaBr}$$

$$\text{Aryl-Na} + \text{Alkyl-Br} \rightarrow \text{Aryl-Alkyl} + \text{NaBr}.$$

2. Grignard Synthesis. In this reaction the reactivity of alkyl sulfonates with a Grignard reagent is utilized to form a saturated hydrocarbon.

$$2\ \text{p-}CH_3C_6H_4SO_2O\text{-Alkyl} + 2\ \text{Aryl MgBr} \rightarrow$$
$$2\ \text{Aryl-Alkyl} + (\text{p-}CH_3C_6H_4SO_3)_2Mg + MgBr_2.$$

Preparation of n-Hexylbenzene by the Fittig Reaction

Five-gram atoms of sodium (115 grams) are sliced into thin (1 mm) pieces under mineral oil, rinsed rapidly in xylene, blotted on cleansing tissue, and dropped, using tweezers or forceps, into a 5-liter, 3-neck flask containing 1 liter of dry cold ethyl ether. The flask was equipped with a thermometer, condenser, calcium chloride drying tube and dropping funnel. Two moles of cold (precooled to $0^{\circ}C$) hexylbromide (330 grams) and 2.2 moles of cold bromobenzene (345 grams) were combined and placed in the dropping funnel and added within 20 minutes to the reaction flask. The reaction was strongly exothermic at first as indicated by vigorous boiling of the solvent. Control was maintained by applying a basin of ice to the outside of the bottom of the flask when the refluxing of ether became

especially vigorous. When spontaneous boiling stopped, and after all the halide mixture had been added, the flask was warmed with a heating mantle for several hours at a temperature sufficient to maintain gentle refluxing of the ether.

Since the rate of reaction depends mainly on the surface area of the metallic sodium, the thickness of the shavings determined how long the reactants should be left in the flask. In the case of large batches such as this it was observed that the mixture could be allowed to stand overnight or longer at which time the sodium, on being changed to the halide, would increase in size and turn a bright blue color indicating an approximate end to the reaction. Of four batches prepared, two took as long as three days to complete the reaction.

Weygand[1] suggested that for high boiling hydrocarbons it is preferable, after the reaction has been completed, to destroy any unchanged sodium with alcohol, then wash the mixture with water to remove sodium salts, dry the organic layer and fractionate. This was done in one batch but with no effect on either yield or purity of the product.

The reaction product was isolated simply by distilling as much liquid as possible from the reaction flask at atmospheric pressure. The product was then purified by fractionation over sodium to remove any unreacted alkylbromide under reduced pressure (125 μ). The boiling point of n-hexylbenzene (226°C) was significantly different from the dialkyl (< 216°C) and diaryl (> 255°C) by-products to permit a positive separation of fractions.

Approximately 670 grams (47% yield) of n-hexylbenzene was obtained from four batches using the Fittig method of synthesis. One batch of n-heptylbenzene was synthesized using the same mole ratios of heptylbromide, bromobenzene and sodium as were used in preparing n-hexylbenzene and resulted in 150 grams (59% yield) of purified product. The results of elemental analysis of the compounds synthesized, as well as measurements for specific gravity, refractive index and flash point, are shown in Table I.

Table I. Composition and Physical Characteristics of Two Alkylbenzenes

	n-Hexylbenzene		n-Heptylbenzene	
	Theoretical*	Found	Theoretical*	Found
Carbon, %	88.8	88.5	88.7	88.2
Hydrogen, %	11.2	11.3	11.3	11.6
d_4^{20}	0.860	0.850	0.859	0.848
n_D^{20}	1.488	1.484	1.486	1.482
B. P., °C.	226	225-227	244	243-245
Flash Point (Cleveland, open cup), °F.	-	208	-	203

*These values are those given by A. W. Francis[2] in his compilation of physical properties of 379 alkylbenzenes. They are selected mean values based on preponderance of agreement of several observations. Observations of density and refractive index at temperatures different from 20°C were corrected to that temperature by the relations of Lipkin and Kurtz.[3]

Preparation of n-Hexylbenzene by the Grignard Reaction

Gilman and Beaber[4] have described the preparation of hydrocarbons by the reaction of alkyl sulfonates with organomagnesium halides. The ester, n-amyl p-toluenesulfonate, was prepared by slowly adding two equivalents of potassium hydroxide pellets to a well-stirred ether solution containing equivalent weights of p-toluenesulfonylchloride and n-amyl alcohol while keeping the mixture below 4°C in an ice-salt bath. The reaction mixture was poured into 1 liter of ice-water and extracted with ether. The ether was washed with water, dried over K_2CO_3 and the ether and unchanged alcohol removed by vacuum distillation. This ester solidified at room temperature.

Benzylmagnesium chloride (Grignard reagent) was prepared as follows: 24 grams (1 mole) of magnesium was placed in a 2-liter, 3-neck flask fitted with dropping funnel, stirrer and condenser (with $CaCl_2$ drying tube in the upper end). 100 ml of dry ethyl ether was added to the flask. 25 ml of a solution of 127 grams (1 mole) of benzylchloride in 1 liter of dry ether was added to the reaction flask. The reaction started on the application of steam from a water bath and was controlled during the dropwise addition of the remaining benzylchloride by cooling now and then in ice-water. The reaction continued for about 15 minutes after all the benzylchloride had

been added and was refluxed gently for an additional 15 minutes.

An ethereal solution was made of 0.23 moles (55 grams) of n-amyl p-toluenesulfonate with 200 ml of dry ethyl ether. To this was slowly added 35 grams of benzylmagnesiumchloride. The reaction, vigorous at first, was controlled by a cooling water bath. The viscous mixture was refluxed and stirred 3 hours. It was then poured onto 100 grams of crushed ice. Dilute hydrochloric acid (30 ml 1:1) was added and the mixture extracted twice with 200 ml of ether. The ether extract was washed with 50 ml of water and dried over potassium carbonate for two hours. The ethereal solution was then decanted into a flask on the steam bath where the ether was evaporated. The resulting oil was vacuum distilled to remove any unchanged ester (which decomposed when heated at too high a temperature). The fraction containing n-hexylbenzene was redistilled at atmospheric pressure. The refractive index of a sample agreed precisely with that given in the literature (1.488). However, the yield of n-hexylbenzene by this method was only 7 grams (< 20 %). This was considerably less than the yields obtained using the Fittig method of synthesizing homologs of benzene (47 to 59%).

The use of the Grignard reagent as a reactant with alkyl sulfonates in preparing alkylbenzenes is considered by the writer to be of limited usefulness as compared with the Fittig method, not only because of the poorer yields but because of the greater number of operations (in the ester and Grignard preparation) and in the much closer control of temperature which is required.

The chief objection to the Fittig method, when preparing large quantities of alkylbenzenes, is that a considerable excess of sodium must be used. This could ultimately lead to a disposal problem. However, no difficulty was encountered by the writer when the excess sodium was slowly and carefully destroyed with isopropyl alcohol following separation of the product by distillation.

References

1. C. Waygand, Organic Preparations, Interscience Publishers, Inc., New York, N. Y. (1945) 381.
2. A. W. Francis, "Properties of Alkylbenzenes," Chem. Rev. 42, 132-136 (1948).
3. M. R. Lipkin and S. S. Kurtz, "Temperature Coefficient of Density and Refractive Index for Hydrocarbons in the Liquid State," Ind. Eng. Chem., Anal. Ed., 13, 291-2 (1941).
4. H. Gilman and N. J. Beaber, "The Preparation of Hydrocarbons by the Reaction Between Alkyl Sulfonates and Organomagnesium Halides," J. Am. Chem. Soc. 47, 518-525 (1925).

Distribution

1. G. E. Boyd
2. M. T. Kelley
3. C. D. Susano
4. J. C. White
5. L. T. Corbin
6. G. W. Leddicotte
7. W. S. Lyon
8. A. S. Meyer
9. P. F. Thomason
10. C. Feldman
11. H. Kubota
12. H. P. Raaen
13. H. L. Holsopple
14. K. B. Brown
15. C. A. Blake
16. J. M. Schmitt
17. M. J. Skinner
18-19. Central Research Library
20. Document Reference Section
21-23. Laboratory Records
24. Laboratory Records - Record Copy
25-39. Division of Technical Information Extension
40. Research and Development Division (ORO)