[CONTRIBUTION FROM KOPPERS COMPANY, INC., MULTIPLE FELLOWSHIP ON TAR SYNTHETICS, MELLON INSTITUTE]

SYNTHESIS OF THE THREE TRIMETHYL- AND CERTAIN OTHER POLYALKYL-BENZENES

J.E. NICKELS AND W. HEINTZELMAN

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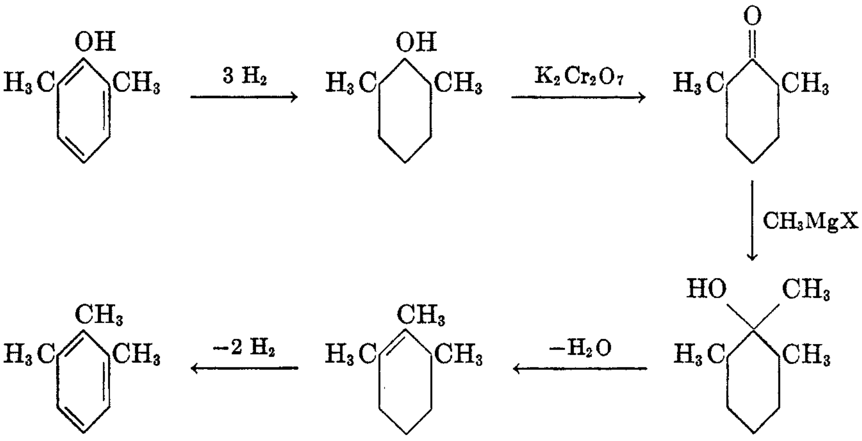
For the development of a spectrographic method of analysis of mixtures of polyalkylbenzene isomers and for a chemical study of the individual isomers and their mixtures, it was necessary to prepare authentic samples of the pure hydrocarbons in quantity for use as reference standards. In the preparation of such authentic compounds it is essential to employ a method of synthesis that avoids reactions that may possibly result in the formation of isomer mixtures. This paper describes a synthesis of the three trimethylbenzene isomers (hemimellitene, pseudocumene, and mesitylene), *o*-diethylbenzene, *m*-xylene, and 1,2,4-triethylbenzene by a method that gives the specific polyalkylbenzene isomer desired in high purity and in good yields. Although the method was used for making polyalkylbenzenes having like alkyl groups, it is equally suitable for the preparation of polyalkylbenzenes containing mixed groups, such as ethyltoluenes and ethylxylenes.

This synthesis involves a combination of known reactions which apparently has not been applied to the preparation of pure polyalkylbenzene isomers from alkylphenols as the starting materials. It comprises the following five distinct steps: (a) hydrogenation of the alkylphenol to an alkylcyclohexanol, (b) oxidation of the cyclohexanol to a ketone, (c) Grignard reaction of the ketone with alkylmagnesium halide, (d) dehydration of the tertiary alcohol to a polyalkylcyclohexene, and (e) dehydrogenation of the latter to a polyalkylbenzene. Although this method may give intermediates comprising geometric and structural isomer mixtures, the product of the final step is a single polyalkylbenzene isomer. The following equations illustrate the synthesis of 1,2,3-trimethylbenzene by this five-step method:



The yields of polyalkylbenzenes obtained by this method were, in general, better than those reported for other methods. For example, the yields of hemimellitene, pseudocumene, and mesitylene were 43, 57, and 61%, respectively, as compared with yields of 24% (1), 35–55% (2, 3, 4) and 14–33% (5, 6), respectively, reported in the literature for other synthetic methods.

TABLE I

ALKYLCYCLOHEXANOL INTERMEDIATES[a]

COMPOUND	B.P.,[b] °C. (20 mm.)	n_D^{20}	d_4^{20}	YIELD,[c] %
2,6-Dimethylcyclohexanol	76–78	1.4600	0.9231	94
3,4-Dimethylcyclohexanol	94	1.4623	.9161	94
3,5-Dimethylcyclohexanol	91	1.4550	.8977	93
2-Ethylcyclohexanol	88–90	1.4660	.9246	93
3-Methylcyclohexanol	82	1.4570	.9158	92
2,4-Diethylcyclohexanol	111.5	1.4658	—	93

[a] Probably mixtures of geometric isomers. [b] Uncorrected distillation temperatures. Based on the alkylphenol.

TABLE II

ALKYLCYCLOHEXANONE INTERMEDIATES[a]

COMPOUND	B.P.,[b] °C. (20 mm.)	n_D^{20}	d_4^{20}	YIELD,[c] %
2,6-Dimethylcyclohexanone	69	1.4470	0.9102	93
3,4-Dimethylcyclohexanone	81	1.4520	.9161	93
3,5-Dimethylcyclohexanone	75	1.4434	.8940	92
2-Ethylcyclohexanone	76	1.4522	.9190	86
3-Methylcyclohexanone	64	1.4460	.9155	88
2,4-Diethylcyclohexanone	104	1.4541	.9021	90

[a] Probably mixtures of geometric isomers. [b] Uncorrected distillation temperatures. [c] Based on the alkylcyclohexanol.

EXPERIMENTAL

Materials. The alkylphenols were, with the exceptions noted, Eastman Kodak Co. chemicals that had been upgraded by distillation and/or crystallization. 2,6-Xylenol was obtained from the Edcan Laboratories. *o*-Ethylphenol was separated from a mixture of ethylphenol isomers by fractional distillation while 2,4-diethylphenol was prepared by Clemmensen reduction of 2-acetyl-4-ethylphenol, obtained by the Fries rearrangement (7) of the acetate of *p*-ethylphenol (8). Hydrogenations were accomplished by means of a powdered nickel catalyst (9) which had been previously reduced at 425° in hydrogen. A 15% chromia-85% alumina catalyst (10) in the form of $\frac{1}{8}''$ × $\frac{1}{8}''$ pills was used for the vapor-phase dehydrogenations.

Procedure. The purified alkylphenols (*ca.* 1 kg.) in the presence of about 5% of nickel catalyst, were hydrogenated at 700–1500 p.s.i. and 150–175° in a rotating autoclave of the Ipatieff type fitted with a glass liner. The alkylcyclohexanols (Table I) were isolated from the filtered catalyzates by fractionation at 20 mm. through a 27-plate, all-glass distillation column packed with glass helices.

For oxidation of the alkylcyclohexanols to alkylcyclohexanones, Sandborn's menthol oxidation method (11) was modified by adding the acid-dichromate solution to the stirred alkylcyclohexanols (instead of the reverse) at such a rate as not to exceed a reaction temperature of 60°. This modification decreased the formation of troublesome emulsions during the subsequent extraction of the ketones with ether and also increased the yields of the ketones by 5–15%. In one instance, when the oxidized mixture remained at room temperature for a day before extraction, a low yield of only about 70–75% was realized. The alkylcyclohexanones (Table II) were purified by fractional distillation through the 27-plate column at 20 mm.

TABLE III

POLYALKYLCYCLOHEXENE INTERMEDIATES[a]

COMPOUND	B.P.,[b] °C. (740 mm.)	n_D^{20}	d_4^{20}	YIELD,[c] %
1,2,3-Trimethylcyclohexene-1	151	1.4641	0.8347	80
1,3,4-Trimethylcyclohexene-1	144	1.4546	.8124	82
1,3,5-Trimethylcyclohexene-1	139	1.4468	.7970	87
1,2-Diethylcyclohexene-1	170.5	1.4635	.8451	88
1,3-Dimethylcyclohexene-1	124.5	1.4493	.8051	88
1,2,4-Triethylcyclohexene-1	98[d]	1.4644	.8370	92

[a] Probably a mixture of geometric and structural isomers. [b] Uncorrected distillation temperatures. [c] Based on the alkylcyclohexanone. [d] Distilled at 20 mm.

TABLE IV

POLYALKYLBENZENE ISOMERS

COMPOUND	B.P.,[a] °C., (740 mm.)	n_D^{20}	d_4^{20}	F.P.,[b] °C.	PURITY,[c] MOLE-%	YIELD,[d] %	OVER-ALL YIELD,[e] %
1,2,3-Trimethylbenzene	170.5	1.5131	0.8943	−26.0	99.0	62	43
1,2,4-Trimethylbenzene	164	1.5047	.8758	−44.9	96.9	80	57
1,3,5-Trimethylbenzene	160	1.4993	.8653	−52.6	98.2	82	61
1,2-Diethylbenzene	177	1.5039	.8797	−32.7	95.7	45	32
1,3-Dimethylbenzene	135.5	1.4969	.8640	−48.2	99.1	80	57
1,2,4-Triethylbenzene	106.5[f]	1.5024	.8738	—[g]	—	53	41

[a] Uncorrected distillation temperatures. [b] Determined in a simplified freezing point apparatus (14, 15) using a copper-constantan thermocouple. [c] Computed from observed freezing points and published data (16, 17). [d] Based on the polyalkylcyclohexene. [e] Based on the starting alkylphenol. [f] Distilled at 20 mm. [g] Forms a "glass" at −78°.

The usual Grignard procedure with ketones was followed; the reaction product was hydrolyzed with dilute sulfuric acid and crushed ice. The resulting ether-extracted tertiary alcohol was usually dehydrated without prior distillation, since some of these alcohols dehydrated partially on distillation. Consequently, the yields of these tertiary alcohols were not determined. Only one of these alcohols, *1,2-diethylcyclohexanol* (b.p. 86.5° at 10 mm.; n_D^{20} 1.4691; d_4^{20} 0.9198; yield, 89%), was isolated and purified.

Dehydration of the tertiary alcohols was accomplished in nearly theoretical yields by following a procedure based on either Cook's (12) conversion of 1-naphthyldimethylcarbinol to 1-isopropenylnaphthalene or the alcohol dehydration method of Bachman and Finholt (13). In the first method the tertiary alcohol was refluxed with an ethanol-hydrochloric acid solution (about 30 ml. of concentrated acid and 750 ml. of ethanol per mole of tertiary alcohol) for 6–10 hours, the product was diluted with a large excess of water and the insoluble olefin layer was separated. In the second method the alcohol was heated with sodium bisulfate and phosphorus pentoxide (about 4 g. of sodium bisulfate and 6 g. of phosphorus pentoxide per mole of tertiary alcohol) at about 210° under such pressure that the olefin and water (but not alcohol) distilled. The resulting polyalkylcyclohexenes (Table III) were dried and fractionated in the 27-plate column at atmospheric pressure.

The polyalkylcyclohexenes were dehydrogenated to the corresponding polyalkylbenzenes in the vapor phase at 525° and 0.5 liquid hourly space velocity (volume of liquid per volume of catalyst per hour), using the equipment and general technique described for the dehydrogenation of isopropylbenzene to α-methylstyrene (10). The liquid catalyzates were distilled through the 27-plate column to effect preliminary purification of the polyalkylbenzenes. The polyalkylbenzenes (Table IV) were further purified by refluxing over sodium at atmospheric pressure for 8–10 hours and by finally fractionating at a reflux ratio of at least 10 to 1 through a 43-plate all-glass distillation column packed with glass helices. The freezing curves (Figure 1) of the polyalkylbenzenes are indicative of their purity.

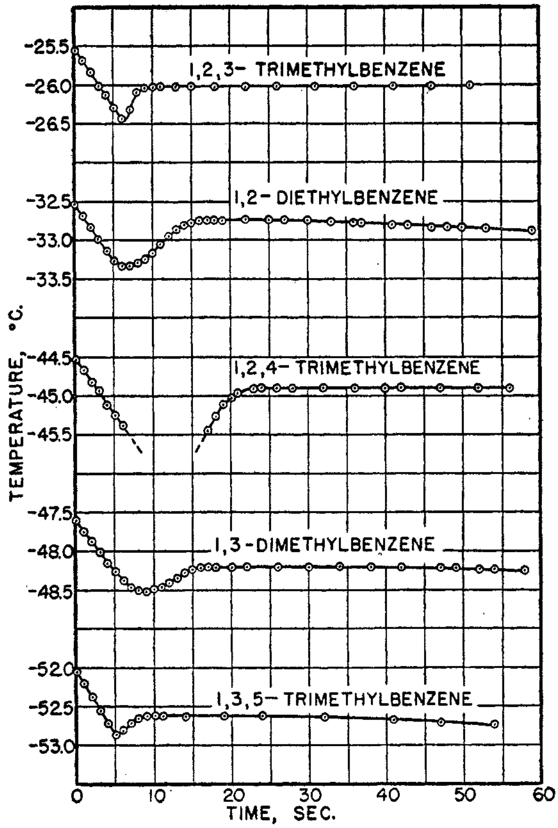


FIGURE 1. FREEZING-POINT CURVES OF POLYALKYLBENZENES

SUMMARY

1. A five-step, improved synthesis for polyalkylbenzenes was applied to the preparation of the three trimethylbenzenes (hemimellitene, pseudocumene, and mesitylene), *o*-diethylbenzene, *m*-xylene, and 1,2,4-triethylbenzene.

2. The intermediate alkylcyclohexanols, alkylcyclohexanones, and polyalkylcyclohexenes were isolated and characterized by boiling point, refractive index, and density.

PITTSBURGH 13, PA.

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