



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](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.

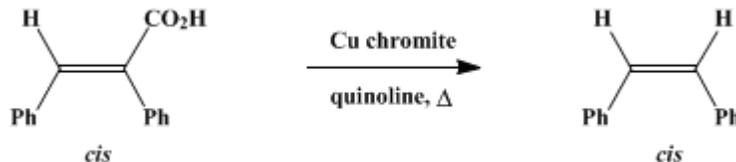
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures 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. 4, p.857 (1963); Vol. 33, p.88 (1953).*

## *cis*-STILBENE



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### 1. Procedure

A 500-ml. three-necked flask is fitted with a reflux condenser and a thermometer, the bulb of which reaches far enough into the flask to be covered by the liquid. A solution of 46.0 g. (0.205 mole) of *α*-phenylcinnamic acid (p. 777) (Note 1) in 280 ml. (307 g., 2.38 moles) of quinoline (Note 2) is added to the flask along with 4.0 g. of copper chromite.<sup>2</sup> The reaction flask is heated by means of a mantle or an oil bath until the temperature of the reaction mixture reaches 210–220°. The mixture is kept within this temperature range for 1.25 hours. The solution is then cooled immediately and added to 960 ml. of 10% hydrochloric acid in order to dissolve the quinoline (Note 3). The product is extracted from this mixture with two 200-ml. portions of ether followed by a 100-ml. portion. The combined ether extracts are filtered to remove particles of catalyst, washed with 200 ml. of 10% sodium carbonate, and dried over anhydrous sodium sulfate. The dry solution is removed from the drying agent by filtration and heated on a steam bath to distil the ether. The residue is dissolved in a hexane fraction, b.p. 60–72° (Skellysolve B); the solution is cooled to 0° and filtered to remove *trans*-stilbene, if any. The hydrocarbon solvent is removed by distillation, and the *cis*-stilbene is distilled. The yield is 23–24 g. (62–65%), b.p. 133–136°/10 mm., 95–97°/1 mm.;  $n_D^{25}$  1.6183–1.6193,  $n_D^{20}$  1.6212–1.6218 (Note 4).

### 2. Notes

1. The isomer of *α*-phenylcinnamic acid of m.p. 172–173° is used (p. 777). The isomer of m.p. 137–139° yields *trans*-stilbene on decarboxylation.<sup>3</sup>
2. Practical grade quinoline containing about 10% of isoquinoline and quinaldine can be used. If the quinoline contains water, the desired temperature can be reached by distillation of a small amount of quinoline directly from the reaction mixture.
3. The quinoline can be recovered by neutralization of the aqueous solution, extraction of the quinoline into ether, and distillation of the dried (over barium oxide) ether extract.
4. The product obtained from this type of decarboxylation is reported to contain only about 5% of *trans*-stilbene.<sup>4</sup> A sample made according to the above directions can be treated with bromine in carbon tetrachloride at room temperature in the dark to give an 80–85% yield of the *dl*-dibromide which arises from *trans* addition to *cis*-stilbene. The *meso*-dibromide, which is very insoluble and easily separated, is obtained only to the extent of 10% or less. Part of the latter product may arise from the action of bromine atoms on *cis*-stilbene rather than from *trans* addition to *trans*-stilbene. The *cis*-stilbene prepared by this method is readily and completely soluble in cold absolute ethanol. It freezes solid at about –5°. Its ultraviolet absorption coefficient ( $\epsilon$ ) is  $1.10 \times 10^4$  at 274 m $\mu$  and  $8.7 \times 10^3$  at 294 m $\mu$ , quite different from *trans*-stilbene.

### 3. Discussion

*cis*-Stilbene has been prepared by the partial hydrogenation of tolan;<sup>5,6</sup> by the electrolytic reduction of tolan;<sup>7</sup> by the reduction of tolan with a copper-zinc couple;<sup>8</sup> by the reduction of the low-melting isomer of *α*-bromostilbene with zinc dust in 90% alcohol;<sup>9</sup> by the illumination of *trans*-stilbene with ultraviolet light;<sup>10</sup> by the decarboxylation of the high-melting isomer of *α*-phenylcinnamic acid in the presence of barium hydroxide;<sup>3</sup> by heating tolan with diisobutylaluminum hydride<sup>11</sup> or zinc and acetic acid;<sup>12</sup> and by the reaction of *cis*-bromostilbene with butyllithium followed by treatment with

methanol.<sup>13</sup> The present method is based on that of Taylor and Crawford.<sup>14</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 777](#)

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## References and Notes

1. State University of Iowa, Iowa City, Iowa.
2. [Org. Syntheses Coll. Vol. 2, 142 \(1943\)](#).
3. Stoermer and Voht, *Ann.*, **409**, 36 (1915).
4. Weygand and Rettberg, *Ber.*, **73B**, 771 (1940).
5. Kelber and Schwarz, *Ber.*, **45**, 1946 (1912).
6. Ott and Schröter, *Ber.*, **60**, 624 (1927).
7. Campbell and Young, *J. Am. Chem. Soc.*, **65**, 965 (1943).
8. Straus, *Ann.*, **342**, 238 (1905).
9. Wislicenus and Jahrmarkt, *Chem. Zentr.*, **1901 I**, 463.
10. Stoermer, *Ber.*, **42**, 4865 (1909).
11. Wilke and Müller, *Chem. Ber.*, **89**, 444 (1956).
12. Rabinovitch and Looney, *J. Am. Chem. Soc.*, **75**, 2652 (1953).
13. Curtin and Harris, *J. Am. Chem. Soc.*, **73**, 4519 (1951).
14. Taylor and Crawford, *J. Chem. Soc.*, **1934**, 1130.

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

[copper-zinc couple](#)

[ethanol \(64-17-5\)](#)

[hydrochloric acid \(7647-01-0\)](#)

[acetic acid \(64-19-7\)](#)

[methanol \(67-56-1\)](#)

[ether \(60-29-7\)](#)

[sodium carbonate \(497-19-8\)](#)

[bromine \(7726-95-6\)](#)

[sodium sulfate \(7757-82-6\)](#)

[barium oxide](#)

[carbon tetrachloride \(56-23-5\)](#)

zinc (7440-66-6)

barium hydroxide (17194-00-2)

Quinoline (91-22-5)

COPPER CHROMITE

$\alpha$ -bromostilbene

quinaldine (91-63-4)

butyllithium (109-72-8)

hexane (110-54-3)

isoquinoline (119-65-3)

diisobutylaluminum hydride (1191-15-7)

$\alpha$ -Phenylcinnamic acid (3368-16-9)

trans-Stilbene (103-30-0)

cis-Stilbene (645-49-8)

cis-bromostilbene