



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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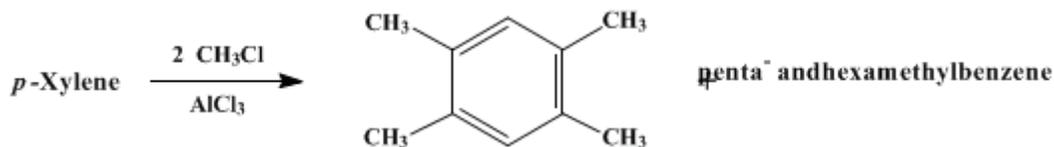
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.248 (1943); Vol. 10, p.32 (1930).

DURENE

[By-products, penta- and hexamethylbenzene]



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1. Procedure

A 5-l. flask, mounted on a steam bath, is fitted with a wide (Note 1) inlet tube reaching to the bottom of the flask, a reflux condenser, and a delivery tube running from the top of the reflux condenser and reaching to the bottom of a heavy glass cylinder containing a column of mercury about 10 cm. high. All stoppers and joints of the apparatus must fit tightly and be wired, as the reaction is carried out under a slight pressure. In the flask are placed 3180 g. (3.7 l., 30 moles) of xylene (Note 2) and 1 kg. of anhydrous aluminum chloride (Note 2). The inlet tube of the flask is then connected to a tank of methyl chloride or to a methyl chloride generator (Note 3), the steam is turned on in the bath, and a fairly rapid stream of methyl chloride is passed into the mixture (Note 4). At first there will be a rapid absorption, and the stream of gas must be regulated so that the mercury in the pressure tube does not suck back. The hydrogen chloride formed may be conveniently disposed of by a trap. As the reaction slows down, the pressure increases until both hydrogen chloride and methyl chloride begin to escape through the mercury. At this point the current of incoming gas should be cut down so that undue loss of methyl chloride is avoided. About one hundred hours is required for the completion of the reaction (Note 5).

When the reaction is completed, the steam is turned off and the flask is disconnected and loosely stoppered. After standing overnight the reaction mixture is decomposed by pouring it slowly onto 5 kg. of chopped ice. The greenish oil which separates from the aqueous layer is removed, dried over calcium chloride, filtered and fractionated twice, using a round-bottomed flask fitted with an efficient column and an air condenser (Note 6).

The fractions are cut as follows:

Fraction	Temp. Range	Distillate	Yield, g.
I and II	Up to 150°	Benzene, xylene	Little
III	150 to 180	Trimethyl benzenes	570
IV	180 to 205	Tetramethyl benzenes	2075
V	Above 205	Mostly pentamethylbenzene	815

Typical yields of the various fractions are given in the table; they may vary 10 to 20 per cent from these figures, owing to slight differences in procedure and materials, and especially to differences in the quality of the aluminum chloride employed. The more efficient the aluminum chloride, the greater is the percentage of the higher-boiling fractions.

The tetramethylbenzene fraction (IV) is rich in durene, which may be frozen out and filtered because of its relatively high melting point (80°). To isolate the durene, fraction IV is thoroughly chilled in an ice-calcium chloride pack, and filtered through a cold filter (Note 7), using good suction and pressing down the solid compactly. When no more liquid drips through the cold filter, the filtration apparatus is allowed to come gradually to room temperature (Note 7) and the suction is continued as

long as any liquid drips through, after which the solid is removed and bottled. The yield is 540 to 610 g.

Fraction III may be methylated to the [tetramethylbenzene](#) stage by heating on the steam bath with 100 g. of anhydrous [aluminum chloride](#) and passing in 225 g. of [methyl chloride](#). The filtrates from the [durene](#) likewise yield more [durene](#) when heated on the steam bath with 50 g. of [aluminum chloride](#). The products are worked up in the usual way; that is, they are decomposed by pouring onto twice their weight of chopped ice, separated from the aqueous layer, fractionated twice, and the [durene](#) frozen out as before. By conducting one methylation of the [trimethylbenzene](#) fraction, and one treatment of the [durene](#) filtrates, the combined yield of crude [durene](#) will average 1 to 1.4 kg. (25–35 per cent of the theoretical amount based on the original 30 moles of [xylene](#)).

To purify the [durene](#), 200 g. of the crude product is placed in a 1-l. round-bottomed flask fitted with a reflux condenser, and melted in a water bath at 95°; 200 cc. of warm (50°) 95 per cent [ethyl alcohol](#) is then added through the top of the condenser, and the mixture is carefully heated until homogeneous. The solution is filtered on a hot-water funnel, allowed to stand tightly covered ([Note 8](#)) in a fairly warm place (35°) overnight, cooled to about 0°, and filtered on a suction filter. The product (about 169 g.) melts at 74–78°. A second recrystallization yields 149 g. melting at 77–79°. A third recrystallization yields 140 g. having a melting point of 79–80°. The alcoholic filtrates are fractionated, and the crude [durene](#) obtained is worked over with the isomers of [durene](#).

Pentamethylbenzene.—Fraction V, and [xylene](#) which is methylated beyond the [tetramethylbenzene](#) stage, may be worked up for [pentamethylbenzene](#). If [xylene](#) is to be methylated to obtain [pentamethylbenzene](#), one more mole of [methyl chloride](#) should be used, and the mixture of [xylene](#) and anhydrous [aluminum chloride](#) should be methylated for one hundred and ten hours instead of the one hundred used for [durene](#). Otherwise the procedure is exactly the same as for [durene](#). The reaction mixture is decomposed and fractionated in the usual way, and the material boiling above 205° (fraction V) is separated into three fractions:

Fraction	Temperature Range	
VI	205–215°	Tetra- and pentamethylbenzene
VII	215–235	Mostly pentamethylbenzene
VIII	Residue above 235	Hexamethylbenzene and tars

The [pentamethylbenzene](#) obtained in this way is nearly pure, and one recrystallization from 95 per cent [alcohol](#) or from a mixture of equal volumes of alcohol and [benzene](#) gives a snow-white product, but the product generally melts over too wide a range for practical purposes. However, if fraction VII is refractionated under diminished pressure and the fraction boiling at 123–133°/22 mm. (practically all at 127–129°) is collected and recrystallized as in the following paragraph, a product melting quite sharply at 52° (true m.p. 53°) is obtained.

Six hundred grams of crude [pentamethylbenzene](#) is heated to 100° and poured slowly with stirring into 1 l. of 95 per cent [ethyl alcohol](#) heated to 70° in a 2-l. beaker, and allowed to stand overnight at a temperature of approximately 30°. The crystals formed are collected on a suction filter and dried at room temperature overnight on a porous plate. The yield is about 250 g. ([Note 9](#)).

Hexamethylbenzene.—Fraction VIII is fractionated in 250-cc. batches in a Claisen flask at 20 mm. pressure, the following fractions being collected:

Fraction	Temperature Range	
IX	80–110°	Mostly tetra- and pentamethyl benzenes
X	110–135	Mostly pentamethylbenzene
XI	135–170	Hexamethylbenzene

This fractionation may be carried out in an ordinary Claisen flask, but there is some difficulty in maintaining the desired pressure owing to the solvent action of the hydrocarbons on the rubber stopper. This difficulty may be avoided by the use of a Claisen flask with very long necks and a wide side tube. The material should be distilled fast enough to prevent it from solidifying in the column and side tube. Prolonged heating of [hexamethylbenzene](#) also causes a considerable amount of decomposition to tars.

The method for the production of large amounts of [hexamethylbenzene](#) is the rapid methylation of [pentamethylbenzene](#) or the [durene](#) filtrates. A mixture of 378 g. of [pentamethylbenzene](#) and 200 g. of anhydrous [aluminum chloride](#) is heated on an oil bath at 190–200° and a rapid stream of dry [methyl chloride](#) is bubbled through for three to four hours, using the same apparatus as for the preparation of [durene](#). The mixture is allowed to stand overnight at room temperature. One liter of hot [xylene](#) is added to dissolve the solidified material, and the reaction mixture is decomposed by pouring it onto 3 kg. of chopped ice. The resulting oil is separated, and the [xylene](#) and other low-boiling material are removed by distillation under reduced pressure (Note 10). The fractions are divided as above. Two refractionations and two recrystallizations (Note 11) give 98–121 g. of white crystals, melting at 157–161° (Note 12).

2. Notes

1. The inner tube of a condenser makes a good inlet tube. It should be placed so that the wide end is inside the large flask.
2. The [xylene](#) should be a good, colorless laboratory grade, b.p. 135–140°. Any moisture present may be removed by distilling and discarding the first 10 per cent of the distillate. The best [aluminum chloride](#) available should be used, for the methylation is very unsatisfactory if the catalyst is of an inferior grade. It should be in small pieces but need not be powdered.
3. The methyl chloride generator consists of a 5-l. flask resting on a sand bath and fitted with a reflux condenser, with a delivery tube running from the top of the condenser to a train of wash bottles, two containing water and two containing concentrated [sulfuric acid](#), with three safety bottles, one at each end of the train, and one between the water and sulfuric acid bottles. To charge for about 45 moles (theoretical) of [methyl chloride](#): 200 g. of water and 2.2 kg. (1.2 l.) of concentrated [sulfuric acid](#) are placed in the flask, and 1.4 kg. (1760 cc.) of [methyl alcohol](#) is added, with cooling, at such a rate that the temperature does not rise above 70°. Then 2.4 kg. of [sodium chloride](#) is added, the apparatus is tightly connected, and the flask is heated on the sand bath so that the gas is evolved at a fairly rapid rate. It has been found in practice that, using materials of the commercial grade, the yield of [methyl chloride](#) is about 55 to 65 per cent of the theoretical amount, so that about double the calculated quantities must be used. This means that the generator has to be charged three times in order to convert 30 moles of [xylene](#) to [tetramethylbenzene](#). If a tank of methyl chloride is available, 65–70 moles of [methyl chloride](#) should be used for this same amount of [xylene](#). The tank should be weighed before starting and the reaction stopped when the tank has lost the proper amount in weight.
4. Experiments have shown that the rapid current of [methyl chloride](#) furnishes sufficient stirring.
5. The normal time of one hundred hours can be shortened by increasing the amount of [aluminum chloride](#). The product is then very viscous, however, and rather difficult to handle in large amounts.
6. Two systematic fractionations (not redistillations) with a good column are absolutely necessary in order to obtain good separations. The more efficient the column the better.
7. The material should be filtered through a large Büchner funnel, which is immersed in a freezing mixture as long as any liquid drips through. It is stated in the literature that the first filtrate obtained in this way is mostly isodurene (1,2,3,5-), whereas the second filtrate, obtained as the material warms slowly to room temperature, is pseudodurene or prehnitene (1,2,3,4-), m.p. -4°.
8. [Durene](#), being quite volatile, should not be allowed to remain exposed to the air any longer than necessary. It is also quite volatile with alcohol, and the mother liquors resulting from the recrystallizations should be distilled: the alcoholic distillate is used for further recrystallizations, and the residues may be worked up for [durene](#) by heating with [aluminum chloride](#).
9. The melting point of [pentamethylbenzene](#) is only slightly affected by recrystallization, because most of the impurity is [hexamethylbenzene](#), which can be removed only by fractionation.

10. **Hexamethylbenzene** decomposes when heated very strongly for any length of time. Therefore better results are obtained if the distillations are carried out under reduced pressure.

11. Small amounts of impurities greatly influence the melting point of **hexamethylbenzene**, and several recrystallizations of a fraction of close boiling range are necessary in order to prepare a sharply melting product.

12. Small amounts (25 g. or less) of **hexamethylbenzene** which is nearly pure are best recrystallized from **ethyl alcohol**. It requires about 600 cc. of boiling **alcohol** to dissolve 25 g., but on cooling 20 g. of pure product will result. **Ether** and **benzene** dissolve the substance much more readily, and larger amounts of materials are best recrystallized from either of these solvents, or from a mixture of one of them with alcohol. One hundred and twenty-five grams of the **hexamethylbenzene** distillate which has been refractionated is melted and poured slowly with stirring into 1.5 l. of 95 per cent **alcohol**. A small amount which remains undissolved may be brought into solution by adding about 300 cc. of hot **benzene**, the beaker being heated on a steam bath and the mixture stirred constantly until all is dissolved. The solution is allowed to stand overnight at approximately 25°. The crystals are filtered by suction and washed with enough 95 per cent **alcohol** to moisten thoroughly (about 25 cc.). After drying, the crystals weigh approximately 112 g. and melt at 155–159°.

3. Discussion

Durene, **pentamethylbenzene** and **hexamethylbenzene** have usually been prepared from benzene or one of its methylated derivatives by the Friedel-Crafts synthesis.¹ **Durene** has been made from bromine derivatives of methylated benzenes by the Fittig reaction.² It has been obtained in 20 per cent yield by passing **methyl alcohol** and **acetone** vapors over heated **aluminum oxide**³ and in 45 per cent yield by the chloromethylation of **xylene** and reduction of the chloromethylated products.⁴ **Hexamethylbenzene** has been obtained by the action of **zinc chloride** on **methyl alcohol**⁵ or on **acetone**.⁶ The method described in the procedure above has been published.⁷

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 254
- Org. Syn. Coll. Vol. 2, 360
- Org. Syn. Coll. Vol. 6, 700

References and Notes

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2. Jannasch and Fittig, Z. Chem. **13**, 161 (1870); Jannasch, Ber. **7**, 692 (1874); **10**, 1354 (1877).
3. Reckleben and Scheiber, *ibid.* **46**, 2363 (1913).
4. v. Braun and Nelles, *ibid.* **67**, 1098 (1934).
5. LeBel and Greene, Compt. rend. **87**, 260 (1878).
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Appendix

Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

penta- and hexamethylbenzene

Tetra- and pentamethylbenzene
tetra- and pentamethyl benzenes
isodurene (1,2,3,5-)
pseudodurene or prehnitene (1,2,3,4-)
benzene or one of its methylated derivatives

ethyl alcohol,
alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

Benzene (71-43-2)

methyl alcohol (67-56-1)

ether (60-29-7)

sodium chloride (7647-14-5)

mercury (7439-97-6)

methyl chloride (74-87-3)

acetone (67-64-1)

aluminum chloride (3495-54-3)

zinc chloride (7646-85-7)

xylene (106-42-3)

Durene (95-93-2)

Hexamethylbenzene (87-85-4)

Pentamethylbenzene (700-12-9)

tetramethylbenzene (488-23-3)

trimethylbenzene (526-73-8)

aluminum oxide (1344-28-1)

