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Working with Hazardous Chemicals

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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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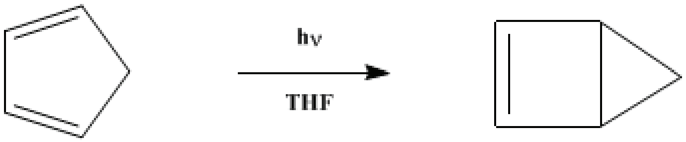
BICYCLO[2.1.0]PENT-2-ENE



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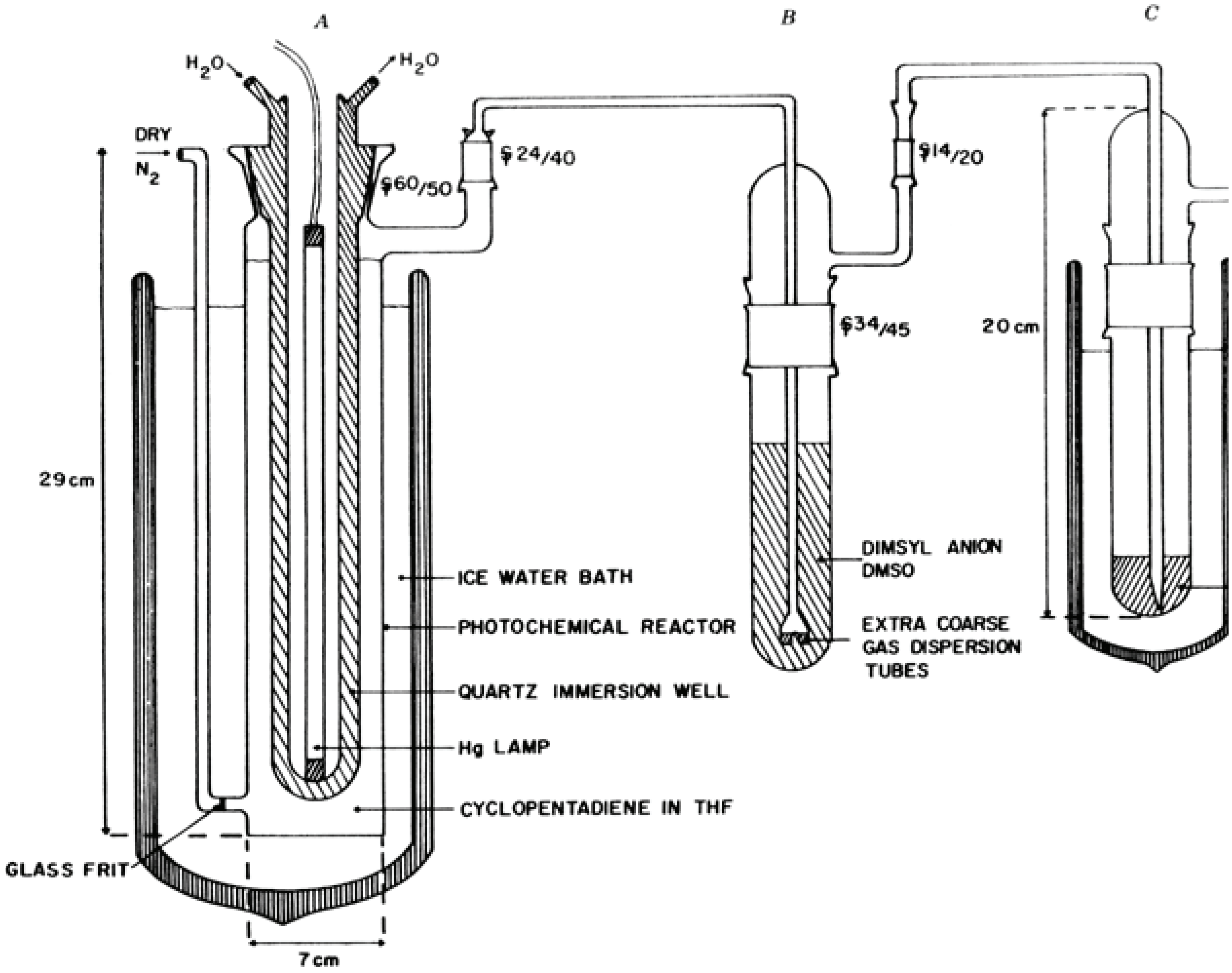
Checked by Keith C. Bishop, III and Kenneth B. Wiberg.

1. Procedure

Caution! The photochemical reaction should be carried out under a light absorbent cover. The operator should wear goggles affording protection from ultraviolet light.

While still slightly warm from the drying oven, a photolysis vessel with a water-jacketed quartz immersion well (Note 1) (section *A* of Figure 1) is charged with 500 ml. of anhydrous tetrahydrofuran (Note 2) and 10.0 ml. (8.05 g., 0.122 mole) of cyclopentadiene (Note 3). The solution is cooled in an ice bath and purged with dry nitrogen for 2 minutes. The vessel is then sealed, the lamp inserted, and the solution irradiated at 0° for 30 minutes. During this period, sections *B* and *C* (see diagram) are removed from the oven to cool slightly. While still warm, the bottom part of *C* is filled with 0.5 ml. of anhydrous tetrahydrofuran and approximately 25 µl. of triethylamine (Note 4), greased, and stoppered. The top parts of *B* and *C* are thoroughly greased and connected to the 24/40 T joint of *A*. The bottom of part *B* is filled rapidly with 200 ml. of an approximately 1 *M* solution of dimsyl anion (Note 5) in dimethyl sulfoxide. The bottom part of *C* is then connected and cooled in a 2-propanol–dry ice bath. The system is irradiated and subjected to a steady flow of nitrogen (approximately 400–500 ml./minute). After the first hour, this flow rate is reduced to 200–250 ml./minute for the remaining 4.5 hours. At the end of a total irradiation period of 6 hours, trap *C* is stoppered and stored at dry ice temperature. This trap contains 15–25 ml. of a 2–5% solution of bicyclopentene in tetrahydrofuran, (Note 6) contaminated with minor amounts (<15%) of tricyclo[2.1.0.0^{2,5}]pentane,[2] which is highly labile and difficult to separate.

Figure 1.



2. Notes

1. The submitters used an unfiltered, Hanovia, 450-watt, medium-pressure mercury vapor lamp (catalog No. 679A, Hanovia Lamp Division, Canrad Precision Industries, 100 Chestnut Street, Newark, N.J. 07105) and a reactor equipped with a nitrogen-inlet containing a glass frit, which enters the bottom of the reactor. All connections (Note 9) were glass with the exception of the rubber tubing between the second trap and the mercury bubbler. All glassware was soaked for 30 minutes in aqueous 30% ammonium hydroxide and oven-dried prior to use without further rinsing. Any polymer formed on the quartz immersion well during this preparation may be removed with nitric acid or with warm water and cleansing powder; if it is not removed, yields in subsequent preparations are significantly diminished.

2. Tetrahydrofuran (purchased from Mallinckrodt Chemical Works) was dried by distillation from lithium aluminum hydride, and stored over Linde 4A Molecular Sieves.

3. Cyclopentadiene was prepared [compare with *Org. Synth.*, **Coll. Vol. 4**, 473, Note 4 (1963) and **Coll. Vol. 5**, 414 (1973)] by heating dicyclopentadiene (purchased from Eastman Organic Chemicals) and a pinch of hydroquinone under a column of glass helices or a Vigreux column at 175° and collecting the distillate in a receiver cooled with a 2-propanol–dry ice bath. The monomer was dried over Linde 4A Molecular Sieves at −20° and could be stored at this temperature for several weeks without excessive dimerization.

4. Triethylamine (purchased from Matheson, Coleman and Bell) was dried over Linde 4A Molecular Sieves.

5. Dimsyl anion[3] was prepared from 10.2 g. (0.241 mole) (Note 10) of 56.8% sodium hydride, which was washed with pentane and vacuum dried, and 200 ml. of anhydrous dimethyl sulfoxide. The mixture was heated at 65–70° for about 50 minutes, until hydrogen evolution ceased. *Caution! This mixture should not be heated above 80° because of the possibility of explosive decomposition.*

6. Analysis and purification of the product solution is best accomplished by GC. The submitters used a 500 cm. by 0.6 cm. aluminum or polyethylene column packed with 21% β,β'-oxydipropionitrile on Chromosorb P with column, injector, and detector operated at 25° and a flow rate of 50 ml./minute. Under these conditions the retention times of bicyclopentene and cyclopentadiene were 3 and 5 minutes, respectively, beyond that of coinjected air. Tricyclopentane elutes in low yield with the bicyclopentene. Since bicyclopentene is extremely labile with respect to acid catalysis, any contact with water, hydroxylic solvents, and aprotic acids should be avoided (Note 11). Bicyclopentene stored at −78° in anhydrous tetrahydrofuran is stable indefinitely.
7. Decalin, benzene, 1,4-dioxane, and ethanol may be used as solvents for the photolysis. In an alternative procedure, volatile materials swept from the photolysis vessel are condensed in a dry ice trap. This cold mixture is added to a flask containing a magnetically stirred solution of dimsyl anion in dimethyl sulfoxide, and fractionation at reduced pressure provides a solution of bicyclopentene in tetrahydrofuran. In both variants additional bicyclopentene remains in the dilute reactor and trap solutions. It may be more fully recovered by using a modified distillation assembly composed of a gently warmed flask, a distillation head with a dry ice condenser filled with ice, an ice-cooled receiver, and a 2-propanol-dry ice vapor trap prior to a vacuum pump. (A rotary evaporator with an ice-filled dry ice condenser also works.) The vacuum is adjusted to rapidly distill the high boiling solvent into the receiver and bicyclopentene past the condenser into the −78° trap. The final distillation should be from the dimsyl anion solution (mainly tetrahydrofuran distills here) to remove codistilled cyclopentadiene.
8. A purified, undiluted sample of bicyclopentene has been reported to explode.[4]
9. All of the connections must be well secured by sturdy rubber bands to avoid leakage caused by substantial back pressure that develops in the course of the reaction.
10. A higher base concentration or substitution of one or two gas-dispersion tubes leads to clogging of the inlet to the trap.
11. Two injections of 10 ml. of ammonia vapors greatly helps to eliminate decomposition on the column during GC collection.

3. Discussion

The present procedure, a modification of that previously reported,[5,6,7,8] permits the ready preparation of a cyclopentadiene-free solution of bicyclopentene on a synthetic scale. Until now, synthetic chemistry involving the use of bicyclopentene has been limited to preparations of bicyclopentane[5,8] and bicyclopentane-2,3-d_2,[8] which is more a reflection of the extraordinary care required in handling this unusually sensitive bicyclic alkene than a lack of interesting potential or useful reactivity.

Most cyclic and acyclic 1,3-dienes, such as cyclopentadiene, undergo photochemical ring-closure to cyclobutenes.[9] Bicyclo[2.1.0]pent-2-ene derivatives have also been prepared *via* photolysis of cyclopentadiene-5-d-, -d_6, and -1,5-$^{13}C_2$;[2,10] 1-, 2-, and 5-methylcyclopentadiene;[2,11] 5,5-dimethylcyclopentadiene;[12] 1,5-dimethyl- and 2,5-dimethyl-1,3-cyclopentadien-5-yl acetic acid;[13] 2,2-dimethylisoindene[14] and 2,3,5-tri-*tert*-butylcyclopentadienone.[15] Substituted thiophenes have been converted photochemically to 5-thia derivatives of bicyclopentene.[16]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 226

References and Notes

1. Department of Chemistry, University of Oregon, Eugene, Oregon 97403.
2. G. D. Andrews and J. E. Baldwin, *J. Am. Chem. Soc.*, **99**, 4851, 4853 (1977); **94**, 1775 (1972) and references therein.
3. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **84**, 866 (1962); **87**, 1345 (1965).
4. T. J. Katz, private communication.
5. J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966).
6. J. I. Brauman and D. M. Golden, *J. Am. Chem. Soc.*, **90**, 1920 (1968).

7. D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, **65**, 464 (1969).
8. P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Am. Chem. Soc.*, **91**, 1684, (1969); **90**, 4746 (1968).
9. G. B. Gill, *Q. Rev. Chem. Soc.*, **22**, 338 (1968); G. J. Fonken, *Org. Photochem.*, **1**, 197 (1967).
10. J. E. Baldwin, R. K. Pinschmidt, Jr., and A. H. Andrist, *J. Am. Chem. Soc.*, **92**, 5249 (1970).
11. J. E. Baldwin, A. H. Andrist, *J. Chem. Soc. D*, 1561 (1970).
12. W. R. Roth, F.-G. Klärner, and H. W. Lennartz, *Chem. Ber.*, **113**, 1818 (1980).
13. F.-G. Klärner, and F. Adamsky, *Angew. Chem. Int. Ed. Engl.*, **18**, 674 (1979).
14. W. R. Dolbier, K. Matsui, H. J. Dewey, D. V. Horak, and J. Michl, *J. Am. Chem. Soc.*, **101**, 2136 (1979).
15. G. Maier, U. Schäfer, W. Sauer, H. Hartan, and J. F. M. Oth, *Tetrahedron Lett.*, 1837 (1978).
16. J. A. Barltrop, A. C. Day, and E. Irving, *J. Chem. Soc. Chem. Commun.*, 966, 881 (1979); H. A. Wiebe, S. Braslavsky, and J. Heicklen, *Can. J. Chem.*, **50**, 2721 (1972).

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

bicyclopentane-2,3-d_2

2,2-dimethylisoindene

ethanol (64-17-5)

ammonia (7664-41-7)

Benzene (71-43-2)

hydrogen (1333-74-0)

hydroquinone (123-31-9)

nitric acid (7697-37-2)

nitrogen (7727-37-9)

ammonium hydroxide (1336-21-6)

Pentane (109-66-0)

Tetrahydrofuran (109-99-9)

lithium aluminum hydride (16853-85-3)

sodium hydride (7646-69-7)

dimethyl sulfoxide (67-68-5)

triethylamine (121-44-8)

CYCLOPENTADIENE (542-92-7)

dicyclopentadiene (77-73-6)

decalin (91-17-8)

Bicyclo[2.1.0]pent-2-ene (5164-35-2)

bicyclopentene

tricyclo[$2.1.0.0^{2,5}$]pentane

1,4-dioxane (123-91-1)

bicyclopentane (1636-39-1)

5-methylcyclopentadiene

5,5-dimethylcyclopentadiene

2,5-dimethyl-1,3-cyclopentadien-5-yl acetic acid

cyclopentadiene-5-d

2,3,5-tri-tert-butylcyclopentadienone