



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

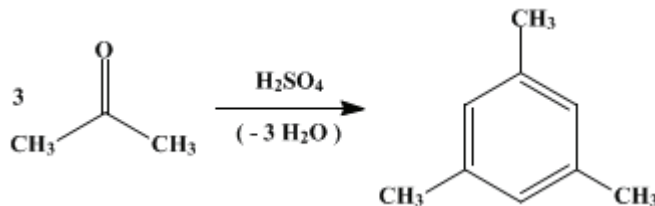
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.341 (1941); Vol. 2, p.41 (1922).*

## MESITYLENE



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### 1. Procedure

In a 12-l. round-bottomed flask, arranged so that the contents can be mechanically stirred, is placed 4600 g. (5750 cc., 79 moles) of technical acetone. The flask is then well cooled with an ice and salt mixture, until the temperature of the acetone is between  $0^\circ$  and  $5^\circ$  (Note 1). Stirring is started, and 4160 cc. of commercial concentrated sulfuric acid is run in at such a rate that the temperature of the mixture never rises above about  $10^\circ$ . This addition is accomplished in about five to ten hours. The stirring is continued for three to four hours longer, while the flask still remains immersed in the original freezing mixture to which no further amount of ice is added. The mixture is then allowed to stand at room temperature for eighteen to twenty-four hours (Note 2).

A 5-l. round-bottomed flask is fitted with a rubber stopper or a cork stopper coated with pitch (Note 3), carrying two glass tubes, one of which (for the entrance of steam) reaches to the bottom of the flask, while the other extends into the open end of a condenser set for downward distillation. The stopper should be wired into the flask. The glass delivery tube into the condenser should not be less than a 12-mm. bore, and the condenser should consist of two 120-cm. water-cooled condensers attached end to end. To the end of the condensing system, an adapter is attached, the small end of which is at least 8 mm. in bore and is fitted tightly into a stopper in a 2-l. suction flask. To the side arm of the suction flask is attached a tube leading to an exhaust fan, in order to carry away the gases which are evolved during the subsequent distillation (Note 4). In the 5-l. flask is placed about 2 l. of the sulfuric acid-acetone reaction mixture (Note 5), and the flask is then heated with a free flame and shaken occasionally. A reaction starts at the end of about fifteen or twenty minutes, as shown by the evolution of gas (chiefly sulfur dioxide), and is allowed to run for about three minutes (Note 6). At the end of this time, a current of steam is passed in and continued for about three minutes. During this period a large proportion of the mesitylene distils and should be kept separate from the subsequent distillate. The steam distillation is continued at such a rate that about 800 cc. distils in twenty-five to thirty minutes and is collected as a second distillate. At the end of this time, the distillation is stopped, the water poured off from the distilling flask, and the tarry material emptied out while hot into waste jars.

The total amount of original reaction mixture requires five distillations similar to the one just described. The first distillates from each of the five distillations are mixed, and the layer of mesitylene is separated from the water. This is shaken with sodium hydroxide solution until no more odor of sulfur dioxide is noticeable, then washed twice with water and distilled. The first portion of the distillate consists of a small amount of water and mesitylene and is added to the combined second distillates. The fraction which distils up to  $210^\circ$  is saved. The second distillates are combined, washed in the same way as the first, and then distilled; the fraction which distils up to  $210^\circ$  is combined with the corresponding fraction from the first distillates.

These combined fractions (which boil up to  $210^\circ$ ) and 15 g. of sodium are placed in a 2-l. distilling flask, the side arm of which is closed with a rubber tube and pinchcock and which is fitted with a reflux condenser. The mixture is heated just below the boiling point for about three hours, during which time the impurities are attacked by the molten sodium, and a gelatinous, reddish mass forms. The reflux condenser is now removed and one set for downward distillation is attached to the side arm. The

mixture is distilled and about two-thirds of the liquid removed in this way. The residue is cooled, the liquid poured off from solid material and distilled up to 210°.

The distillates from the sodium treatment are now fractionated with a good column (at least 30 cm. long), and the portion which boils at 163–167° is collected. The yield of this fraction varies from 430 to 470 g. (13–15 per cent of the theoretical amount), but very often will be as high as 500 g., and has reached, in certain experiments, 600 g. (Note 7) and (Note 8).

## 2. Notes

1. The cooling of the reaction flask must be very efficient, a 10–15 cm. blanket of a thorough mixture of ice and salt being used. If this precaution is not employed, the time for the addition of the sulfuric acid is greatly increased, provided the temperature of the reaction mixture is still kept within the limits mentioned.

2. While the original reaction mixture is standing, the temperature gradually rises to 40° or 50° in the course of six to ten hours, and then gradually cools off again. It is probable that at the end of this time (when the flask has cooled again) the reaction mixture could be distilled with nearly as good a yield as is obtained after standing eighteen to twenty-four hours.

3. If a cork is used for the steam distillation of the reaction mixture of acetone and sulfuric acid, it should be coated well with pitch and wired into the flask. This is necessary because the vapors of the reaction mixture attack an ordinary cork very badly, and soften it so much that it is necessary to rewire it to prevent it from slipping out. A rubber stopper is satisfactory and may be used in several runs.

4. The evolved gases may be disposed of by means of a gas-absorption trap (Fig. 7 on p. 97). However, the trap may be inadequate when large volumes of gas are liberated in a short time.

5. The evolution of gas is so vigorous that it is not possible to distil more than 2 l. of the original reaction mixture at one time in the apparatus described. The connections on the apparatus, in which the mesitylene is obtained from the crude reaction mixture, should be tight, since the fumes evolved during the heating are very irritating.

6. The product which distils during the initial heating and the three minutes of steam distillation is mainly satisfactory material; the rest of the steam distillation yields only a small amount of pure product. The two portions of the distillate are, therefore, kept separate, since the second distillate always contains a considerable amount of high-boiling product which tends to cause emulsification of the alkali in the purification. No recovery of acetone is made.

The mechanism of the reaction is undoubtedly as follows: when the sulfuric acid and acetone are in contact for long periods of time, several molecules of the acetone condense to form aldol condensation products. These do not break down into mesitylene until the temperature is raised in the second part of the experiment.

7. The wide variation in yields which is mentioned in the experimental part is probably due to a slight change in the grade of the chemicals which are used in this preparation. The average yield of a large number of runs made in recent years is 510 g. This improvement is due in part to a better grade of technical acetone.

8. An alternative method for the purification of the crude material has been employed by the checkers, and yields a slightly higher-grade product than the sodium method. It is as follows:

The combined distillates are treated with an equal volume of concentrated sulfuric acid and the solution warmed on a water bath for one hour, under a reflux condenser, with occasional shaking or, better, with mechanical stirring. Upon cooling, mesitylenesulfonic acid crystallizes and the unsulfonated material remains as an oil on the surface. The mixture is filtered through flannel or a filter plate, and the crystals are washed with 60–70 per cent sulfuric acid. The oily layer is again warmed with sulfuric acid, as before. The acid and oily filtrates from the two sulfuric acid treatments are steam distilled, and the distillate combined with the next batch of material. The crystals are mixed with 2 l. of 15 per cent hydrochloric acid and heated under a reflux condenser for two to three hours. The reaction mixture is now steam distilled, the mesitylene separated, dried over calcium chloride and fractionated; the portion which boils at 163–167° is collected.

## 3. Discussion

Mesitylene can be prepared by the action of sulfuric acid<sup>1</sup> on acetone; by the action of hydrochloric

acid on acetone, under pressure and at temperatures varying from 100 to 200°;<sup>2</sup> by the condensation of acetone using silica gel or alumina as a catalyst;<sup>3</sup> and by the methylation of benzene, toluene, or *m*-xylene.<sup>4</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 95
- Org. Syn. Coll. Vol. 2, 449

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## References and Notes

1. Kane, J. prakt. Chem. (1) **15**, 129 (1838); Fitting, Ann. **141**, 131 (1867); Fittig and Brueckner, Ann. **147**, 43 (1868); Varenne, Bull. soc. chim. (2) **40**, 266 (1883); Orndorff and Young, Am. Chem. J. **15**, 256 (1893); Käster and Stallberg, Ann. **278**, 210 (1893); Noyes, Am. Chem. J. **20**, 807 (1898); Tistchenko, Bull. soc. chim. **47**, 1137 (1930).
  2. Ipatiev, Dolgov, and Wolnow, Ber. **63**, 3072 (1930); Sucharda and Kuczynski, Roczniki Chem. **14**, 1182 (1934) [C. A. **29**, 6214 (1935)].
  3. Mitchell and Reid, J. Am. Chem. Soc. **53**, 330 (1931); I. G. Farbenind. A.-G., Ger. pat. 597,059 [C. A. **28**, 5082 (1934)].
  4. Smith and Cass, J. Am. Chem. Soc. **54**, 1603 (1932); Norris and Ingraham, *ibid.* **60**, 1422 (1938); Norris and Vaala, *ibid.* **61**, 2131 (1939); Norris and Arthur Jr., *ibid.* **62**, 874 (1940).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alumina

silica gel

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium hydroxide (1310-73-2)

sulfur dioxide (7446-09-5)

acetone (67-64-1)

toluene (108-88-3)

sodium (13966-32-0)

Mesitylene (108-67-8)

sulfuric acid-acetone

mesitylenesulfonic acid

m-xylene (108-38-3)

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