



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.

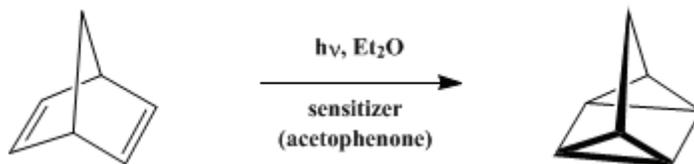
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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. 6, p.962 (1988); Vol. 51, p.133 (1971).

QUADRICYCLANE

[Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane]



Submitted by Claibourne D. Smith¹

Checked by A. J. Taggi and J. Meinwald.

1. Procedure

A Hanovia, 550-watt, immersion photochemical reactor (Note 1) equipped with a magnetic stirrer and water condenser (Note 2) is charged with 1 l. of diethyl ether, 180 g. (1.96 moles) of bicyclo[2.2.1]hepta-2,5-diene (2,5-norbornadiene, (Note 3), and 8 g. of acetophenone. The system is flushed briefly with a stream of nitrogen, then irradiated for about 36–48 hours (Note 4). After irradiation, the ether is removed by distillation through a 20-cm. Vigreux column (Note 5). The residue, a clear liquid weighing about 185 g., is distilled through a spinning-band column under reduced pressure (Note 6), yielding 126–145 g. (70–80%) of quadricyclane as a colorless liquid, b.p. 70° (200 mm.) (Note 7).

2. Notes

1. The reactor, manufactured by the Hanovia Division of Engelhard Industries, consists of a water-jacketed Pyrex well through which a stream of water is continuously passed. The well is placed in an appropriately shaped flask containing the solution to be irradiated [*Org. Synth.*, **Coll. Vol. 5**, 528 (1973)]. The essentially cylindrical flask is equipped with a sidearm near the top which is connected to a water-cooled condenser. There should be sufficient clearance between the bottom of the well and the flask for a magnetic stirring bar. The flask is so designed that the liquid level is above the top of the lamp.

2. A source of nitrogen is attached to the top of the condenser, protecting the system from oxygen. The condenser serves as a safeguard in case the temperature of the system exceeds the boiling point of the solvent.

3. Bicyclo[2.2.1]hepta-2,5-diene was obtained from Shell Chemical Company and can be used as supplied. However, if the diene is distilled it should be used at once. The uninhibited diene may form a white, insoluble polymer or peroxide if allowed to stand in the presence of air and light. The use of undistilled diene results in a slightly lower yield of quadricyclane. The checkers used bicyclo[2.2.1]hepta-2,5-diene supplied by the Aldrich Chemical Company, Inc., which was distilled prior to use, giving a pure sample, b.p. 89–90.5°, $n_D^{26.5}$ 1.4680.

4. Other sensitizers (acetone, benzophenone) can be used, but with slightly reduced yields. The reaction may be monitored by removing aliquots and analyzing by GC or ¹H NMR. For GC analysis a 2-m. column containing 20% by weight of 1,2,3-tris(2-cyanoethoxy)propane suspended on Gas Chrome R (60–80 mesh) is used at a temperature of 75° with a flow rate of 85 ml./minute of helium. The retention time for quadricyclane is 5.2 minutes. For ¹H NMR analysis the disappearance of the absorption of the olefinic protons at δ 6.75 is monitored.

Lower wattage lamps can be used, although the irradiation time would be somewhat longer. The checkers found this reaction to be almost complete in about half this time; lamp age and other factors will cause appreciable variation in the irradiation time required.

5. Rapid distillation of the solvent may slightly reduce the yield of product.

6. The only volatile impurity at this point is bicyclo[2.2.1]hepta-2,5-diene. If the irradiation has been carried out for a sufficient period of time, the amount of diene present is less than 2%. Distillation through an efficient column will remove most of the diene, b.p. 91° (760 mm.) or 51° (200 mm.) Traces

of acid² or noble metal ions and complexes³ may cause quadricyclane to isomerize to the diene. The checkers used a 60-cm., Teflon-coated, spinning-band column available from Nester-Faust Corporation. The submitter used a similar 43-cm. column.

7. The checkers found n_D^{26} 1.4830 (lit.,⁴ 1.4830) for the distillate. The ¹H NMR spectrum² shows peaks at δ 1.41 (6H) and δ 2.00 (2H). No olefinic absorption was detectable. The IR spectrum (CCl₄) shows three unusually well-resolved bands in the C-H stretching region at 3069, 2929, and 2852 cm.⁻¹.

3. Discussion

Quadricyclane may be prepared by direct irradiation of bicyclo[2.2.1]hepta-2,5-diene² and 2,3-diazatetracyclo[4.3.0.0^{4,8}.0^{7,9}]non-2-ene,⁴ or by photosensitized isomerization of bicyclo[2.2.1]hepta-2,5-diene.^{5,6} Several substituted quadricyclanes have been prepared by direct irradiation^{7,8,9,10} and by photosensitization.^{11,12,13} The procedure described above can be used to isomerize substituted bicycloheptadienes to the corresponding quadricyclanes when traces of sensitizers can be conveniently removed or their presence does not interfere with further use of the quadricyclane.

Quadricyclane is a highly strained and reactive compound. It reacts readily with acetic acid, giving a mixture of nortricycyl acetate and *exo*-norbornyl acetate and with bromine, yielding a mixture of 2,6-dibromonortricycene and *exo*-5-*anti*-7-dibromonorbornene.² Quadricyclane undergoes cycloaddition reactions with a variety of dienophiles, giving 1:1 adducts.¹⁴

References and Notes

1. Contribution No. 1222 from the Central Research Department, E. I. du Pont de Nemours & Co. (Inc.), Experimental Station, Wilmington, Delaware 19898. [Present address: Fabrics and Finishes Department, E. I. du Pont de Nemours & Co. (Inc.), Marshall Laboratory, Philadelphia, Pennsylvania 19146.]
2. W. G. Dauben and R. L. Cargill, *Tetrahedron*, **15**, 197 (1961).
3. H. Hogeveen and H. C. Volger, *J. Am. Chem. Soc.*, **89**, 2486 (1967).
4. R. M. Moriarty, *J. Org. Chem.*, **28**, 2385 (1963).
5. G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.*, **83**, 4674 (1961).
6. G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *J. Am. Chem. Soc.*, **86**, 2532 (1964).
7. S. J. Cristol and R. L. Snell, *J. Am. Chem. Soc.*, **76**, 5000 (1954).
8. H. G. Richey, Jr. and N. C. Buckley, *J. Am. Chem. Soc.*, **85**, 3057 (1963).
9. J. A. Claisse, D. I. Davies, and C. K. Alden, *J. Chem. Soc. C*, 1498 (1966).
10. D. I. Davies and P. J. Rowley, *J. Chem. Soc. C*, 2245 (1967).
11. P. R. Story and S. R. Fahrenholtz, *J. Am. Chem. Soc.*, **86**, 527 (1964).
12. P. G. Gassman, D. H. Aue, and D. S. Patton, *J. Am. Chem. Soc.*, **86**, 4211 (1964).
13. H. Prinzbach and J. Rivier, *Tetrahedron Lett.*, 3713 (1967).
14. C. D. Smith, *J. Am. Chem. Soc.*, **88**, 4273 (1966).

Appendix

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

Nortricycyl acetate

Quadricyclane

20-cm. Vigreux column

quadricyclanes

2,6-dibromonortricyclene
exo-5-anti-7-dibromonobornene
acetic acid (64-19-7)
ether,
diethyl ether (60-29-7)
bromine (7726-95-6)
oxygen (7782-44-7)
nitrogen (7727-37-9)
acetone (67-64-1)
Acetophenone (98-86-2)
Benzophenone (119-61-9)
peroxide (7722-84-1)
helium (7440-59-7)
bicyclo[2.2.1]hepta-2,5-diene,
2,5-norbornadiene
Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (278-06-8)
2,3-diazatetracyclo[4.3.0.0^{4,8}.0^{7,9}]non-2-ene
1,2,3-tris(2-cyanoethoxy)propane (2465-93-2)
exo-norbornyl acetate