



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.

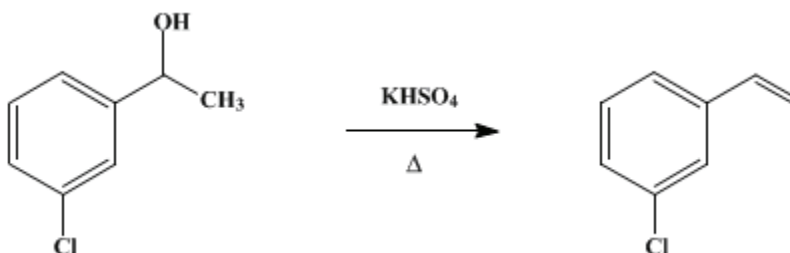
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 3, p.204 (1955); Vol. 28, p.31 (1948).

***m*-CHLOROSTYRENE**

[Styrene, *m*-chloro-]



Submitted by C. G. Overberger and J. H. Saunders.

Checked by Arthur C. Cope and Theodore T. Foster.

1. Procedure

A 500-ml. three-necked round-bottomed flask is attached to a 250-ml. dropping funnel and a total-condensation variable take-off fractionating column with a 20 by 1.2 cm. section packed with glass helices (Note 1). The fractionating column is fitted to a 500-ml. receiving flask. In the reaction flask are placed 12.5 g. of powdered fused potassium acid sulfate and 0.05 g. of *p*-*tert*-butylcatechol. The flask is immersed in an oil bath maintained at 220–230°, and 145 g. (0.925 mole) of *m*-chlorophenylmethylcarbinol (p. 200) and 0.05 g. of *p*-*tert*-butylcatechol (Note 2) are placed in the dropping funnel. The system is evacuated to a pressure of 125 mm., maintained by a manostat, and the *m*-chlorophenylmethylcarbinol is added dropwise at a rate (15–20 drops per minute) which maintains a vapor temperature at 110–120° at the top of the column. The *m*-chlorostyrene and water formed are collected in a receiver. When the addition is completed (5.5–8.5 hours) the pressure is held constant until distillation stops, and it is then reduced to 20 mm. until no more liquid distills.

The distillate is rinsed into a separatory funnel with 25 ml. of ether, and the organic layer is separated and dried over 10 g. of anhydrous magnesium sulfate. The drying agent is separated and rinsed with 25 ml. of ether, and 0.1 g. of *p*-*tert*-butylcatechol is added to the solution. The ether is removed, and the product is distilled under reduced pressure. *m*-Chlorostyrene is obtained in a yield of 102–106 g. (80–82.5%), boiling at 55–57°/3 mm.; n_D^{20} 1.5625 (Note 3) and (Note 4). A small amount (3–8 g.) of *m*-chlorophenylmethylcarbinol can be recovered as a higher-boiling fraction.

2. Notes

1. Effective separation of *m*-chlorostyrene from *m*-chlorophenylmethylcarbinol is possible with the short column specified. If a fractionating column is not used, lower conversions result and the crude product contains *m*-chlorophenylmethylcarbinol, which can be separated by fractional distillation and used in a subsequent preparation.
2. The submitters state that hydroquinone is not a satisfactory polymerization inhibitor for use in this preparation but that picric acid is very effective (less than 0.01 g. is required).
3. The submitters have used a similar procedure to prepare the following substituted styrenes from arylmethylcarbinols. The reactions were conducted more rapidly (addition rate about 2 drops per second), and no fractionating column was used in the initial distillation. A lower pressure (100 mm.) was used in dehydration of the dichlorophenylmethylcarbinols. The yields cited are based on the weights of arylmethylcarbinols which reacted; varying amounts of the carbinols were recovered in the distillation of the products.

	Boiling Point	% Yield
<i>o</i> -Chlorostyrene	67–69°/3–3.5 mm.	64–66.5

<i>p</i> -Chlorostyrene	65°/4 mm.	57
<i>o</i> -Bromostyrene	64–65°/3 mm.	64.5
<i>m</i> -Bromostyrene	74–75°/3 mm.	56
<i>p</i> -Bromostyrene	87–88°/12 mm.	50
<i>m</i> -Fluorostyrene	30–32°/2 mm.	45
2,3-Dichlorostyrene	92–94°/4–5 mm.	44
2,4-Dichlorostyrene	81°/6 mm.	33
3,4-Dichlorostyrene	95°/5 mm.	63.5
2,6-Dichlorostyrene	64–65°/3 mm.	31.5
3,5-Dichlorostyrene	59°/1 mm.	43.5

The dehydration procedure of this preparation is stated to be unsatisfactory for substituted phenylmethylcarbinols which have a strongly electronegative group, such as the nitro or trifluoromethyl group, in the *meta* position.

4. Some color due to small amounts of iodine may be present in substituted styrenes prepared by this procedure from arylmethylcarbinols synthesized from the corresponding aldehyde and methylmagnesium iodide. If present, iodine may be removed by shaking the crude product with 1 g. of powdered zinc and 25 ml. of water.

3. Discussion

m-Chlorostyrene has been prepared by dehydration of *m*-chlorophenylmethylcarbinol by modifications of this procedure,^{1,2,3} and by the vapor-phase dehydration in the presence of alumina at reduced pressure.⁴

References and Notes

1. Marvel and Schertz, *J. Am. Chem. Soc.*, **65**, 2054 (1943).
 2. Brooks, *J. Am. Chem. Soc.*, **66**, 1295 (1944).
 3. Ushakov and Matuzov, *J. Gen. Chem. U.S.S.R.*, **14**, 120 (1944) [*C. A.*, **39**, 916 (1945)].
 4. Emerson and Lucas, *J. Am. Chem. Soc.*, **70**, 1180 (1948).
-

Appendix

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

alumina

potassium acid sulfate

ether (60-29-7)

hydroquinone (123-31-9)

iodine (7553-56-2)

zinc (7440-66-6)

picric acid (88-89-1)

methylmagnesium iodide (917-64-6)

magnesium sulfate (7487-88-9)

2,3-Dichlorostyrene

2,4-Dichlorostyrene

3,4-Dichlorostyrene (2039-83-0)

2,6-Dichlorostyrene (28469-92-3)

3,5-Dichlorostyrene

p-tert-butylcatechol (98-29-3)

o-Bromostyrene (2039-88-5)

m-Chlorophenylmethylcarbinol (5182-44-5)

m-Chlorostyrene,
Styrene, m-chloro- (2039-85-2)

o-Chlorostyrene (2039-87-4)

p-Chlorostyrene (1073-67-2)

m-Bromostyrene (2039-86-3)

p-Bromostyrene (2039-82-9)

m-Fluorostyrene (350-51-6)