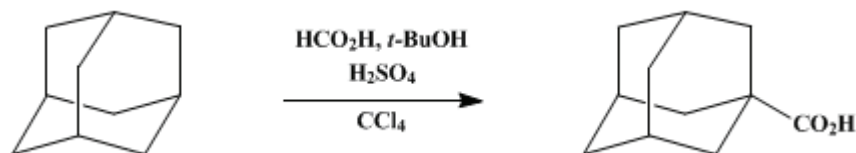


1-ADAMANTANECARBOXYLIC ACID



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1. Procedure

Caution! Because carbon monoxide is evolved, the reaction should be carried out in a good hood.

A 1-l. three-necked flask equipped with stirrer, thermometer, dropping funnel, and gas-outlet tube is charged with 470 g. (255 ml., 4.8 moles) of 96% sulfuric acid (Note 1), 100 ml. of carbon tetrachloride (Note 2), and 13.6 g. (0.100 mole) of adamantane.² The well-stirred mixture is cooled to 17–19° in an ice bath, and 1 ml. of 98% formic acid is added. Then a solution of 29.6 g. (38 ml., 0.40 mole) of *t*-butyl alcohol in 55 g. (1.2 moles) of 98–100% formic acid is added dropwise; the rate of addition and the cooling are regulated so that the addition requires 1–2 hours, and the temperature of the reaction mixture is kept at 17–25°. The reaction mixture is stirred for an additional 30 minutes and poured onto 700 g. of crushed ice. The layers are separated, and the upper, acid layer is extracted with three 100-ml. portions of carbon tetrachloride.

The combined carbon tetrachloride layers are shaken with 110 ml. of 15*N* ammonium hydroxide (Note 3), and the crystalline ammonium 1-adamantanecarboxylate that separates is collected on a Büchner funnel having a coarse fritted disk. The salt is washed with 20 ml. of cold acetone and suspended in 250 ml. of water. The suspension is made strongly acidic with 25 ml. of 12*N* hydrochloric acid and extracted with 100 ml. of chloroform. The chloroform layer is dried over anhydrous sodium sulfate and evaporated to dryness on a steam bath (Note 4). The residue is crude 1-adamantanecarboxylic acid; weight 12–13 g. (67–72%) (Note 5); m.p. 173–174°. Recrystallization of this product from a mixture of 30 ml. of methanol and about 10 ml. of water gives 10–11 g. (56–61%) of pure acid, m.p. 175–176.5° (Note 6).

2. Notes

1. Acid concentrations of 95–98% are satisfactory. The yield falls with concentrations lower than 95%.
2. Cyclohexane or *n*-hexane can be used in place of carbon tetrachloride. Technical "normal hexane" may contain substantial amounts of methylcyclopentane and isohexane that lower the yield through formation of C₇-acids that are hard to remove.
3. A large amount of trimethylacetic acid and a small amount of at least one C₉-acid and one C₁₃-acid are formed from the *t*-butyl alcohol. The treatment with ammonia separates 1-adamantanecarboxylic acid from these acids, the ammonium salts of which remain in solution.
4. Acid that is satisfactory for most purposes may be obtained by interrupting the evaporation of the chloroform solution when crystals start to appear, cooling the concentrated chloroform solution to 0–5°, and collecting the acid on a Büchner funnel. The acid melts at 173–174°.
5. The checkers obtained similar yields when the quantity of reactants was increased fivefold.
6. As an alternative purification procedure, the checkers have esterified the crude acid by refluxing it for 2 hours with three times its weight of methanol and 2 ml. of 98% sulfuric acid. The solution is poured into 10 volumes of water and extracted with the minimum amount of chloroform required to give a clean separation of layers. The chloroform solution is washed with water, dried over calcium chloride, and distilled from a Claisen flask with an indented neck. Methyl 1-adamantanecarboxylate is collected at 77–79° (1 mm.); m.p. 38–39°. Hydrolysis of the ester with the calculated amount of 1*N* potassium

hydroxide followed by acidification yields 1-adamantanecarboxylic acid; m.p. 175–176.5°; 90% overall recovery.

3. Discussion

1-Adamantanecarboxylic acid can be prepared by carboxylation of 1-adamantanol³ or 1-bromoadamantane^{3,4} by formic acid and 96% sulfuric acid; by carboxylation of adamantane by formic acid, *t*-butyl alcohol, and 96% sulfuric acid;⁵ and by carboxylation of adamantane by formic acid and 130% sulfuric acid.⁶

4. Merits of the Preparation

This procedure illustrates a general method of carboxylating saturated hydrocarbons that have a tertiary hydrogen.⁷ It has been used to convert isopentane to 2,2-dimethylbutanoic acid, 2,3-dimethylbutane to 2,2,3-trimethylbutanoic acid, and methylcyclohexane to 1-methylcyclohexanecarboxylic acid. The preparation of 1-methylcyclohexanecarboxylic acid by a variation of this procedure is described on p. 739 of this volume.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 739

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References and Notes

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3. H. Stetter, M. Schwarz, and A. Hirschhorn, *Ber.*, **92**, 1629 (1959).
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6. C. Wulff, Doctoral Thesis, Technische Hochschule, Aachen, Germany, "Über Substitutionsreaktionen des Adamantans," September, 1961, p. 65.
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Appendix

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

ammonium 1-adamantanecarboxylate

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methanol (67-56-1)

hydrogen (1333-74-0)

carbon monoxide (630-08-0)

chloroform (67-66-3)

sodium sulfate (7757-82-6)

formic acid (64-18-6)

carbon tetrachloride (56-23-5)

cyclohexane (110-82-7)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

ammonium hydroxide (1336-21-6)

methylcyclohexane (108-87-2)

Trimethylacetic acid (75-98-9)

isopentane (78-78-4)

n-hexane (110-54-3)

t-butyl alcohol (75-65-0)

Adamantane (281-23-2)

1-Adamantanecarboxylic acid (828-51-3)

methylcyclopentane (96-37-7)

isohexane (107-83-5)

Methyl 1-adamantanecarboxylate (711-01-3)

1-Adamantanol (768-95-6)

1-bromoadamantane (768-90-1)

2,2-dimethylbutanoic acid (595-37-9)

2,3-dimethylbutane (79-29-8)

2,2,3-trimethylbutanoic acid

1-Methylcyclohexanecarboxylic acid (1123-25-7)

