Synthesis of 1,2,3-Trimethylbenzene, 1-Ethyl-3-Methylbenzene, and *m*-Xylene

BY DEHYDROGENATION OF CORRESPONDING CYCLOHEXENE INTERMEDIATES

THAINE W. REYNOLDS, EARL R. EBERSOLE[1],
JOSEPH M. LAMBERTI, HENRY H. CHANAN[2],
AND PAUL M. ORDIN
National Advisory Committee for Aeronautics, Cleveland, Ohio

Methods of synthesis for 1-ethyl-3-methylbenzene, 1,2,3-trimethylbenzene, and *m*-xylene which are applicable to the production of 10-gallon quantities of pure hydrocarbon are described. The three compounds were prepared by the dehydrogenation of suitable cyclohexene intermediates. Physical constants and freezing or melting curves for the three aromatic hydrocarbons are reported.

IN CONJUNCTION with a program at this laboratory to study aromatic hydrocarbons as possible components of aviation gasoline, the development of methods of synthesis readily adaptable to the preparation of 10-gallon quantities of the pure hydrocarbons was necessary. This paper presents the methods developed for the large scale syntheses of 1,2,3-trimethylbenzene (*5*), 1-ethyl-3-methylbenzene (*2*), and *m*-xylene by the dehydrogenation of the corresponding cyclohexene intermediates.

1,2,3-Trimethylbenzene was prepared according to a general method outlined by Tom and Boord (*9*) in which piperylene (1,3-pentadiene) and crotonaldehyde were condensed to the 2,6- and 5,6-dimethyl-3-cyclohexene-1-carboxaldehydes, followed by hydrogenation to the 2,3- and 2,6-dimethylcyclohexylcarbinols, dehydration to the 1,2,3-trimethylcyclohexenes, and dehydrogenation to the 1,2,3-trimethylbenzene.

1-Ethyl-3-methylbenzene and *m*-xylene were synthesized through the preparation of intermediate cyclohexyl alcohols which were dehydrated to the corresponding cyclohexenes and then dehydrogenated to the aromatic hydrocarbons.

In the synthesis of 1-ethyl-3-methylbenzene the intermediate 1-ethyl-3-methyl-1-cyclohexanol was prepared by hydrogenation of commercial *m*-cresol to 3-methyl-1-cyclohexanol, oxidation of the alcohol to 3-methyl-1-cyclohexanone, and condensation of the ketone with ethylmagnesium bromide. In the synthesis of *m*-xylene the intermediate 3,5-dimethyl-1-cyclohexanol was prepared by hydrogenation of commercial 3,5-dimethyl-1-hydroxybenzene (3,5-xylenol, 3,5-dimethylphenol).

Table I. Physical Constants

Aromatic Hydrocarbon	F.P., ° C.	B.P., 760 Mm., ° C.	Density, G./Ml. at 20° C.	n_D^{20}	Literature Cited
1,2,3-Trimethylbenzene	−25.41	176.09	0.8944	1.5138	This work
	−25.75[a]	.....	0.8944	1.5138	(*4*)
	−25.41	.....	0.8944	1.5130	(*7*)
	−25.450	176.15	0.8950	1.5139	(*1*)
	−25.375[b]	.....	.....	.....	(*8*)
1-Ethyl-3-methylbenzene	−95.62[c]	161.25	0.8644	1.4965	This work
	−95.55	161.30	0.8646	1.4965	(*1*)
	−95.81[d]	.....	0.8648	1.4965	(*4*)
m-Xylene	−47.91	139.11	0.8642	1.4972	This work
	−47.872	139.104	0.86412	1.49715	(*1*)

[a] Calcd. purity, 99.4 ± 0.2 mole %.
[b] Freezing point calculated for 0.0% impurity.
[c] Melting point.
[d] Calcd. purity, 99.2 ± 0.3 mole %.

In the large scale preparation of these compounds several runs were made at each stage before the next step was begun. For this reason typical quantities of reactants used are given under experimental details for the stepwise synthesis of the hydrocarbons.

Physical constants of the 1,2,3-trimethylbenzene, 1-ethyl-3-methylbenzene, and *m*-xylene are listed in Table I together with selected literature values. The properties were obtained by methods previously described (*3*). Freezing curves for 1,2,3-trimethylbenzene and *m*-xylene, and a melting curve for 1-ethyl-3-methylbenzene are presented in Figure 1.

1,2,3-TRIMETHYLBENZENE

Condensation of Crotonaldehyde and Piperylene. Commercial piperylene, 5.6 kg. (82.4 moles), and commercial crotonaldehyde, 4.5 kg. (64.3 moles), were condensed in a 20-liter rocking autoclave at 200° C. for 5 hours. Pressures developed in the autoclave were usually of the order of 400 pounds per square inch and dropped to 250 pounds per square inch at the end of the condensation. However, in some runs pressures of 2000 pounds per square inch developed. No explanation of this behavior can be given as the temperature remained at 200° ± 5° C.

The reaction mixture was stripped at atmospheric pressure and the fraction (4.8 kg., 54% of theoretical) boiling between 170° and 190° C. was taken as crude 2,6- and 5,6-dimethyl-3-cyclohexene-1-carboxaldehydes. No attempt was made to separate the piperylene dimer from the crude product at this stage of the synthesis.

Hydrogenation of 2,6- and 5,6-Dimethyl-3-cyclohexene-1-carboxaldehydes. The crude aldehyde mixture, 9.1 kg. (66.0 moles), was hydrogenated with 454 grams of nickel-on-kieselguhr in the 20-liter autoclave at 120° C. and a maximum pressure of 1800 pounds per square inch in 10 to 12 hours. The hydrogenated product amounted to 9.1 kg. (97% of the theoretical).

A small portion of the product was distilled and gave 10% of low-boiling material, 20% of hydrogenated piperylene dimer and 70% of the desired 2,3- and 2,6-dimethylcyclohexylcarbinols distilling at 207° to 215° C. at atmospheric pressure.

Dehydration of 2,3- and 2,6-Dimethylcyclohexylcar-

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[1] Present address, Pocatello, Idaho.
[2] Present address, Farchan Research Laboratories, Cleveland, Ohio.

BINOLS. The crude alcohol mixture, 8.3 kg. (58.5 moles), was passed through a 2-inch by 10-foot column packed with alumina catalyst at 380° to 400° C. over a period of 10 hours. The resulting hydrocarbon mixture (6.6 kg.) on distillation through a 2-inch by 12-foot helix-packed column of forty theoretical plates gave 4.2 kg. (58% of theoretical) of trimethylcyclohexene isomers boiling at 146° to 156° C. The hydrogenated piperylene dimer (boiling point approximately 172° C.) was removed by the fractionation.

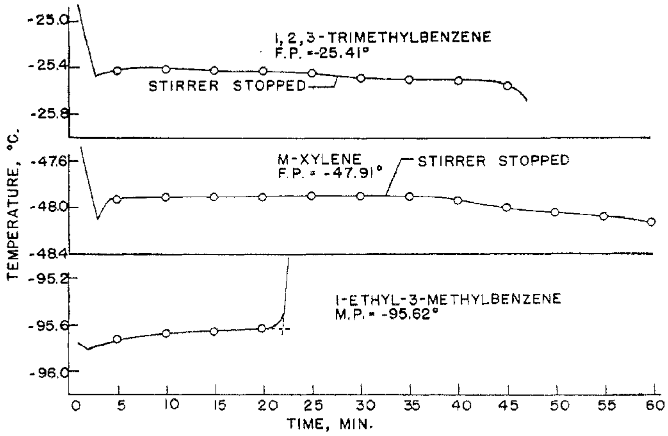

Figure 1. Time-Temperature Freezing or Melting Curves of Three Aromatic Hydrocarbons

Dehydrogenation of Trimethylcyclohexene Isomers. The trimethylcyclohexene isomers, 19.2 kg. (155.0 moles), were passed through a 2-inch by 10-foot column packed with commercial chrome-alumina catalyst (0.125-inch pellets, approximately 11 to 13% chromic oxide) at 450° to 470° C. over a period of 65 hours. The product obtained (17.3 kg.) was fractionated through a 100-theoretical plate column and gave 14.7 kg. (79% of theoretical) of 1,2,3-trimethylbenzene (24% over-all yield). The material was then stripped over sodium to remove the slight yellow color of the product.

1-ETHYL-3-METHYLBENZENE

Hydrogenation of *m*-Cresol. Ninety-eight per cent *m*-cresol, 10.4 kg. (96.3 moles), was completely hydrogenated with 250 grams of nickel-on-kieselguhr to 3-methyl-1-cyclohexanol in the 20-liter autoclave at 160° C. and a maximum pressure of 1800 pounds per square inch in 12 hours.

Oxidation of 3-Methyl-1-cyclohexanol. Approximately 35 gallons of water, 14.1 liters of concentrated sulfuric acid, and 31.7 kg. (106.4 moles) of sodium dichromate were mixed with stirring in a 100-gallon glass-lined reactor. The mixture was heated to 55° to 60° C., 17.2 kg. (151 moles) of 3-methyl-1-cyclohexanol were added slowly over a period of 3 hours and stirring was continued for an additional 15 hours. The mixture was steam distilled and gave 10.6 kg. (63% of theoretical) of crude 3-methyl-1-cyclohexanone. Analysis of a sample of this crude product by the acetylation method of Shaefer (*6*) indicated that approximately 20% of the material was unconverted 3-methyl-1-cyclohexanol. An attempt to purify the 3-methyl-1-cyclohexanone by fractional distillation was unsuccessful, so the crude ketone, dried over alumina, was used in the condensation with the Grignard reagent.

Preparation of 1-Ethyl-3-methyl-1-cyclohexanol. Ethylmagnesium bromide was prepared in a 100-gallon glass-lined reactor from 10 kg. (412 moles) of magnesium turnings and 46.4 kg. (426 moles) of ethyl bromide in 25 gallons of ethyl ether. Crude 3-methyl-1-cyclohexanone, 31.8 kg. (284 moles), in 10 gallons of ether was added to the ethylmagnesium bromide over a period of 6 hours. The mixture was stirred overnight and hydrolyzed with dilute hydrochloric acid. The ether layer was washed once with a sodium bicarbonate solution and twice with water. The ether was stripped from the mixture and the residual oil distilled under reduced pressure. The material (31.8 kg., 79% of theoretical) distilling at 95° to 120° C. at 50 mm. was collected as crude 1-ethyl-3-methyl-1-cyclohexanol.

Dehydration of 1-Ethyl-3-methyl-1-cyclohexanol. The crude alcohol, 31.8 kg. (224 moles), was dehydrated by one pass through alumina catalyst at 250° to 270° C. over a period of 18 hours in the column previously described and gave 27.5 kg. of unsaturated hydrocarbons. The mixture of olefins was fractionated through the 12-foot column and gave 71% (70% of theoretical) of isomeric 1-ethyl-3-methylcyclohexenes and approximately 20% of methylcyclohexenes. The amount of methylcyclohexenes agreed well with the amount of 3-methyl-1-cyclohexanol found by analysis in the oxidation product.

Dehydrogenation of the 1-Ethyl-3-methylcyclohexenes. The isomeric 1-ethyl-3-methylcyclohexenes, 19.2 kg. (155 moles), were dehydrogenated by one pass through chrome-alumina catalyst at 450° to 470° C. over a period of 60 hours. The product obtained was fractionated through a 100-theoretical plate column and the fraction from 160° to 161° C. was combined and refluxed over sodium to remove the yellow color. Redistillation of this material gave 15.3 kg. (82% of theoretical) of 1-ethyl-3-methylbenzene (28% over-all yield).

m-XYLENE

Hydrogenation of 3,5-Dimethylphenol. Commercial 3,5-dimethylphenol (3,5-xylenol) melting point 58° to 62° C., 5.3 kg. (43.5 moles), was hydrogenated with 80 grams of Raney nickel in the 20-liter autoclave at 200° C. and a maximum pressure of 1800 pounds per square inch over a period of 5 hours. The hydrogenated product was stripped and gave 5.2 kg. (93% of theoretical) of 3,5-dimethyl-1-cyclohexanol boiling at 180° to 190° C.

Dehydration of 3,5-Dimethyl-1-cyclohexanol. The 3,5-dimethyl-1-cyclohexanol, 8.7 kg. (68 moles) was dehydrated by one pass through alumina catalyst at 350° to 370° C. over a period of 10 hours. The product was stripped and gave 6.6 kg. (88% of theoretical) of 2,4-dimethyl-1-cyclohexene distilling at 120° to 127° C.

Dehydrogenation of 2,4-Dimethyl-1-cyclohexene. The 2,4-dimethyl-1-cyclohexene, 6.4 kg. (58.2 moles), was dehydrogenated by two passes over chrome-alumina catalyst at 450° to 470° C. over a total period of 29 hours. The product obtained was fractionated through a 100-theoretical plate column and gave 5.4 kg. (88% of theoretical) of *m*-xylene (72% over-all yield).

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