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Preparation of Highly Purified 1,3-Dimethyl-5-*t*-butylbenzene by Normal Freezing

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NOTE

Preparation of Highly Purified 1,3-Dimethyl-5-*t*-butylbenzene by Normal Freezing

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Summary

A combination of fractional distillation and normal freezing was used to purify 1,3-dimethyl-5-*t*-butylbenzene. Analysis by gas chromatography indicates that the final product was >99.999% pure. A number of physical constants are given of the pure material.

INTRODUCTION

Normal freezing is an excellent, simple, and versatile method to prepare high-purity organic compounds (*1*,*2*). Although this technique is now already several years old, it is surprising to note that it has not been used on a more extensive scale. In combination with high-efficiency fractional distillation (where separations are based on vapor–liquid equilibria), normal freezing (which is based on liquid–solid equilibria) is a very effective follow-up purification method to isolate compounds in very high purity.

An indication of the potential of this technique is obtained from a recent paper where a >99.99% pure hexafluorobenzene was obtained by six consecutive controlled crystallizations (3). Stirring, an essential operation to reduce the stagnant liquid boundary layer, was not employed. It is obvious, as the authors also point out, that still higher purities would have been obtained if the product were agitated during crystallization.

In this note we report on the purification of 1,3-dimethyl-5-*t*-butylbenzene. The pure material was needed as a standard for physical measurements in our studies on the alkylation of *m*-xylene with isobutene (*4*). The final product was >99.999% pure as analyzed by gas chromatography. This is one of the purest organic compounds purified by normal freezing ever reported.

EXPERIMENTAL

A 99.51% pure heart cut was obtained from a 90% stock by careful distillation through a 3 ft by 1 in. i.d. column packed with 0.16- by 0.16-in. stainless steel protruded packing (5). The chief impurity was 1,2-dimethyl-4-*t*-butylbenzene. Other identified impurities were *m*-xylene, 1,3-dimethyl-4-*sec*-butylbenzene, 1-methyl-4-*t*-butylbenzene, 1-methyl-3-*t*-butylbenzene, 1,3-dimethyl-5-*t*-amylbenzene, 1-ethyl-3-*t*-butylbenzene, and 1-ethyl-4-*t*-butylbenzene. In addition, there were also some very minor amounts of unidentified components.

This heart cut was then subjected to eight consecutive normal freezing runs, with 10–20% of the material being discarded after each run. The normal freezing apparatus used in these experiments has been described earlier (6). Normal freezing was carried out at different lowering rates and temperatures of the coolant, but a typical run would be carried out under the following conditions:

Lowering speed, inch/hour	$\frac{1}{2}$
Stirrer speed, rpm	1800
Coolant temperature, °C	−38 (isothermal)
Discards, %	10–20

Starting with approximately 500 ml of the 99.51% pure heart cut, about 100 ml of the highly purified product was obtained.

ANALYSES

Control analyses were carried out with a Perkin-Elmer 800 gas chromatograph on a 200 ft by 0.02 in. i.d. stainless steel capillary column coated with GE-SF 96 silicone at 100°C. A 100:1 splitter was used on the 0.4-μl sample. The position of the peaks and the identification of the impurities were determined on the chromatograms of the discards on run 1. As the purification progressed, the relative peaks on the subsequent chromatographs decreased sharply in size. No new peaks were observed. This indicated that no artifacts were being introduced during the purification process. This and the knowledge of the position of all possible peaks on the chromatograms made it possible to determine the purity of the major peak more accurately than would otherwise be possible with this analytical system. Chromatograms of the discards of the last two runs indicated almost no deflections at all at those places where the impurities in the starting material were known to be present. The purity of the major compound can, therefore, be estimated to within 0.001%.

An additional analysis of the purity was carried out with an F & M 810 gas chromatograph on a 200 ft by 0.02 in. i.d. support-coated open tubular column packed with squalane. A 100:1 splitter was used on the 25-μl sample. This column has a much larger β value and is, therefore, more suitable for handling the large sample size necessary to determine the very low levels of impurities. The flame ionization detector–electrometer system of this chromatograph had a linear range of approximately 10^9. Under isothermal conditions at 115°C and with a helium flow rate of 5 ml/min, the main peak was eluted in about 130 min. The maximum ion current during elution of the major peak was 0.8×10^{-8} A, with a background noise of less than 0.8×10^{-12} A. In addition, the width of the major peak can be expected to be 10–50 times larger than the impurity peak width; hence, impurities on the order of a few parts per million would have been observed. To check for impurities which may not be resolved on the squalane column, the product was also analyzed with the same chromatograph on a 1000-ft by 0.02-in. stainless steel capillary column packed with Ucon HB 2000 Polar as the liquid substrate. The column was held isothermally at 100°C. With a flow rate of 10 ml of He per minute, the major peak was eluted in 120 min. The lower limits of detection of a resolved impurity would be 5–10 ppm in this case. No impurity peaks could be discerned on the chromatogram.

Melting Points

These were determined on 15-ml samples with a platinum resistance thermometer which had been calibrated by the National Bureau of Standards. The maximum error of the method is 0.05°C. The melting point of the products of the last two runs (see Table 1)

TABLE 1

Purity and Physical Properties of 1,3-Dimethyl-5-*t*-butylbenzene

	Top: Discards		Bottoms: Product				
Run no.	Purity by GLC	mp, °C	Purity by GLC	mp, °C	n_D^{20}	d_4^{20}	d_4^{25}
Starting material			99.51	−18.05			
1	98.7	−19.00	99.87				
2	99.26		99.91	−17.73			
3							
4				−17.69			
5	98.90	−18.46	99.99	−17.57			
6	99.27		99.995	−17.49			
7	99.92		99.999	−17.41			
8	99.99	−17.51	99.999	−17.43	1.49595	0.86507	0.86129

may, therefore, be considered to be essentially the same. The apparatus used has been described earlier (7).

Refractive Index

This was measured with a Bausch and Lomb precision refractometer. Accuracy of the readings is approximately 0.00005 unit, depending on the wavelength. Temperature control of the sample was better than 0.01°C. The refractometer was calibrated against a special test piece calibrated by the National Bureau of Standards.

Densities

These were measured in 25-ml Bingham pycnometers calibrated with distilled water at the temperatures of measurement. Temperature control of the thermostatic bath was within 0.01°C of the stated temperatures, which were checked against a platinum resistance thermometer calibrated by the National Bureau of Standards. The accuracy of these measurements is approximately 0.00002 unit.

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