



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.

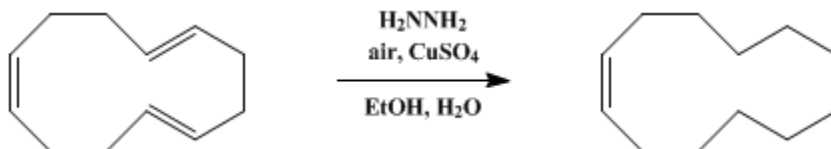
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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. 5, p.281 (1973); Vol. 49, p.30 (1969).*

## *cis*-CYCLODODECENE



Submitted by Masaji Ohno and Masaru Okamoto<sup>1</sup>.  
Checked by Frederick J. Sauter and Herbert O. House.

### 1. Procedure

In a 2-l., three-necked, round-bottomed flask equipped with a mechanical stirrer, an efficient condenser, and an air inlet tube (Note 1) are placed 60.0 g. (0.370 mole) of *cis,trans,trans*-1,5,9-cyclododecatriene (Note 2), 224.4 g. (7.00 moles) of 95% hydrazine (Note 3), 350 ml. of 95% ethanol, and 3.0 g. (0.012 mole) of copper(II) sulfate pentahydrate (Note 4). Air is bubbled through the reaction mixture (Note 5) with vigorous stirring for 8–12 hours or longer until the reaction mixture contains primarily the desired *cis*-monoolefin (Note 6). During the early stages in the reaction a considerable amount of heat is generated and the temperature of the reaction mixture rises to 50–60°.<sup>2</sup>

When the reaction has progressed to the desired stage (Note 6), the flow of air is stopped and the mixture is filtered. After the filtrate has been extracted with two 350-ml. portions of petroleum ether (b.p. 30–60°), the combined hydrocarbon extracts are washed successively with two 100-ml. portions of 2*N* hydrochloric acid and three 100-ml. portions of water. The petroleum ether is distilled from the solution, heated in a water bath, through a 60-cm. Vigreux column, and the residual liquid is distilled under reduced pressure. The fraction, b.p. 64–65° (1.0 mm.) or 132–134° (35 mm.), is collected as 39.5–52.0 g. (64–85%) of colorless liquid, *n*<sub>D</sub><sup>25</sup> 1.4846–1.4850. This distillation fraction contains (Note 6) 80–90% of the *cis*-cyclododecene (51–76%) accompanied by 10–20% of a mixture of cyclododecane and *cis,trans*-1,5-cyclododecadiene (Note 7). If desired, the *cis*-cyclododecene may be further purified by preparative chromatography or separation of the silver nitrate-olefin addition complex (Note 8).

### 2. Notes

1. An air inlet tube with a sintered-glass disk or cylinder at the end immersed in the solution is recommended.
2. The submitters used material available from Hüls Company in Germany. This material was contaminated with 1–3% of the more easily reduced *trans,trans,trans*-1,5,9-cyclododecatriene. The checkers purchased the starting triene from Aldrich Chemical Company, Inc. The gas chromatogram (see (Note 6)) of this material exhibited no peak corresponding to the all-*trans*-triene, an indication that less than 1% of this contaminant was present.
3. The submitters had specified the use of either hydrazine hydrate (aqueous 85% hydrazine) or aqueous 80% hydrazine. The checkers observed only partial reduction of the triene and intermediate diene under these conditions, apparently because sufficient water was present in the reaction mixture to prevent adequate partitioning of the olefins between the hydrocarbon layer and the aqueous ethanolic layer containing the diimide. The checkers avoided this difficulty by use of hydrazine containing less than 5% water (95+ % hydrazine) available from Olin Mathieson Chemical Company or from Eastman Organic Chemicals. This difficulty could probably also be avoided by use of absolute ethanol rather than 95% ethanol.
4. Copper(II) acetate can also be used.
5. The rate of air flow, measured with a precalibrated mercury flow meter in the gas inlet tube, was adjusted to 400–450 ml. per minute.
6. In order to stop the reaction when the amount of monoolefinic product in the reaction mixture is highest, aliquots of the reaction mixture are removed at intervals and analyzed by infrared spectrometry or by gas chromatography. In the infrared spectrum the relative intensities of bands at 965 cm.<sup>-1</sup> (*trans*-

CH=CH) and  $702\text{ cm}^{-1}$  (*cis*-CH=CH) are observed in successive aliquots. The reaction is stopped when the band at  $965\text{ cm}^{-1}$ , attributable to the *trans* double bonds of the starting triene, has almost completely disappeared and the band at  $702\text{ cm}^{-1}$  (*cis*-olefin) remains.

Gas chromatographic analyses are obtained at about  $120^\circ$  with a  $2\text{ m.} \times 7\text{ mm.}$  column packed with a suspension of 5% (by weight) of silver nitrate and 15% (by weight) of Carbowax 6000 (polyethylene glycol) on either Chromosorb P or Celite 545. With this column the relative retention times of the various possible components in the reaction mixture are: cyclododecane, 1.00; *trans,trans,trans*-1,5,9-cyclododecatriene, 1.20; *trans*-cyclododecene, 1.13; *cis*-cyclododecene, 1.33; *cis,trans*-1,5-cyclododecadiene, 1.51; *cis,trans-trans*-1,5,9-cyclododecatriene, 1.72. The reaction should be stopped when the rate of reduction of *cis,trans*-1,5-cyclododecadiene to *cis*-cyclododecene has become approximately equal to the rate of conversion of the *cis*-monoolefin to cyclododecane.

7. The submitters reported obtaining a product after a 60–72 hour reaction period which contained 91%–95% of the *cis*-monoolefin and 5–9% of cyclododecane with no *trans*-monoolefin being detected. The checkers found the maximum amount of *cis*-monoolefin was present in the reaction mixture after a reaction period of 8–12 hours. At this time the resulting distilled product had the approximate composition: cyclododecane, 8%; *trans*-cyclododecene, 3%; *cis*-cyclododecene, 80%; and *cis,trans*-1,5-cyclododecadiene, 9%. The use of longer reaction times resulted in the further reduction of the *cis*-monoolefin to cyclododecane more rapidly than it was produced from the residual *cis,trans*-diene.

8. The conversion of the *cis*-monoolefin to its silver nitrate complex<sup>3</sup> was accomplished by adding 1.66 g. (0.010 mole) of the distilled reaction product to a solution of 1.70 g. (0.010 mole) of silver nitrate in 50 ml. of boiling methanol. The resulting solution, when cooled, deposited the complex as white needles, m.p.  $79^\circ\text{ dec.}$ ; recrystallization from methanol separated 1.0 g. of the complex, m.p.  $80^\circ\text{ dec.}$  After this complex had been partitioned between water and ether, the ether phase was separated, dried over magnesium sulfate, and concentrated. Distillation of the residual liquid in a short path still separated 0.45 g. of the pure (Note 6) *cis*-cyclodecene, b.p.  $70^\circ$  (1.0 mm.),  $n_D^{25}$  1.4852.

### 3. Discussion

Cyclododecene may be prepared from 1,5,9-cyclododecatriene by the catalytic reduction with Raney nickel and hydrogen diluted with nitrogen,<sup>4</sup> with nickel sulfide on alumina,<sup>5</sup> with cobalt, iron, or nickel in the presence of thiophene,<sup>6</sup> with palladium on charcoal,<sup>7</sup> with palladium chloride in the presence of water,<sup>8</sup> with palladium on barium sulfate,<sup>9</sup> with cobalt acetate in the presence of cobalt carbonyl,<sup>10</sup> and with cobalt carbonyl and tri-*n*-butyl phosphine.<sup>11</sup> It may also be obtained from the triene by reduction with lithium and ethylamine,<sup>12</sup> by disproportionation,<sup>13,14</sup> by epoxidation followed by isomerization to a ketone and Wolff-Kishner reduction,<sup>15</sup> and from cyclododecanone by the reaction of its hydrazone with sodium hydride.<sup>16</sup>

These methods generally afford a mixture of *cis*- and *trans*-cyclododecene. *cis*-Cyclododecene has also been prepared by the reduction of cyclododecyne with Lindlar catalyst,<sup>17,3</sup> and from 1,5-cyclododecadiene<sup>18</sup> or from 1,2-dichlorocyclododecane.<sup>19</sup> The *cis*-olefin is usually obtained as a minor product from the Hofmann degradation of cyclododecyltrimethylammonium hydroxide<sup>17</sup> and from the pyrolysis of cyclododecyl acetate.

The procedure described is based on the selective reduction with diimide described by Ohno and Okamoto<sup>2</sup> and by Nozaki and Noyori.<sup>20</sup> It illustrates the generation of diimide from the air oxidation of hydrazine and the use of diimide for the selective reduction of the *trans* double bond in *cis,trans,trans*-1,5,9-cyclododecatriene, the product of trimerization of butadiene.<sup>21</sup>

The use of diimide provides a particularly convenient and general method for the selective reduction of *trans* double bonds of medium ring systems.<sup>22</sup> The *cis*-cyclododecene produced in this selective reduction is thermodynamically less stable than the corresponding *trans*-isomer.<sup>23</sup>

---

### References and Notes

1. Basic Research Laboratories, Toray Industries, Inc., Kamakura, Japan.
2. M. Ohno and M. Okamoto, *Tetrahedron Lett.*, 2423 (1964); M. Ohno, M. Okamoto, and S.

- Torimitsu, *Bull. Chem. Soc. Japan*, **39**, 316 (1966).
3. M. Svoboda and J. Sicher, *Chem. Ind. (London)*, 290 (1959).
  4. Fr. Patent 1,357,114 (1964) [*Chem. Abstr.*, **61**, 5536 (1964)].
  5. Belg. Patent 634,763 (1964) [*Chem. Abstr.*, **61**, 13214 (1964)].
  6. Ger. Patent 1,226,568 (1966) [*Chem. Abstr.*, **66**, 10657 (1967)].
  7. Neth. Appl. 6,412,540 (1964) [*Chem. Abstr.*, **63**, 11390 (1965)].
  8. Neth. Appl. 6,507,159 (1965) [*Chem. Abstr.*, **64**, 19448 (1966)].
  9. L. I. Zakharkin and V. V. Korneva, *Zh. Organ. Khim.*, **1**, 1608 (1965) [*Chem. Abstr.*, **64**, 611 (1966)].
  10. U.S. Patent 3,308,177 [*Chem. Abstr.*, **67**, 21504 (1967)].
  11. A. Misono and I. Ogata, *Bull. Chem. Soc. Japan*, **40**, 2718 (1967).
  12. U.S. Patent 3,173,964 (1965) [*Chem. Abstr.*, **63**, 515 (1965)].
  13. U.S. Patent 3,182,093 (1965) [*Chem. Abstr.*, **63**, 515 (1965)].
  14. Fr. Patent 1,389,362 (1965) [*Chem. Abstr.*, **63**, 514 (1965)].
  15. W. Stumpf and K. Rombusch, *Ann.*, **687**, 136 (1965).
  16. A. P. Krapcho and J. Diamanti, *Chem. Ind. (London)*, 847 (1965).
  17. V. Prelog and M. Speck, *Helv. Chim. Acta*, **38**, 1786 (1955).
  18. U.S. Patent 3,294,853 (1966) [*Chem. Abstr.*, **66**, 46145 (1967)].
  19. W. Ziegenbein and W. M. Schneider, *Ber.*, **98**, 824 (1965).
  20. H. Nozaki and R. Noyori, *J. Org. Chem.*, **30**, 1652 (1965).
  21. G. Wilke, *Angew. Chem.*, **75**, 10 (1963).
  22. J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967).
  23. A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960).
- 

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

alumina

petroleum ether

cis-monoolefin

silver nitrate-olefin

trans-monoolefin

cis-olefin

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

ether (60-29-7)

hydrogen (1333-74-0)

iron (7439-89-6)

silver nitrate (7761-88-8)

nitrogen (7727-37-9)

nickel,  
Raney nickel (7440-02-0)

barium sulfate (7727-43-7)

charcoal (7782-42-5)

palladium (7440-05-3)

Copper(II) acetate (142-71-2)

hydrazine hydrate (7803-57-8)

hydrazine (302-01-2)

palladium chloride (7647-10-1)

Thiophene (110-02-1)

lithium (7439-93-2)

magnesium sulfate (7487-88-9)

butadiene (106-99-0)

copper(II) sulfate pentahydrate (7758-99-8)

sodium hydride (7646-69-7)

cobalt (7440-48-4)

ethylamine (75-04-7)

cyclododecanone (830-13-7)

cyclododecane (294-62-2)

Cyclododecene,  
cis- and trans-cyclododecene (1501-82-2)

1,5,9-cyclododecatriene

nickel sulfide

cobalt acetate

cobalt carbonyl  
cyclododecyne (1129-90-4)  
1,5-cyclododecadiene  
1,2-dichlorocyclododecane  
cyclododecyltrimethylammonium hydroxide  
cyclododecyl acetate  
tri-n-butyl phosphine (998-40-3)  
trans-Cyclododecene (1486-75-5)  
cis-Cyclododecene (1129-89-1)  
cis,trans,trans-1,5,9-cyclododecatriene,  
cis,trans-trans-1,5,9-cyclododecatriene  
cis,trans-1,5-cyclododecadiene  
trans,trans,trans-1,5,9-cyclododecatriene (676-22-2)  
cis-cyclodecene