



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.

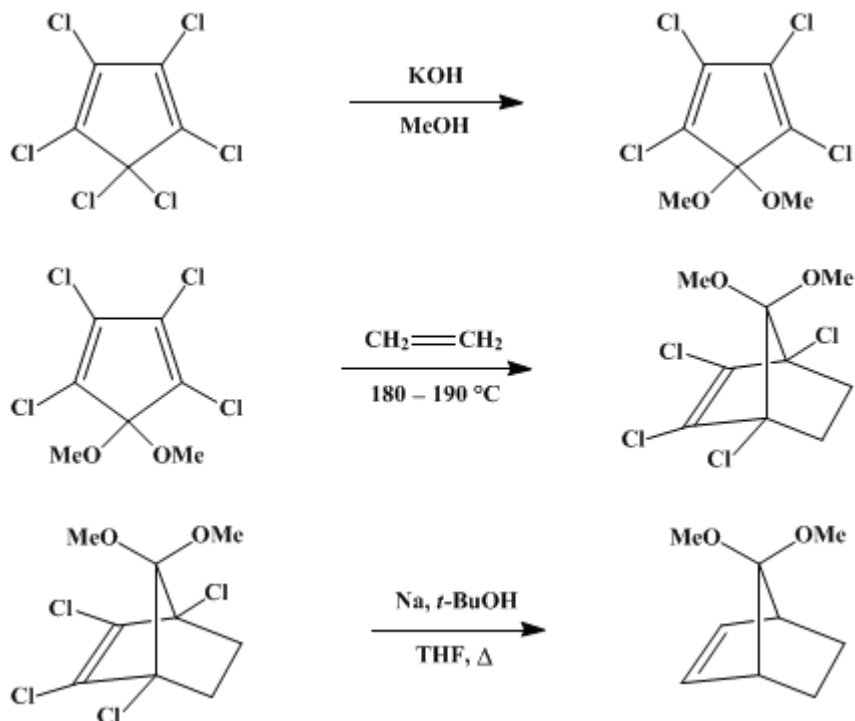
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.424 (1973); Vol. 48, p.68 (1968).*

## 7,7-DIMETHOXYBICYCLO[2.2.1]HEPTENE

### [2-Norbornen-7-one dimethyl acetal]



Submitted by P. G. Gassman and J. L. Marshall<sup>1</sup>.  
Checked by William G. Dauben and James L. Chitwood.

### 1. Procedure

*Caution! Most polychlorinated compounds show some toxicity. These compounds should be handled in a hood.*

A. *5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene*. In a 3-l. three-necked flask fitted with a condenser (Note 1), an addition funnel, and a mechanical stirrer (Note 2) are placed 254 g. (0.93 mole) of *hexachlorocyclopentadiene* (Note 3) and 800 ml. of *methanol* (Note 4). The stirrer is started, and a solution of 120 g. (2.14 moles) of *potassium hydroxide* in 600 ml. of *methanol* is added dropwise over a period of 2 hours (Note 5). The reaction mixture is stirred for an additional 2 hours and then poured over 3 l. of chopped ice. After the ice has melted, the mixture is extracted with three 250-ml. portions of *dichloromethane*. The combined extracts are dried over anhydrous *magnesium sulfate* and concentrated to a yellow syrup on a rotary evaporator (Note 6). The residue is distilled through a 12-in. vacuum-jacketed Vigreux column to yield 187–189 g. (76–77%) of *5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene* as a viscous, yellow-tinted oil, b.p. 79–84° (0.6 mm.) (Note 7).

B. *7,7-Dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene*. A large Pyrex gas washing bottle with fritted-glass inlet (Note 8) is fitted with a condenser and a drying tube. In the bottle is placed 189 g. (0.72 mole) of *5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene*, and a slow stream of *nitrogen* and *ethylene* is passed through the fritted-glass inlet (Note 9). The bottle is heated to 180–190° by means of an oil bath. The color of the liquid changes from yellow to reddish brown as *ethylene* is bubbled through the reaction mixture at this temperature for 6 hours (Note 10). The reaction mixture is cooled and distilled through a 12-in. vacuum-jacketed Vigreux column to yield 155–165 g. (73–78%) of a yellow

syrup, b.p. 70–75° (0.15 mm.) (Note 11).

C. *7,7-Dimethoxybicyclo[2.2.1]heptene*. A 3-l. three-necked flask is equipped with a sealed Hershberg stirrer,<sup>2</sup> a condenser fitted with a nitrogen inlet to maintain a slight positive pressure, and a pressure-equalizing dropping funnel. The flask is placed in a heating mantle, and into it are placed 1.5 l. of *tetrahydrofuran*, 130 g. (5.7 g. atoms) of *sodium* chopped into 5-mm. cubes, and 190 ml. (150 g., 2.0 moles) of *t-butyl alcohol*. This mixture is stirred vigorously and brought to gentle reflux (Note 12). As soon as refluxing occurs, 106 g. (0.36 mole) of *7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene* is added dropwise over a 2-hour period (Note 13). The mixture is heated under reflux for 38 hours, cooled to room temperature, and filtered through a wire screen to remove the unreacted *sodium*. The dark filtrate is refiltered by suction through Celite in a Buchner funnel (Note 14). The filtrate is mixed with 2 l. of chopped ice and 500 ml. of *ether*. The aqueous phase is separated (Note 15), and the organic phase is washed with 500-ml. portions of saturated aqueous *sodium chloride* until the washings are clear. The ethereal solution is dried over anhydrous *magnesium sulfate* and concentrated to a dark oil by removal of the *ether* by fractional distillation. The oil is fractionally distilled through a 6-in. Vigreux column to yield 17–24 g. (31–43%) of colorless liquid, b.p. 58–68° (17 mm.),  $n_D^{25}$  1.4598 (Note 16) and (Note 17).

## 2. Notes

1. If the directions are carefully followed, the condenser will not be utilized since it serves mainly as a safety device in case the reaction should become too exothermic.
2. A Hershberg nichrome wire stirrer<sup>2</sup> is well suited for this reaction.
3. The *hexachlorocyclopentadiene* was used as obtained from Matheson, Coleman and Bell.
4. Commercial grade *methanol* was used.
5. This reaction mixture should not be cooled initially because an uncontrollable exothermic reaction will occur if a large concentration of alkoxide builds up.
6. Concentration at 100° (30 mm.) is necessary for removal of most of the *dichloromethane*.
7. The submitters have obtained an 86% yield of product, b.p. 79–91° (0.6 mm.). They have also found that the reaction may be scaled up fivefold if 4 hours is taken for the addition of the methanolic base. No danger exists if the temperature is maintained between 50° and 60°.
8. Pyrex gas washing bottle, Corning No. 31750, was used.
9. The checkers found that best results were obtained when the slowest detectable *nitrogen* flow was used with a fairly rapid *ethylene* flow (about 1 in. of foam in the gas washing bottle at the reaction temperature).
10. The course of the reaction is readily followed by n.m.r. spectroscopy. The spectrum of the starting material has a singlet at  $\delta$  3.30 p.p.m., whereas that of the product has two singlets at  $\delta$  3.50 and 3.55 p.p.m. The time required for complete reaction depends on the flow rate of *ethylene* and *nitrogen*. The reaction should be allowed to continue until all the starting material is consumed.
11. The distillation should be conducted carefully since the yield in the next step depends on the purity of the material used.
12. Occasionally the pieces of *sodium* may start to fuse together. This difficulty may be avoided by bringing the mixture to a gentle reflux and stirring vigorously. Once the addition of the chlorinated compound is started, fusing of the *sodium* ceases. When the reaction is finished, the *sodium* pieces often fuse into a single large chunk.
13. Unless the reaction mixture is heated *before* the addition process is started, there may be an initial induction period that may cause the reaction to become extremely vigorous once the mixture heats to reflux temperature.
14. The checkers found this last filtration to be a very time-consuming and cumbersome operation. They found it preferable to omit it; they cautiously added *methanol*<sup>3</sup> to decompose any traces of *sodium* and poured the resulting solution directly onto the chopped ice.
15. In the separation of the organic and aqueous phases it is often initially very difficult to discern the phase separation because of the dark color of the reaction mixture. The submitters found that, if the phase separation cannot be detected under ordinary light, it can usually be seen by the use of an ultraviolet scanning lamp.
16. The submitters report that 65% yields of product, b.p. 61–71° (18 mm.), can be obtained by workers with experience with this reaction.

17. The product is rather volatile, and care should be taken in its handling and storing.

### 3. Discussion

The procedures described for the preparation of [5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene](#) and [7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo\[2.2.1\]hept-2-ene](#) are essentially those of Newcomer and McBee<sup>4</sup> and of Hoch,<sup>5</sup> respectively. The dechlorination is a modification of an analogous dechlorination carried out by Bruck, Thompson, and Winstein.<sup>3</sup> The overall procedure is that of Gassman and Pape.<sup>6</sup>

### 4. Merits of the Preparation

The reactions include an unusual Diels-Alder reaction and a very useful synthetic method, the dechlorination of polychlorinated compounds. At the present time this procedure is the best one available for the removal of [chlorine](#) from an organic molecule. The end product, [7,7-dimethoxybicyclo\[2.2.1\]heptene](#), is an interesting and useful intermediate in bicyclic chemistry; it has a reactive double bond and a protected carbonyl group in the 7-position.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 91](#)
- [Org. Syn. Coll. Vol. 6, 82](#)

---

### References and Notes

1. Department of Chemistry, The Ohio State University, Columbus, Ohio 43210.
  2. [P. S. Pinkney, \*Org. Syntheses, Coll. Vol. 2\*, 116 \(1943\).](#)
  3. [P. Bruck, D. Thompson, and S. Winstein, \*Chem. Ind. \(London\)\*, 405 \(1960\).](#)
  4. [J. S. Newcomer and E. T. McBee, \*J. Am. Chem. Soc.\*, \*\*71\*\*, 946 \(1949\).](#)
  5. [P. E. Hoch, \*J. Org. Chem.\*, \*\*26\*\*, 2066 \(1961\).](#)
  6. [P. G. Gassman and P. G. Pape, \*J. Org. Chem.\*, \*\*29\*\*, 160 \(1964\).](#)
- 

### Appendix

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

[methanol \(67-56-1\)](#)

[ether \(60-29-7\)](#)

[sodium chloride \(7647-14-5\)](#)

[nitrogen \(7727-37-9\)](#)

[chlorine \(7782-50-5\)](#)

[potassium hydroxide \(1310-58-3\)](#)

[sodium \(13966-32-0\)](#)

[ethylene \(9002-88-4\)](#)

dichloromethane (75-09-2)

magnesium sulfate (7487-88-9)

Tetrahydrofuran (109-99-9)

5,5-Dimethoxy-1,2,3,4-tetrachlorocyclopentadiene (2207-27-4)

7,7-dimethoxy-1,2,3,4-tetrachlorobicyclo[2.2.1]hept-2-ene (19448-78-3)

t-butyl alcohol (75-65-0)

7,7-Dimethoxybicyclo[2.2.1]heptene,  
2-Norbornen-7-one dimethyl acetal (875-04-7)

hexachlorocyclopentadiene