



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.

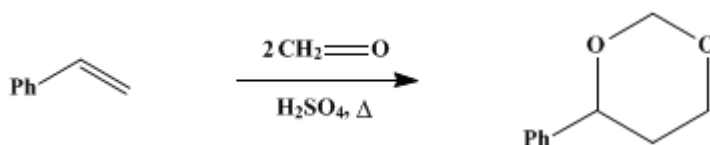
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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4-PHENYL-*m*-DIOXANE

[*m*-Dioxane, 4-phenyl-]



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1. Procedure

In a 2-l. round-bottomed flask, fitted with a reflux condenser and mechanical stirrer, are placed 675 g. (8.3 moles) of 37% formalin, 48 g. of sulfuric acid (sp. gr. 1.84), and 312 g. (3 moles) of styrene. The resulting mixture is gently refluxed and stirred for 7 hours. The mixture is cooled, and 500 ml. of benzene is stirred in. The layers are separated, and the aqueous layer is extracted with 500 ml. of benzene. The benzene solutions are combined and washed with two 750-ml. portions of water. The benzene is removed by distillation, and the residual liquid is fractionated under reduced pressure. At 2 mm. pressure a forerun is collected separately, up to a temperature of 96° (Note 1); then the main fraction is collected at 96–103°/2 mm. The yield of 4-phenyl-*m*-dioxane amounts to 353–436 g. (72–88%): n_D^{20} 1.5300–1.5311; d_4^{20} 1.092–1.093 (Note 2).

2. Notes

1. The amount of fore-run and the yield depend on the efficiency of the fractionation. With a 7-cm. distilling head, a fore-run of 75 g. boiling at 84–96°/2 mm. was collected, whereas with a heated Vigreux column (2 cm. by 35 cm.) the fore-run amounted to only 11 g. and the higher yields were obtained. The fore-run may be refractionated to obtain additional product. The checkers used a 2 cm. by 20 cm. column packed with stainless-steel helices, and collected their product (72–75% yield) over a 1° boiling range (94–95°/2 mm., n_D^{20} 1.5300).

2. This modification of the Prins² reaction has been applied to other olefins.³ The aryl olefins give the best yields; see the tabulation.

Aryl Olefin	Yield of Substituted <i>m</i> -Dioxane, %
α -Methylstyrene	58
Propenylbenzene	66
Anethole	89
Isosafrole	84
1-(3',4'-Dimethoxyphenyl)-1-propene	68
1-(<i>p</i> -Cumyl)-1-propene	96

3. Discussion

4-Phenyl-*m*-dioxane was obtained by Prins² by the reaction between styrene and formaldehyde in the presence of sulfuric acid. The correct structure was pointed out by Fourneau, Benoit, and Firmenich.⁴ The above procedure is essentially that given by Shortridge⁵ and by Beets³ and mentioned in a patent.⁶ Methylphenylcarbinol has been substituted for styrene.³

This preparation is referenced from:

References and Notes

1. State University of Iowa, Iowa City, Iowa.
 2. Prins, *Chem. Weekblad*, **14**, 932 (1917); **16**, 1072, 1510 (1919); *Proc. Acad. Sci. Amsterdam*, **22**, 51 (1919).
 3. Beets, *Rec. trav. chim.*, **70**, 20 (1951); Beets and Van Essen, *Rec. trav. chim.*, **70**, 25 (1951); Drukker and Beets, *Rec. trav. chim.*, **70**, 29 (1951).
 4. Fourneau, Benoit, and Firmenich, *Bull. soc. chim. France*, **47**, 858 (1930).
 5. Shortridge, *J. Am. Chem. Soc.*, **70**, 873 (1948).
 6. Engel, U. S. pat. 2,417,548 [*C. A.*, **41**, 3493 (1947)].
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Appendix

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

1-(p-Cumyl)-1-propene

sulfuric acid (7664-93-9)

Benzene (71-43-2)

formaldehyde,
formalin (72/22/2)

styrene (100-42-5)

methylphenylcarbinol (98-85-1)

propenylbenzene isosafrole (120-58-1)

α -methylstyrene (98-83-9)

Anethole (104-46-1)

m-Dioxane (505-22-6)

4-Phenyl-m-dioxane,
m-Dioxane, 4-phenyl- (3141-24-0)

1-(3',4'-Dimethoxyphenyl)-1-propene