



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). 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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

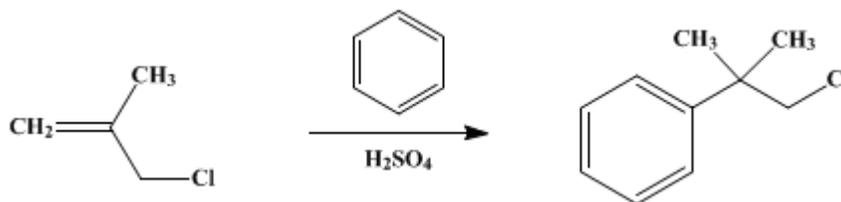
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.702 (1963); Vol. 32, p.90 (1952).

NEOPHYL CHLORIDE

[Benzene, (2-chloro-1,1-dimethylethyl)-]



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1. Procedure

In a 2-l. three-necked flask equipped with a mechanical stirrer, thermometer, and dropping funnel are placed 500 g. (570 ml., 6.4 moles) of [benzene](#) ([Note 1](#)) and 34.6 g. (18.8 ml.) of concentrated [sulfuric acid](#) (sp. gr. 1.84). The resultant mixture is brought to 20°. To this is added dropwise 201 g. (219 ml., 2.22 moles) of [methallyl chloride](#) ([Note 2](#)) over a period of 12 hours, during which time vigorous stirring is maintained and the temperature is kept at 20° with the aid of a water bath. The mixture, which becomes an amber color, is stirred for an additional 12 hours.

The reaction mixture is then transferred to a 1-l. separatory funnel, and the [sulfuric acid](#) layer is removed. The remaining [benzene](#) solution is then washed with four 200-ml. portions of distilled water ([Note 3](#)). In this step the amber color disappears and the liquid becomes colorless. The [benzene](#) solution is dried with anhydrous [sodium sulfate](#) and transferred to a 1-l. distilling flask. The [benzene](#) is removed by distillation under a pressure of about 45 mm. The liquid residue is poured into a 500-ml. flask and distilled through a 40-cm. Vigreux column under reduced pressure. The yield of [neophyl chloride](#) boiling at 97–98° /10 mm. is 262–275 g. (70–73%) ([Note 4](#)) and ([Note 5](#)); n_D^{20} 1.5250.

2. Notes

1. The [benzene](#) is purified by washing with three 80-ml. portions of concentrated [sulfuric acid](#) and then drying with anhydrous [sodium sulfate](#). It is used directly after removal of the [sodium sulfate](#) by filtration.
2. The [methallyl chloride](#) used was a redistilled commercial sample and had the following properties: b.p. 71–72° /760 mm., n_D^{20} 1.4274, d_4^{20} 0.918.
3. To ensure good results it is necessary to remove all of the [sulfuric acid](#) by washing the mixture thoroughly with water. The final washing should be neutral to litmus.
4. If the residue in the distilling flask is dissolved in [ether](#), treated with activated [carbon](#), and evaporated to dryness, the solid so obtained can be recrystallized from about 25 ml. of 95% [ethanol](#) to give 10 g. (2.7%) of *p*-di(chloro-*tert*-butyl)benzene; m.p. 54.5–55.0°.
5. In a run in which the temperature was kept at 10–15° during the addition of [methallyl chloride](#), the [methallyl chloride](#) was added over a period of 1 hour. Stirring was continued for 1 hour, and the reaction mixture was worked up as described above to give a 53% yield.

3. Discussion

(Chloro-*tert*-butyl)benzene has been prepared by the direct chlorination of *tert*-butylbenzene in the presence of strong light;² by chlorination of *tert*-butylbenzene with [sulfuryl chloride](#) in the presence of [benzoyl peroxide](#);³ by the action of [thionyl chloride](#) on the corresponding alcohol;⁴ and by the hydrogen fluoride-catalyzed alkylation of [benzene](#) with [methallyl chloride](#).⁵ The sulfuric acid-catalyzed alkylation described here is based on the procedure of Whitmore, Weisgerber, and Shabica.⁶ A variation using a shorter reaction time has also been described.⁷

References and Notes

1. State University of Iowa, Iowa City, Iowa.
 2. Truce, McBee, and Alfieri, *J. Am. Chem. Soc.*, **71**, 752 (1949).
 3. Kharasch and Brown, *J. Am. Chem. Soc.*, **61**, 2147 (1939).
 4. Haller and Ramart, *Compt. rend.*, **174**, 1211 (1922).
 5. Calcott, Tinker, and Weinmayr, *J. Am. Chem. Soc.*, **61**, 1010 (1939).
 6. Whitmore, Weisgerber, and Shabica, *J. Am. Chem. Soc.*, **65**, 1469 (1943).
 7. Schmerling and Ipatieff, *J. Am. Chem. Soc.*, **67**, 1862 (1945).
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Appendix

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

ethanol (64-17-5)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

thionyl chloride (7719-09-7)

sodium sulfate (7757-82-6)

carbon (7782-42-5)

sulfuryl chloride (7791-25-5)

benzoyl peroxide (94-36-0)

methallyl chloride (563-47-3)

Neophyl chloride,
Benzene, (2-chloro-1,1-dimethylethyl)-,
(Chloro-tert-butyl)benzene (515-40-2)

tert-butylbenzene (98-06-6)

p-di(chloro-tert-butyl)benzene