



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.

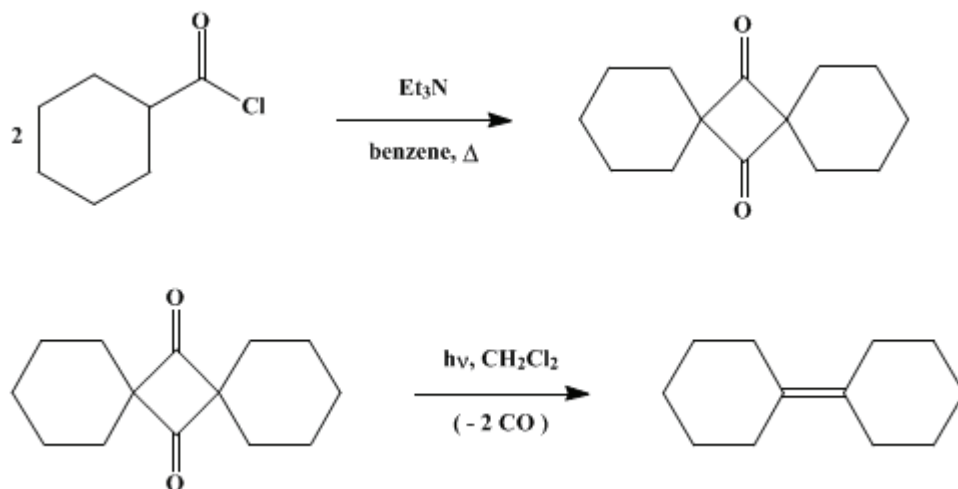
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.297 (1973); Vol. 47, p.34 (1967).

CYCLOHEXYLIDENECYCLOHEXANE

[Bicyclohexylidene]



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1. Procedure

A. *Dispiro[5.1.5.1]tetradecane-7,14-dione*. Cyclohexanecarbonyl chloride (Note 1) (30.0 g., 0.205 mole) and 250 ml. of dry benzene are placed in a three-necked, round-bottomed flask equipped with a stirrer, condenser, and dropping funnel. A nitrogen atmosphere is maintained in the system. Dry triethylamine (35.0 g., 0.35 mole) is slowly added, and the mixture is heated under reflux overnight. The amine hydrochloride is then filtered, and the filtrate is washed with dilute hydrochloric acid and with water. Solvent is removed on a steam bath, and the residue is recrystallized from ligroin-ethanol; yield 11–13 g. (49–58%), m.p. 161–62°.

B. *Cyclohexylidenecyclohexane*. In a Hanovia 450-watt immersion photochemical reactor (Note 2), equipped with a side arm attachment to monitor gas evolution, is placed 15 g. (0.068 mole) of dispiro [5.1.5.1]tetradecane-7,14-dione dissolved in 150 ml. of methylene chloride. The sample is irradiated, and carbon monoxide starts to evolve rapidly after a few minutes. Irradiation is continued until gas evolution has ceased, usually about 8–10 hours (Note 3). After the irradiation most of the solvent is removed on a steam bath. The residual oil is transferred to a sublimator. The sublimator, with the cold finger removed, is placed in a vacuum desiccator, and the system is evacuated to remove any remaining methylene chloride. The semisolid residue is then sublimed at 45° (1 mm.) to yield 7 g. (63%) of crude cyclohexylidenecyclohexane. The product after recrystallization from methanol weighs 5.5 g. (49%), m.p. 53–54°.

2. Notes

1. Cyclohexanecarbonyl chloride was obtained from Eastman Organic Chemicals.
2. The reactor, manufactured by the Hanovia Division of Engelhard Industries, consists of a water-jacketed Vycor well through which a stream of water is continuously passed. Since wavelengths shorter than 3000 Å are not needed, the immersion well may be made of Pyrex instead. Within the well is a No. 679A-36 450-watt medium-pressure mercury lamp, also manufactured by Hanovia, and a cylindrical Pyrex filter which surrounds the lamp. The well is placed in an appropriately shaped flask containing the solution to be irradiated. The flask is essentially cylindrical and is equipped with a side arm near the top through which gas can escape and be bubbled through a container of water. The flask is so designed that the liquid level is above the top of the lamp. The reaction vessel is quite similar to that shown in

Fig. 1 (p. 65).

The same synthesis could be carried out in an ordinary flask using one or two sunlamps or sunlight, but the irradiation time would necessarily be much longer.

3. The system should be relatively free of oxygen during irradiation. Oxygen apparently combines with a photochemical intermediate to form cyclohexanone.³ Under the conditions recommended in the procedure, oxygen is prevented from entering the system by the water trap which also serves as a monitor for gas evolution.

3. Discussion

Ethyl 1-bromocyclohexanecarboxylate, when treated with magnesium in anhydrous ether-benzene with subsequent addition of cyclohexanone, yields ethyl 1-(1-hydroxycyclohexyl)cyclohexanecarboxylate. Dehydration and saponification give rise to 1-(1-cyclohexenyl)cyclohexanecarboxylic acid, which upon decarboxylation at 195° yields cyclohexylidenecyclohexane in 8% overall yield, m.p. 54°.⁴ This olefin has also been prepared by the debromination of 1,1'-dibromobicyclohexyl with zinc in acetic acid.⁵

The preparation of the dispiro[5.1.5.1]tetradecane-7,14-dione intermediate is essentially that of Walborsky and Buchman.⁶

4. Merits of the Preparation

The most obvious features of this synthesis are its simplicity and overall yield, which appear to be superior to those of any other published report. An important merit lies in the generality of the reaction, and the fact that it is an example of a reasonably large-scale photochemical preparation. Tetramethylethylene is readily produced from commercially available tetramethyl-1,3-cyclobutanedione by an identical route.⁷

This preparation is referenced from:

- Org. Syn. Coll. Vol. 7, 470

References and Notes

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6. H. M. Walborsky and E. R. Buchman, *J. Am. Chem. Soc.*, **75**, 6339 (1953).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

ligroin-ethanol

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

methanol (67-56-1)

ether (60-29-7)

carbon monoxide (630-08-0)

magnesium (7439-95-4)

Cyclohexanone (108-94-1)

oxygen (7782-44-7)

nitrogen (7727-37-9)

zinc (7440-66-6)

methylene chloride (75-09-2)

tetramethylethylene (563-79-1)

tetramethyl-1,3-cyclobutanedione (933-52-8)

triethylamine (121-44-8)

cyclohexanecarbonyl chloride (2719-27-9)

Cyclohexylidenecyclohexane,
Bicyclohexylidene (4233-18-5)

Dispiro[5.1.5.1]tetradecane-7,14-dione (950-21-0)

Ethyl 1-bromocyclohexanecarboxylate

ethyl 1-(1-hydroxycyclohexyl)cyclohexanecarboxylate

1-(1-cyclohexenyl)cyclohexanecarboxylic acid

1,1'-dibromobicyclohexyl