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.

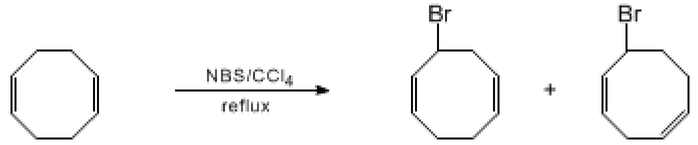
September 2014: The paragraphs above replace the section "Handling and Disposal of Hazardous Chemicals" in the originally published version of this article. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.073.0240

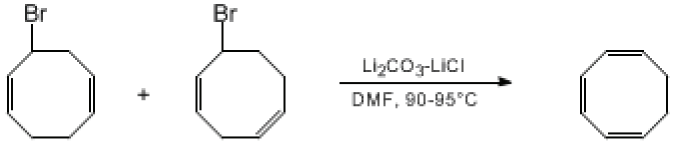
Organic Syntheses, Coll. Vol. 9, p.191 (1998); Vol. 73, p.240 (1996).

1,3,5-CYCLOOCTATRIENE

A.



B.



Submitted by Masaji Oda, Takeshi Kawase, and Hiroyuki Kurata[1].
Checked by Daniel V. Paone and Amos B. Smith, III.

1. Procedure

CAUTION. The handling of carbon tetrachloride must be done in a well-ventilated hood using glass. It must be disposed of properly. See Waste Disposal Information.

A. *Allylic bromination of 1,5-cyclooctadiene*. A 2-L, three-necked, round-bottomed flask, equipped with a mechanical stirrer, reflux condenser, and a heating mantle, is charged with 216.4 g (2.0 mol) of 1,5-cyclooctadiene (Note 1), 44.5 g (0.25 mol) of N-bromosuccinimide (NBS), 0.5 g of benzoyl peroxide, and 700 mL of carbon tetrachloride. The mixture is heated to gentle reflux with stirring. When the reaction starts, a rapid reflux is observed. Three more 44.5-g portions (0.25 mol) of NBS are added at 30-min intervals (total 178 g, 1.0 mol). Heating is continued for 1.5 hr after addition of the final portion of NBS. The mixture is cooled to room temperature and suction filtered and the filter cake is washed with 150 mL of carbon tetrachloride (Note 2). The filtrate is washed once with 150 mL of water, dried over calcium chloride, and filtered with suction. A vacuum distillation apparatus consisting of a 500-mL, two-necked, round-bottomed flask, a stoppered pressure-equalizing dropping funnel, a distilling head (25 cm long) packed with Pyrex glass tips or helices, a condenser, and receivers is assembled (Note 3). The dried carbon tetrachloride solution is transferred to the dropping funnel, the system is evacuated to 150 mm, and the solution is introduced continuously from the dropping funnel resulting in removal of the bulk of the solvent (Note 4). The pale yellow residue is then fractionally distilled first at 30 mm to remove the unreacted 1,5-cyclooctadiene (Note 5), and then at 5 mm to distill the bromocyclooctadienes to give 113–121 g (60–65%) of a mixture of 3-bromo-1,5-cyclooctadiene and 6-bromo-1,4-cyclooctadiene,[2] bp 66–69°C at 5 mm (Note 6),(Note 7),(Note 8).

B. *1,3,5-Cyclooctatriene*. A 1-L, three-necked, round-bottomed flask, equipped with a magnetic stirring bar, pressure-equalizing dropping funnel, immersion thermometer, and a condenser bearing a gas inlet vented through a mineral oil bubbler, is charged with 25.9 g (0.35 mol) of lithium carbonate, 2.0 g (0.047 mol) of lithium chloride (Note 9), and 400 mL of dry dimethylformamide (DMF) (Note 10). The magnetically stirred mixture is heated to 90°C in an oil bath (Note 11) and 113.5 g (0.607 mol) of the bromocyclooctadiene mixture (Part A) is added dropwise via the dropping funnel over 50 min. During the addition, rapid evolution of gas (carbon dioxide) is observed via the bubbler. After completion of the addition, heating is continued for 1 hr at 90–95°C. The mixture is cooled to room temperature, diluted with 1 L of ice water, and the mixture extracted twice with 200-mL portions of pentane. The combined organic phase is washed twice with 100-mL portions of water, dried over sodium sulfate, and filtered. The filtrate is distilled at atmospheric pressure to remove the pentane, and the residue is distilled under reduced pressure, employing a short (12 cm) Vigreux column, to give 54–58 g (84–90%) of almost pure 1,3,5-cyclooctatriene, bp 63–65°C at 48 mm (Note 12).

2. Notes

1. All reagents and solvents are commercially available and are used without further purification.
2. The solids consisted of 94.0 g of succinimide (0.95 mol, 95% of theoretical).
3. The distillation system was connected to a closed-tube manometer and a Cartesian diver-type pressure regulator employed to control the pressure.
4. When a rotary evaporator was used for the concentration, the recovery of 1,5-cyclooctadiene decreased substantially.
5. Approximately 88.5 g (0.82 mol, 82% of theoretical) of 1,5-cyclooctadiene, bp 55–57°C at 30 mm, is recovered and can be recycled.
6. Care must be taken during fractionation of 1,5-cyclooctadiene and the bromocyclooctadienes, because contamination of the bromide with 1,5-cyclooctadiene leads to contamination of 1,3,5-cyclooctatriene with the diene. A 1–2-mL intermediate fraction effects clean separation. The distillation took the checkers 6–8 hr. The bromides are extremely light sensitive, turning yellow to red-brown quickly. To avoid product coloration all product receiving flasks were wrapped in aluminum foil.
7. When NBS was added in two portions instead of four, the yield of bromocyclooctadienes decreased slightly to 60%. A preparation using 500 g (2.80 mol) of NBS (five-portion addition) gave a higher yield (78%).
8. The spectral data for the mixture of bromocyclooctadienes is as follows: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 1.7–3.4 (m, 12 H), 4.6–5.25 (m, 2 H), 5.3–5.9 (m, 8 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 25.0, 27.7, 28.3, 28.7, 34.3, 36.8, 48.0, 49.9, 124.7, 127.0, 128.3, 128.8, 129.2, 130.4, 130.6, 131.7; IR (thin film) cm^{-1}: 3000, 2940, 2890, 2820, 1640, 1480, 1450, 1440, 1420, 1220, 1150, 1140, 990, 910, 860, 805, 670.
9. Lithium carbonate and lithium chloride were dried under reduced pressure at 80–100°C for 3 hr before use.
10. DMF dried azeotropically with benzene is sufficient for the present reaction.
11. The checkers employed a heating mantle.
12. 1,3,5-Cyclooctatriene exists in equilibrium with bicyclo[4.2.0]octa-2,4-diene, its valence isomer (ratio = ~7:1).[3] [4] [5] [6] 1,3,5-Cyclooctatriene exhibits the following spectral data: ^{1}H NMR (500 MHz, $CDCl_3$) δ: 2.43 (s, 4 H), 5.50–6.00 (m, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 28.0, 125.9, 126.7, 135.5; IR (thin film) cm^{-1}: 3000, 2920, 2875, 2830, 1635, 1605, 1445, 1425, 1220, 690, 635. Signals for the minor valence isomer may be observed. No signals for 1,3,6-cyclooctatriene, another possible isomer, are observed.

Waste Disposal Information

All toxic materials were disposed of in accordance with "Prudent Practices in the Laboratory"; National Academy Press; Washington, DC, 1995.

3. Discussion

Mixtures of 1,3,5- and 1,3,6-cyclooctatriene were obtained by partial reduction of cyclooctatetraene in ways such as protonation of cyclooctatetraene dianion[6,7] and reduction with zinc-alkali.[2,8] 1,3,6-Cyclooctatriene is the major product in these reductions. However, since 1,3,6-cyclooctatriene isomerizes to 1,3,5-cyclooctatriene on treatment with base, quenching cyclooctatetraene dianion with methanol and subsequent heating affords 1,3,5-cyclooctatriene in an 80% yield.[6] Reduction of cyclooctatetraene with sodium hydrazide and hydrazine also produces 1,3,5-cyclooctatriene.[9] Therefore, when cyclooctatetraene is available in quantity, these procedures are the methods of choice.

The present two-step procedure for the synthesis of 1,3,5-cyclooctatriene uses commercially available 1,5-cyclooctadienes as starting material. Although allylic bromination of 1,5-cyclooctadiene with N-bromosuccinimide produces a mixture of 3-bromo-1,5-cyclooctadiene and 6-bromo-1,4-cyclooctadiene,[2] dehydrobromination of this mixture with LiCl-Li_2CO_3/DMF affords only 1,3,5-cyclooctatriene, which is in equilibrium with its valence isomer bicyclo[4.2.0]octa-2,4-diene.

References and Notes

1. Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan.
2. Echter, T.; Meier, H. *Chem. Ber.* **1985**, *118*, 182.
3. Cope, A. C.; Haven, A. C., Jr.; Ramp. F. L.; Trumbull, E. R. *J. Am. Chem. Soc.* **1952**, *74*, 4867;
4. Kröner, M. *Chem. Ber.* **1967**, *100*, 3172;
5. Huisgen, R.; Boche, G.; Dahmen, A.; Hechtl, W. *Tetrahedron Lett.* **1968**, 5215;
6. Adam, W.; Gretzke, N.; Hasemann, L.; Klug, G.; Peters, E. M.; Peters, K.; von Schnering, H. G.; Will, B. *Chem. Ber.* **1985**, *118*, 3357.
7. Reppe, W.; Schlichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1; Cope, A. C.; Hochstein, F. A. *J. Am. Chem. Soc.* **1950** *72*, 2515.
8. Jones, W. O. *J. Chem. Soc.* **1954**, 1808; Sanne, W.; Schlichting, O. *Angew. Chem.* **1963**, *75*, 156.
9. Kauffmann, T.; Kosel, C.; Schoeneck, W. *Chem. Ber.* **1963**, *96*, 999.

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

NBS

1,3,5- and 1,3,6-cyclooctatriene

LiCl

Li_2CO_3

calcium chloride (10043-52-4)

Benzene (71-43-2)

methanol (67-56-1)

bromide (24959-67-9)

sodium sulfate (7757-82-6)

carbon tetrachloride (56-23-5)

aluminum (7429-90-5)

carbon dioxide (124-38-9)

Pentane (109-66-0)

hydrazine (302-01-2)

benzoyl peroxide (94-36-0)

Succinimide (123-56-8)

dimethylformamide,
DMF (68-12-2)

N-bromosuccinimide (128-08-5)

lithium carbonate (554-13-2)

Lithium chloride (7447-41-8)

1,5-cyclooctadiene

sodium hydrazide

1,3,5-Cyclooctatriene (1871-52-9)

cyclooctatetraene

3-Bromo-1,5-cyclooctadiene (23346-40-9)

6-Bromo-1,4-cyclooctadiene (23359-89-9)

bromocyclooctadiene

bicyclo[4.2.0]octa-2,4-diene

1,3,6-cyclooctatriene