



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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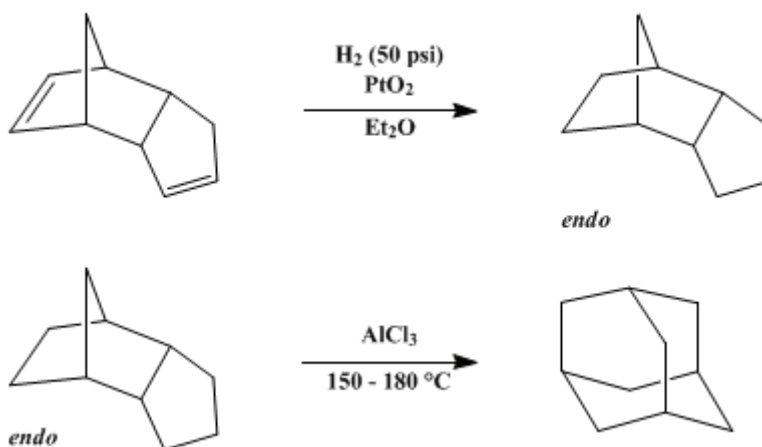
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.16 (1973); Vol. 42, p.8 (1962).

ADAMANTANE

[Tricyclo[3.3.1.1^{3,7}] decane]



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1. Procedure

A. *endo*-Tetrahydrodicyclopentadiene. A solution of 200 g. (1.51 moles) of purified dicyclopentadiene (Note 1) in 100 ml. of dry ether containing 1.0 g. of platinum oxide is hydrogenated at 50 p.s.i. hydrogen pressure using a Parr apparatus. The reaction mixture becomes quite warm during the initial stage of the hydrogenation,² and the uptake of 2 mole equivalents of hydrogen requires 4–6 hours. The catalyst is removed by suction filtration, and the filtrate is distilled at atmospheric pressure through a 30-cm. Vigreux column.

When the removal of the ether is complete, the condenser at the top of the column is replaced by a wide-diameter adapter the bottom of which is placed in a receiver flask immersed in an ice bath. The adapter is heated (Note 2) to prevent premature solidification of the distillate. The distillation is continued and the *endo*-tetrahydrodicyclopentadiene, b.p. 191–193°, is collected. The yield is 196–200 g. (96.5–98.4%). The melting point depends on the purity of the starting material but generally is above 65°.

B. *Adamantane*. In a 500-ml. Erlenmeyer flask having a 24/40 standard taper joint are placed 200 g. (1.47 moles) of molten *endo*-tetrahydrodicyclopentadiene and a magnetic stirring bar. A well-greased inner joint (2.2 × 15 cm., 24/40) is fitted into the top of the flask to serve as an air condenser, and 40 g. of anhydrous aluminum chloride is added through the opening (Note 3). The reaction mixture is simultaneously stirred and heated at 150–180° (Note 4), (Note 5) by means of a combination magnetic stirrer-hot plate. Aluminum chloride sublimes to the top of the flask, especially at the beginning of the reaction, and the accumulated sublimate is, from time to time, pushed down into the reaction liquid. After the mixture has been heated for 8–12 hours, the flask is removed from the hot plate-stirrer and the black contents upon cooling separate into two layers. The upper layer, a brown mush of adamantane and other products, is decanted carefully from the lower black tarry layer into a 600-ml. beaker. The Erlenmeyer flask is rinsed five times with a total of 250 ml. of petroleum ether (b.p. 30–60°) with decantation into the same beaker (Note 6), (Note 7). The petroleum ether suspension is warmed until all the adamantane is in solution; there should be an appreciable excess of solvent. The solution is decolorized by careful addition of 10 g. of chromatography-grade alumina, the hot solution filtered, and the alumina and the beaker washed thoroughly with solvent. The nearly colorless filtrate (Note 8) is concentrated to a volume of about 200 ml. by distillation and then cooled in a Dry Ice-acetone bath. The solid adamantane is removed by suction filtration and there results 27–30 g. (13.5–15.0%) of crystals,

melting point about 255–260° (Note 9), (Note 10). One recrystallization from petroleum ether raises the melting point to 268–270° (Note 11), (Note 12).

2. Notes

1. Technical grade [dicyclopentadiene](#) is purified by distillation at water pump pressure through a 30-cm. Vigreux column, and the fraction boiling at 64–65°/14 mm. (72–73°/22 mm.) is used in the reaction. The best material is solid or semisolid at room temperature.
2. The adapter can readily be heated by placing an infrared lamp above it.
3. The evolution of heat initially observed is due to the exothermic rearrangement of [endo-tetrahydrodicyclopentadiene](#) to its *exo*-isomer.³
4. The temperature of the reaction is followed by inserting a thermometer into the reaction flask through the joint.
5. Other methods of heating and stirring may be used but are more troublesome because of the tendency of [aluminum chloride](#) to sublime and clog top-mounted stirrers.
6. If appreciable amounts of tar have been transferred to the beaker, repeat the decantation and washing process into a clean beaker.
7. The tarry flasks and beakers can be cleaned easily with [acetone](#). *Do not use water* until all the tar has been removed.
8. If necessary, the filtrate should be warmed to dissolve all the [adamantane](#).
9. The melting point must be taken in a sealed capillary, and the sealed portion must be completely immersed in the liquid of the melting-point bath.
10. Additional [adamantane](#), 2–6 g., can be obtained by distilling the mother liquors through a 10-cm. Vigreux column and chilling the fraction boiling between 180° and 200°. The filtrate from the collection of the second portion of [adamantane](#) consists mostly of [exo-tetrahydrodicyclopentadiene](#).³ The amount of this fraction, 30–100 g., depends on the severity of the rearrangement conditions. Much non-distillable residue is obtained. Conversion of the 180–200° fractions to [adamantane](#) is brought about by treating them with [aluminum chloride](#) as before, and the yields are comparable.
11. The recrystallization is not necessary unless material of the highest purity is desired.
12. [1-Methyladamantane](#) and [1,3-dimethyladamantane](#) can be prepared by analogous isomerizations.⁴

3. Discussion

[Adamantane](#) can be isolated from petroleum, where it is found in minute yield.⁵ Two multistep syntheses starting with [tetraethylbicyclo\[3.3.1\]nonane-2,6-dione-1,3,5,7-tetracarboxylate](#) have been reported.⁶ Also, starting with [endo-tetrahydrodicyclopentadiene](#), it has been found that a catalyst composed of [aluminum chloride](#) and [hydrogen chloride](#) will bring about the rearrangement to [adamantane](#) in 30–40% yield, but the reaction must be performed in a [hydrogen](#) atmosphere at high pressure.⁷ A recent patent describes the conversion in up to 30% yield using a [boron trifluoride-hydrogen fluoride](#) catalyst under pressure.⁸ The present method is based on the published procedure of the submitters and is the preferred method by virtue of the greater convenience.⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 20](#)
- [Org. Syn. Coll. Vol. 6, 48](#)
- [Org. Syn. Coll. Vol. 6, 378](#)

References and Notes

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4. P. von R. Schleyer, *Tetrahedron Lett.*, 305 (1961).

5. S. Landa and V. Macháček, *Collection Czechoslov. Chem. Commun.*, **5**, 1 (1960); S. Landa and S. Hála, *Collection Czechoslov. Chem. Commun.*, **24**, 93 (1959).
 6. V. Prelog and R. Seiwerth, *Ber.*, **74**, 1644, 1769 (1941); H. Stetter, O. E. Bänder, and W. Neumann, *Ber.*, **89**, 1922 (1956).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

alumina

petroleum ether

hydrogen chloride (7647-01-0)

ether (60-29-7)

hydrogen (1333-74-0)

platinum oxide

hydrogen fluoride (7664-39-3)

acetone (67-64-1)

aluminum chloride (3495-54-3)

boron trifluoride (7637-07-2)

dicyclopentadiene (77-73-6)

Adamantane,
Tricyclo[3.3.1.1^{3,7}] decane (281-23-2)

1-Methyladamantane (768-91-2)

1,3-dimethyladamantane (702-79-4)

tetraethylbicyclo[3.3.1]nonane-2,6-dione-1,3,5,7-tetracarboxylate

endo-Tetrahydrodicyclopentadiene,
exo-tetrahydrodicyclopentadiene (6004-38-2)