Organic Syntheses

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.

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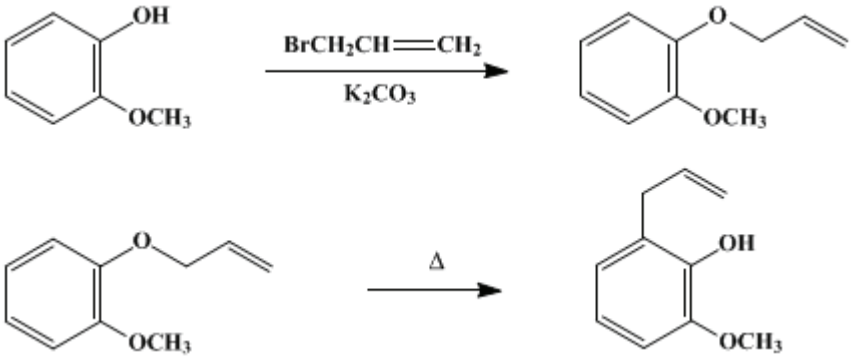
o-EUGENOL



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1. Procedure

A. *Guaiacol allyl ether*. A mixture of 63 g. (0.5 mole) of guaiacol, 66 g. (0.55 mole) of allyl bromide, 70 g. of anhydrous potassium carbonate (0.5 mole), and 100 ml. of dry acetone in a 500-ml. round-bottomed flask is refluxed on a steam bath for 8 hours and cooled. The mixture is diluted with 200 ml. of water and extracted with two 100-ml. portions of ether. The combined extracts are washed with two 100-ml. portions of 10% sodium hydroxide (Note 1) and dried with 50 g. of anhydrous potassium carbonate. After removal of the solvent, the residual oil (Note 2) is distilled under reduced pressure. The yield of guaiacol allyl ether boiling at 110–113°/12 mm. is 66–75 g. (80–90%).

B. *o-Eugenol*. The allyl ether (70 g.) is cautiously (Note 3) brought to boiling in a 500-ml. round-bottomed flask, refluxed for 1 hour, and cooled. The oil is dissolved in 100 ml. of ether (Note 4), and the solution is extracted with three 100-ml. portions of 10% sodium hydroxide. The combined alkaline extracts are then acidified with 100 ml. of concentrated hydrochloric acid diluted with 100 ml. of water, and the mixture is extracted with three 100-ml. portions of ether. The combined ether extracts are dried with 50 g. of anhydrous sodium sulfate and evaporated, and the residual oil is distilled under reduced pressure. The yield of *o*-eugenol boiling at 120–122°/12 mm. (Note 5) is 56–63 g. (80–90%).

2. Notes

1. A small amount of guaiacol may be recovered by acidifying the alkaline wash and extracting with ether.
2. When this crude guaiacol allyl ether was rearranged without prior distillation, the yields of *o*-eugenol were about 10% lower than those obtained with the distilled ether.
3. This rearrangement is sometimes quite vigorous and needs little heat once it is started. Dimethylaniline is said to be a good solvent for use in this type of rearrangement.[1]
4. Benzene may be substituted for ether throughout.
5. Other boiling points are 250–251°/760 mm., 125°/14 mm., and 115°/9 mm.

3. Discussion

Guaiacol allyl ether has been prepared from guaiacol, ethanolic potassium hydroxide, and allyl iodide;[2] or from guaiacol, allyl bromide, and potassium carbonate in acetone.[3,4] *o*-Eugenol has been prepared by the rearrangement of guaiacol allyl ether;[3,4] from 3-methoxy-2-allyloxybenzaldehyde by heating to 210°;[5] and from 3-methoxy-2-allyloxybenzoic acid by heating above 110°.[6]

References and Notes

1. Tarbell, *Org. Reactions*, **2**, 24 (1944).
2. Marfori *Annali di chimica e di farmacologia*, (5), **12**, 115; *Jahresb.*, **1890**, 1196.
3. Claisen and Eisleb, *Ann.*, **401**, 52 (1913).
4. Claisen, *Ber.*, **45**, 3161 (1912); Ger. pat. 268,099 [*Chem. Zentr.*, **1914**, I, 308; *Frdl.*, **11**, 181 (1912–1914)].
5. Claisen and Eisleb, *Ann.*, **401**, 112, 114 (1913).
6. Claisen, *Ann.*, **418**, 117 (1919).

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

ethanolic potassium hydroxide

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

Allyl bromide (106-95-6)

sodium sulfate (7757-82-6)

allyl iodide (556-56-9)

acetone (67-64-1)

Guaiacol (90-05-1)

dimethylaniline (121-69-7)

Guaiacol allyl ether (4125-43-3)

3-methoxy-2-allyloxybenzaldehyde

3-methoxy-2-allyloxybenzoic acid

o-Eugenol (579-60-2)