



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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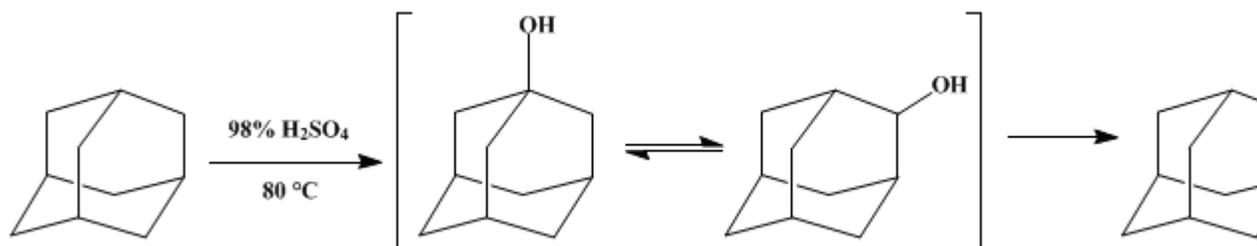
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.48 (1988); Vol. 53, p.8 (1973).

ADAMANTANONE

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



Submitted by H. W. Geluk and V. G. Keizer¹.
Checked by L. Foley, W. Jackson, and A. Brossi.

1. Procedure

Caution! This procedure should be carried out in an efficient hood to avoid exposure to sulfur dioxide.

Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A 1-l., three-necked, round-bottomed flask equipped with an efficient mechanical stirrer (Note 1), a thermometer, and a vent (Note 2) is placed in a water bath and charged with 600 ml. of 98% sulfuric acid (Note 3). Powdered adamantane [*Org. Synth.*, **Coll. Vol. 5**, 16 (1973)], (100 g., 0.735 mole), is added in one portion to the stirred acid, and the mixture is heated rapidly (with the water bath) to an internal temperature of 70°. The internal temperature is then raised gradually to 80° over a 2-hour period (Note 4) while vigorous stirring is maintained (Note 5). After stirring at 80° is continued for an additional 2 hours, the temperature is raised to 82°. When almost all the adamantane is dissolved, the residual sublimed material is scraped and rinsed from the walls of the flask (Note 1) and (Note 6). When GC analysis indicates that 2–3% of adamantanol is present (Note 6), the hot reaction mixture is poured immediately onto 800 g. of crushed ice, giving a 1500-ml. suspension containing crude adamantanone.

A 750-ml. portion of this suspension of crude adamantanone is transferred to a 2-l., round-bottomed flask, equipped for steam distillation (Note 7) and (Note 8), which is placed in a heating mantle. The contents of the distillation flask are heated to 70°; the external heating is turned off (Note 9) and steam is introduced carefully through both inlet tubes (Note 10). The two layers of distillate are separated, and the aqueous layer is extracted with two 75-ml. portions of dichloromethane. This steam distillation procedure is then repeated with the second half of the suspension of crude adamantanone. The organic extracts are combined, washed with 100 ml. of aqueous, saturated sodium chloride, dried over anhydrous sodium sulfate, and evaporated under reduced pressure, yielding 52–53 g. (47–48%) of adamantanone (Note 11), (Note 12), and (Note 13).

2. Notes

1. The stirrer should be placed just under the surface of the sulfuric acid. The flask should be filled to at least three-quarters of its volume so the sublimed material can be rinsed from the walls with vigorous stirring.
2. Sulfur dioxide generated during the reaction can escape through the third neck of the flask. This neck should be wide enough to prevent clogging by subliming adamantane.

3. The required amount of 98% sulfuric acid is prepared by adding 53 ml. of fuming sulfuric acid (65% free sulfur trioxide) to 530 ml. of 96% sulfuric acid, or by adding 120 ml. of fuming sulfuric acid (30–33% free sulfur trioxide) to 480 ml. of 96% sulfuric acid.
4. During this part of the reaction a vigorous evolution of sulfur dioxide takes place. Care should be taken to ensure that the internal temperature does not rise too fast to prevent an uncontrollable increase in the evolution of the sulfur dioxide.
5. An adamantane layer floating on the sulfuric acid, caused by ineffective stirring or too rapid evolution of sulfur dioxide, can lead to heavy foaming and subsequent losses. This layer, if formed, may be brought into contact with the reaction mixture by increasing the speed of the stirrer or by lowering the bath temperature to 65–70°.
6. At this stage the reaction should be monitored carefully by GC. For this purpose samples are taken periodically from the reaction mixture, poured onto ice, extracted with dichloromethane, washed with water, and subjected to GC. The submitters used an F and M Model 700 gas chromatograph equipped with a 2 m. by 3 mm. glass column, filled with 80/100 mesh Chromosorb-W-Hp impregnated with 9.5% Apiezon-L and 0.5% Carbowax-20 M, at 120° with a flame ionization detector and nitrogen as carrier gas. To obtain a good yield of a fairly pure product, the reaction should be stopped when the amount of 1-adamantanol remaining is between 2% and 3%. Prolonged heating will give a further reduction in the 1-adamantanol content but it should be emphasized that concurrently the yield of the adamantanone will diminish rapidly.
7. The flask is fitted with two inlet tubes, one narrow and adjustable positioned above the surface of the adamantanone suspension, and the other reaching half-way between the bottom of the flask and the surface. Both tubes are connected to the steam supply. The flask is connected through a splash head and a short adapter to a 1-l., three-necked, round-bottomed flask equipped with two very efficient reflux condensers each stoppered with a wad of cotton. The receiving flask is charged with 100 ml. of benzene, which, during the course of the steam distillation, begins to reflux and rinses the adamantanone from the condensers. *Added in proof.* Because of the toxicity of benzene the submitters advise replacement of this solvent with ethyl acetate at this point and in (Note 8).
8. The checkers found that it is advisable to use superheated steam and also to distill each portion twice. Thus when the first receiving flask fills with distillate, it is replaced with a second 1-l., round-bottom flask charged with 100 ml. of benzene and distillation is resumed.
9. Prolonged external heating will stimulate the foaming. Insulation by the heating mantle is sufficient to prevent extensive steam condensation in the distilling flask.
10. The short inlet tube above the surface (Note 7) will break the foam and enable smooth removal of the adamantanone. When foaming is very heavy, steam is introduced only through this short inlet tube.
11. The checkers found that an additional 3 g. of adamantanone could be obtained by extracting the combined contents of the two distillation flasks with dichloromethane, removing the solvent under reduced pressure and steam-distilling the residue, resulting in a total yield of 55–56 g. (50–51%).
12. The product is 97–98% pure by GC (Note 6) and is satisfactory for most purposes. If desired, the adamantanone may be purified by either column chromatography (alumina, activity grade IV; eluent: ether) or by treatment with fuming sulfuric acid (20% free sulfur trioxide). For example, 8.0 g. of adamantanone is added portionwise to 40 ml. of ice-cold, fuming sulfuric acid, and the solution is heated to 40° and maintained at this temperature for one hour. After pouring the mixture onto ice, the adamantanone is recovered by extraction with dichloromethane.
13. The IR spectrum (KBr) shows a strong band at 1717 with minor peaks or shoulders at 1670, 1690, 1725, and 1740 cm^{-1} ; ^1H NMR (CDCl_3), δ 2.04 (broad s, 12H, 2CH, 5CH₂) and 2.55 (broad s, 2H, 2CHC=O).

3. Discussion

Adamantanone is a very versatile starting material for the preparation of adamantane derivatives, especially those substituted at secondary carbon atoms.

The preparative method presented is a slight modification of that reported by Geluk and co-workers,^{2,3} who also give a detailed account of the several reactions of adamantane, 1-adamantanol, and 2-adamantanol that take place in sulfuric acid.^{2,4} Adamantanone can be prepared essentially as described herein starting with 1-adamantanol instead of adamantane²—the yield is better (70%) and the reaction time is shorter, but adamantane is a more suitable starting material.

Adamantane can also be oxidized to adamantanone with ozone,⁵ and the oxime can be made directly from adamantane by photoöximation.⁶

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 41](#)

References and Notes

1. Philips-Duphar B. V. Research Laboratories, Weesp, The Netherlands.
 2. H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5361 (1968).
 3. H. W. Geluk and V. G. Keizer, *Synth. Commun.*, **2**, 201 (1972). This preparation appears in *Org. Synth., Coll. Vol. 6, 48 (1988)*, by courtesy of Marcel Dekker, Inc., New York.
 4. H. W. Geluk and J. L. M. A. Schlatmann, *Tetrahedron*, **24**, 5369 (1968).
 5. S. Landa and L. Vodicka, Czech. Pat. 119,348 (1966) [*Chem. Abstr.*, **67**, P21508v (1967)].
 6. E. Müller and G. Fiedler, *Chem. Ber.*, **98**, 3493 (1965).
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Appendix

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

[sulfuric acid \(7664-93-9\)](#)

[Benzene \(71-43-2\)](#)

[ethyl acetate \(141-78-6\)](#)

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

[sulfur trioxide \(7446-11-9\)](#)

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

[sulfur dioxide \(7446-09-5\)](#)

[sodium sulfate \(7757-82-6\)](#)

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

[carbon \(7782-42-5\)](#)

[dichloromethane \(75-09-2\)](#)

[ozone \(10028-15-6\)](#)

[Adamantane \(281-23-2\)](#)

[1-Adamantanol,
adamantanol \(768-95-6\)](#)

Adamantanone,
Tricyclo[3.3.1.1^{3,7}]decanone (700-58-3)

2-adamantanol (700-57-2)

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