



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.

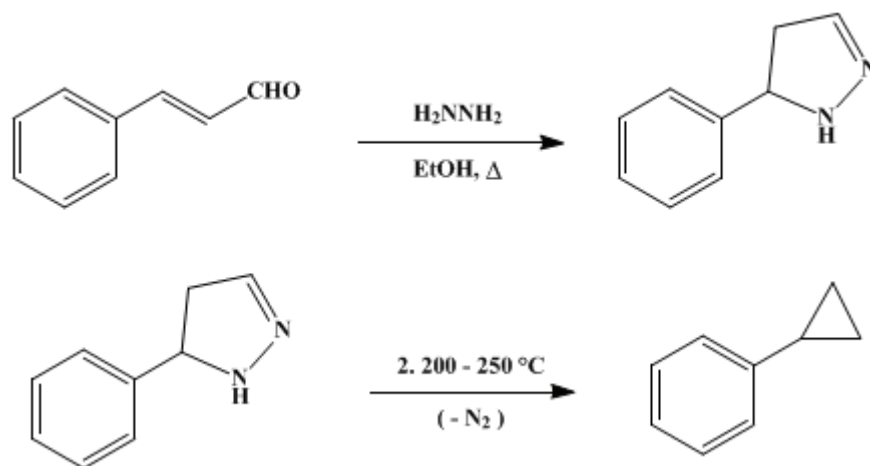
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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PHENYLCYCLOPROPANE

[Benzene, cyclopropyl-]



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Checked by Thomas R. Lynch and Peter Yates.

1. Procedure

Caution! This reaction should be carried out behind a safety screen.

A 1-l. three-necked flask is fitted with a reflux condenser, an addition funnel, and a thermometer. It is charged with 450 ml. of 95% ethanol, 230 ml. (236 g.) of 85% hydrazine hydrate (Note 1), and several porcelain boiling chips. The solution is brought to reflux with a heating mantle. Cinnamaldehyde (200 g., 1.51 moles) (Note 2) is added dropwise over a period of 45 minutes to the refluxing solution, while the mixture turns orange because of the formation of cinnamalazine in a side reaction (Note 3). After an additional 30 minutes at reflux, the flask is fitted with a simple takeoff head, and ethanol, water, and hydrazine hydrate are slowly removed by distillation. After approximately 3 hours the pot temperature rises to 200°, and phenylcyclopropane begins to codistil with the last of the hydrazine hydrate (Note 4). The distillate from this point is collected in a 250-ml. receiver, the main fraction coming over at 170-80°. When the pot temperature exceeds 250°, the decomposition is essentially complete (Note 5), (Note 6).

The crude, cloudy distillate (110–130 g.) is washed twice with 100-ml. portions of water and dried over anhydrous potassium carbonate. Distillation at reduced pressure, b.p. 60° (13 mm.), 79–80° (37 mm.), through a 12-in. Vigreux column gives phenylcyclopropane pure enough for most purposes; yield 80–100 g. (45–56%), n_D^{25} 1.5309.

2. Notes

1. Matheson, Coleman and Bell technical grade 85% hydrazine hydrate was used.
2. Eastman Organic Chemicals cinnamaldehyde gave satisfactory results. If colorless crystals are present in the neck of the bottle or on the walls above the liquid, the cinnamaldehyde is seriously contaminated with cinnamic acid and should be distilled before use. A small amount of cinnamic acid apparently does not affect the yield of phenylcyclopropane.
3. Reversal of the addition procedure results in formation of cinnamalazine as a major product.
4. Earlier investigators employed strong bases (sodium hydroxide, potassium hydroxide) or platinum on asbestos to catalyze the decomposition of 5-phenylpyrazoline. These catalysts are not necessary and

should be avoided because they also cause the reduction of cinnamaldehyde to propenylbenzene. Phenylcyclopropane can be freed from propenylbenzene only with great difficulty.

5. The checkers found in a full-scale run that the pot temperature had to be raised to close to 250° before the onset of reaction, which was then very vigorous.

6. Pyrazoline vapors are known to be rather flammable. It is advisable, therefore, to cool the pyrolysis flask somewhat before dismantling the apparatus. The syrupy residue in the flask sets to a hard mass on cooling; it can be removed by heating under dimethylformamide on a steam bath overnight.

3. Discussion

Phenylcyclopropane has been prepared by the base-catalyzed decomposition of 5-phenylpyrazoline (33%),² by the reaction of 1,3-dibromo-1-phenylpropane with magnesium (68%),³ and by the reaction of 3-phenylpropyltrimethylammonium iodide with sodium amide in liquid ammonia (80%).⁴ However, the method frequently used at present is the reaction of styrene with the methylene iodide-zinc reagent (32%).⁵

4. Merits of the Preparation

The procedure outlined is much quicker and simpler than previous methods. Starting materials are readily available, and the preparation can be run on any scale in the length of a day. Because exclusion of a basic catalyst eliminates the Wolff-Kishner reduction of the cinnamaldehyde, separation of the 5-phenylpyrazoline from cinnamaldehyde, or of phenylcyclopropane from propenylbenzene, does not have to be effected. The present procedure can also be used to convert other ring-substituted cinnamaldehydes to the corresponding arylcyclopropanes.

References and Notes

1. Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania.
2. S. G. Beech, J. H. Turnbull, and W. Wilson, *J. Chem. Soc.*, 4686 (1952).
3. P. J. C. Fierens and J. Nasielski, *Bull. Soc. Chim. Belges*, **71**, 187 (1962).
4. C. L. Bumgardner, *J. Am. Chem. Soc.*, **83**, 4420 (1961).
5. H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, **81**, 4256 (1959).

Appendix

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

cinnamalazine

cinnamaldehyde

ethanol (64-17-5)

potassium carbonate (584-08-7)

ammonia (7664-41-7)

sodium hydroxide (1310-73-2)

magnesium (7439-95-4)

platinum (7440-06-4)

potassium hydroxide (1310-58-3)

hydrazine hydrate (7803-57-8)

cinnamic acid (621-82-9)

cinnamaldehyde

styrene (100-42-5)

propenylbenzene

sodium amide (7782-92-5)

dimethylformamide (68-12-2)

Benzene, cyclopropyl-,
Phenylcyclopropane (873-49-4)

1,3-Dibromo-1-phenylpropane (17714-42-0)

5-phenylpyrazoline

3-phenylpropyltrimethylammonium iodide (2125-48-6)

pyrazoline

methylene iodide-zinc