



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.

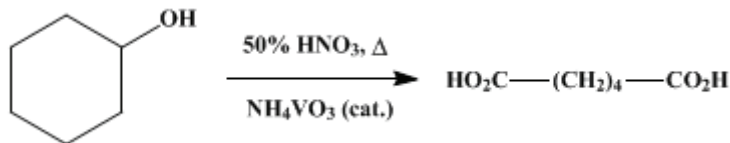
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.18 (1941); Vol. 5, p.9 (1925).*

## ADIPIC ACID



Submitted by B. A. Ellis

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### 1. Procedure

In a 5-l. round-bottomed flask fitted with a mechanical stirrer, a thermometer, and a 1-l. separatory funnel, is placed 2100 g. (16.6 moles) of 50 per cent [nitric acid](#) (sp. gr. 1.32) (Hood). The acid is heated nearly to boiling, and 1 g. of [ammonium vanadate](#) ([Note 1](#)) is added. The stirrer is started, and 500 g. (5 moles) of [cyclohexanol](#) ([Note 2](#)) is introduced slowly through the separatory funnel. At first 40–50 drops of [cyclohexanol](#) are admitted and the reaction mixture is stirred until the reaction has started (four to five minutes) as is indicated by the evolution of oxides of nitrogen ([Note 3](#)). Then the reaction flask is placed in an ice-water bath and cooled until the temperature of the oxidizing mixture is 55–60°. The [cyclohexanol](#) is then added as rapidly as possible while the temperature of the mixture is kept within these limits. Toward the end of the oxidation (after about 475 g. of [cyclohexanol](#) has been added) the ice bath must be removed and sometimes heat must be applied in order to maintain the temperature and avoid crystallization of [adipic acid](#).

Stirring is continued for about one hour after the addition of the last of the [cyclohexanol](#). Then the mixture is cooled to about 0° and the [adipic acid](#) is collected on a suction filter, washed with 500 cc. of ice water, and dried in the air overnight. The yield is 395–410 g. of white crystals which melt at 146–149°. Evaporation of the [nitric acid](#) mother liquors yields an additional 30–40 g. of product which melts at 141–144° ([Note 4](#)). The total yield of crude [adipic acid](#) is 425–440 g. (58–60 per cent of the theoretical amount) ([Note 5](#)). This product is pure enough for most purposes. However, a purer product may be obtained by recrystallizing this crude material from 700 cc. of concentrated [nitric acid](#) (sp. gr. 1.42). The loss in this purification is about 5 per cent. The recrystallized acid melts at 151–152° ([Note 6](#)) and ([Note 7](#)).

### 2. Notes

1. It is suggested that no catalyst is necessary if the temperature of the reaction mixture, once the reaction has started, is maintained at 85–90°. (W. W. Hartman, private communication.)
2. The [cyclohexanol](#) used was a commercial grade, which contained practically no [phenol](#). Over 90 per cent of the product boiled between 158–163°.
3. It is important that the oxidation start before a large amount of [cyclohexanol](#) has been added or the reaction will become violent. The reaction must be carried out in a good hood.
4. The [nitric acid](#) mother liquors contain considerable amounts of [adipic acid](#) mixed with glutaric and succinic acids. It has not proved practicable to separate these acids by crystallization. However, if the [nitric acid](#) is removed by evaporation and the resulting mixture of acids is esterified with [ethyl alcohol](#), a mixture of [ethyl succinate](#) (b.p. 121–126°/20 mm.), [ethyl glutarate](#) (b.p. 133–138°/20 mm.), and [ethyl adipate](#) (b.p. 142–147°/20 mm.) can be obtained. These esters can be separated quite satisfactorily by distillation.
5. The following modified procedure is reported to give better yields. In a 3-l. three-necked flask provided with a stirrer, reflux condenser, and dropping funnel set in asbestos-sodium silicate stoppers, are placed 1900 cc. of 50 per cent [nitric acid](#) (1262 cc. of [nitric acid](#), sp. gr. 1.42, diluted to 1900 cc.) and 1 g. of [ammonium vanadate](#). The flask is surrounded by a water bath heated to 50–60°, and, while the mixture is stirred, 357 g. (3.5 moles) of commercial [cyclohexanol](#) is added very slowly so that the temperature of the bath is maintained at 50–60°. This requires about six to eight hours. The reaction is

completed by heating the water bath to boiling until the evolution of nitrogen oxides has ceased (about one hour). The hot reaction mixture is siphoned off and allowed to cool. The yield of crude adipic acid is 372 g. (72 per cent of the theoretical amount). (Duncan G. Foster, private communication.)

The asbestos-sodium silicate stoppers are prepared by cutting thin asbestos paper into strips about 2.5 cm. wide, moistening the strips in water-glass solution, and then winding them around the end of the condenser, for example, until a stopper of the correct size is obtained. After the apparatus is assembled the stoppers are coated with water-glass and allowed to harden overnight.

6. The nitric acid mother liquors from the crystallization may be used as part of the acid for a subsequent oxidation.

7. Adipic acid may also be recrystallized from 2.5 times its weight of water or 50 per cent alcohol. However, these solvents are less satisfactory than nitric acid.

### 3. Discussion

Adipic acid can be prepared by the oxidation of cyclohexanol and cyclohexanone with nitric acid<sup>1</sup> or potassium permanganate.<sup>2</sup> The procedure described is adapted from the patent of the Deutsche Hydrierwerke A.-G.<sup>1</sup>

Other methods of preparing adipic acid are the oxidation of cyclohexene with dichromate and sulfuric acid<sup>3</sup> and the interaction of  $\gamma$ -bromobutyric ester with sodium malonic ester followed by hydrolysis and decarboxylation of the resulting triethyl 1,4,4-butanetricarboxylate.<sup>4</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 123
- Org. Syn. Coll. Vol. 1, 192
- Org. Syn. Coll. Vol. 1, 289
- Org. Syn. Coll. Vol. 2, 169

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### References and Notes

1. Zelinsky, J. Russ. Phys. Chem. Soc. **35**, 1280 (1903) [Bull. soc. chim. (3) **34**, 208 (1905)]; Holleman, Van Der Laan and Slijer, Rec. trav. chim. **24**, 23 (1905); Bouveault and Locquin, Bull. soc. chim. (4) **3**, 438 (1908); Chavanne and Simon, Compt. rend. **168**, 1326 (1919); Thorpe and Kon, Org. Syn. **5**, 9; Deutsche Hydrierwerke A.-G., Ger. pat. 473,960 (1926) [C. A. **23**, 2988 (1929)]; Claasen, Fr. pat. 32,991 (1927) [C. A. **23**, 846 (1929)]; Edwards and Reid, J. Am. Chem. Soc. **52**, 3235 (1930); E. I. du Pont de Nemours and Co., U. S. pat. 1,921,101 [C. A. **27**, 5084 (1933)].
2. Rosenlew, Ber. **39**, 2202 (1906); Mannich and Hâncu, Ber. **41**, 575 (1908); Blaise and Koehler, Bull. soc. chim. (4) **5**, 682 (1909); v. Braun and Lemke, Ber. **55B**, 3529 (1922); Wagner, J. Chem. Education **10**, 114 (1933); D. A. Howes (private communication) prepared adipic acid in quite satisfactory yields by the permanganate oxidation method.
3. Zal'kind and Markov, Russ. pat. 50,394 [C. A. **31**, 8548 (1937)]; Zal'kind and Markov, C. A. **31**, 3875 (1937).
4. Boorman, Linstead, and Rydon, J. Chem. Soc. **1933**, 573.

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### Appendix

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

oxides of nitrogen

glutaric

succinic acids

asbestos-sodium silicate

nitrogen oxides

$\gamma$ -bromobutyric ester

sodium malonic ester

ethyl alcohol,  
alcohol (64-17-5)

sulfuric acid (7664-93-9)

Adipic acid (124-04-9)

nitric acid (7697-37-2)

ammonium vanadate (7803-55-6)

Cyclohexanol (108-93-0)

phenol (108-95-2)

ethyl succinate

ethyl glutarate (1070-62-8)

Ethyl adipate (626-86-8)

Cyclohexanone (108-94-1)

potassium permanganate (7722-64-7)

Cyclohexene (110-83-8)

dichromate

triethyl 1,4,4-butanetricarboxylate