



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.

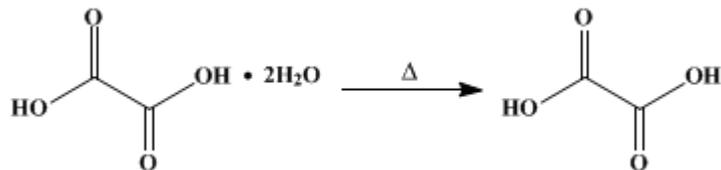
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 1, p.421 (1941); Vol. 1, p.67 (1921).*

## OXALIC ACID (ANHYDROUS)

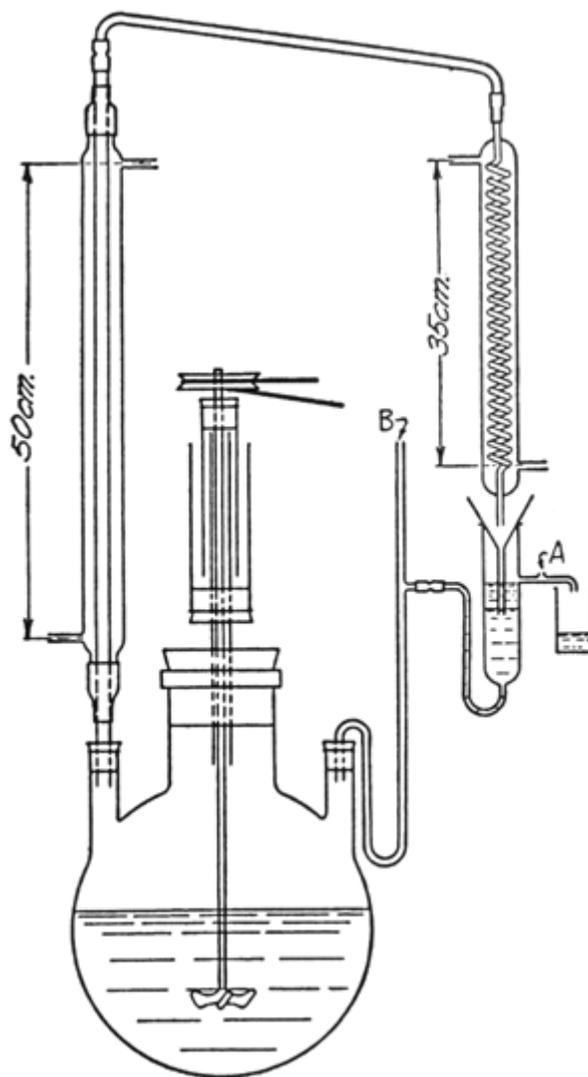


Submitted by H. T. Clarke and Anne W. Davis.  
Checked by Roger Adams and V. Voorhees.

### 1. Procedure

In a 5-l. round-bottomed flask are placed 2 kg. (15.9 moles) of pure crystallized oxalic acid which has been passed through a 10-mesh sieve, and 3 l. of carbon tetrachloride (Note 1). The flask is then fitted (Note 2) with a mechanical stirrer and the apparatus shown in Fig. 22.

Fig. 22.



This apparatus consists of an upright water condenser through the jacket of which steam is passed. A connecting tube leads from the top of this condenser to the top of a second efficient spiral condenser

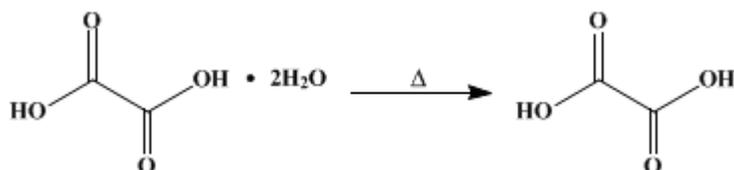
(Note 3), the bottom of which extends into a gravity separator. The water runs off into a receiver, and the heavier carbon tetrachloride layer returns to the reaction flask. A few essential points in the apparatus should be mentioned: it is necessary that the return arm of the gravity separator be below the tube through which the water flows into the receiver; the bottom of the funnel should be below the water outlet as in the diagram; the openings A and B are necessary to prevent siphoning in the respective tubes; and the last bend in the return tube before entering the reaction flask serves as a trap to prevent vapors from entering that tube.

The flask is placed up to its neck (Note 4) in hot water, stirring is started, and the steam is allowed to flow through the first upright condenser. The heating of the flask (Note 5) and vigorous stirring are continued until no more water passes through into the condenser. This point is indicated by the fact that no more water flows from the side arm of the separator. A slight milkiness in the carbon tetrachloride, which persists even when practically no more water comes over, need not be considered. The time of heating depends to a large extent on the rate with which the vapors are distilled over, and this rate in turn depends largely on the efficiency of the condenser. With an ordinary apparatus, such as that described, the time necessary will be approximately eighteen to twenty-four hours.

The reaction mixture is now filtered with suction, care being taken that any oxalic acid which is crusted above the surface of the carbon tetrachloride is not removed with the main portion of the product. The carbon tetrachloride may be used again for another run (Note 6), and the anhydrous oxalic acid is dried by short exposure to a warm dry atmosphere. The yield of product amounts to more than 90 per cent of the theoretical amount.

## 2. Notes

1. Carbon tetrachloride is in every way the most suitable liquid. It is not inflammable; the boiling temperature is such that water is readily evolved but sublimation of anhydrous acid is slight; and, inasmuch as the density is near to that of oxalic acid, an efficient mixing can be obtained. In benzene, the first and third conditions are not fulfilled; in toluene, apparently none of them, for although the water is more rapidly driven off than with carbon tetrachloride the sublimation is so great as to be troublesome, and, owing to the less efficient stirring in the liquid of lower density, the acid shows a great tendency to clump. However, toluene has been used.<sup>1</sup>
2. The stopper should be of good cork, covered if desired with tin foil. Rubber stoppers are rapidly attacked by the carbon tetrachloride vapors and rendered useless after one run.
3. As the time necessary for the dehydration depends almost entirely on the rate of boiling, care must be taken to select an efficient condenser. If a long spiral condenser is not available, a very successful device is to join the top of the upright tube to an ordinary long condenser placed in a slanting position, with its lower end connected by a bent tube of rather large bore to another condenser also in a slanting position, and leading back to the top of the gravity separator, the arrangement being > shaped.
4. It is well to place as much liquid in the flask as consistent with rapid boiling, since a slight crust of partially dehydrated acid is likely to collect around the upper edges of the carbon tetrachloride; this stays behind when the anhydrous acid is filtered off and must not be included in the main product. Complete immersion of the flask in hot water will greatly minimize this trouble, and it is therefore recommended.
5. The heat may be applied to the flask either by direct flame, water bath, or steam bath.
6. A considerable portion of carbon tetrachloride is lost in the experiment, and this is the chief disadvantage in the procedure. It is almost impossible to filter the oxalic acid and recover more than about 80 per cent of the carbon tetrachloride. About 18 per cent remains attached to the anhydrous oxalic acid and evaporates when the oxalic acid is dried. The last 2 per cent is lost by evaporation during the dehydration.



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## 1. Procedure

A laboratory oven (Note 1) is equipped with as many clay plates or enameled pie plates or trays as it will accommodate and is adjusted to operate at 98–99° (Note 2) and (Note 3). When the temperature has become constant the plates are removed, rapidly covered with a layer (not over 3–4 mm. deep) of pulverized (Note 4) hydrated oxalic acid, and then quickly replaced in the oven. The temperature will drop slightly for a few minutes (Note 5). After the oven has regained the temperature for which it was adjusted, it is heated for two hours longer at this temperature. The product is then removed, crushed if slightly caked, and quickly bottled. The yield from 100 g. of hydrated oxalic acid is 69–70 g. (96–98 per cent of the theoretical amount) (Note 6). The product is 99.5–100 per cent pure, as indicated by titration with standard alkali (Note 7).

## 2. Notes

1. Any type of oven may be used, but the automatic electric requires least attention. As many trays may be used as there are shelves in the oven. The trays are heated with the oven to decrease the subsequent first drop in temperature.
2. Some *slight* sublimation is always noticed, and the acid tends to cake. At higher temperatures heavy losses are caused by sublimation, and the caked material is very imperfectly dehydrated; there is also some darkening. Under the conditions described a white product is formed.
3. The dehydration is faster at higher temperatures. Numerous experiments showed that one hour and twenty minutes at a temperature of 113–115° gave a nearly theoretical yield of slightly colored material containing 97 per cent of oxalic acid. A one-hour heating at the same temperature gave an apparent yield of 102 per cent containing 94 per cent of oxalic acid. This result applies to a c.p. starting material; technical acid gives somewhat less favorable results.
4. The acid should be powdered so that 50 per cent will pass a 60-mesh sieve and all will pass a 40-mesh sieve. A 23-cm. plate can be used for about 50 to 100 g. of acid.
5. The oven temperature always drops a few degrees, owing to the cooling effect of the cold acid and the evaporation of a relatively large quantity of water. This drop in temperature is much less noticeable in a large oven than in a small one, and in one having thermostatic control in contrast to manual control.
6. The amount of material which may be dried will depend entirely on the size of the oven and the size and number of trays used. By repeating the runs several kilograms of material may be dried in a day with very little attention.
7. The success of this method of dehydration depends upon an exact control of all conditions specified.

## 3. Discussion

Oxalic acid can be dehydrated by heating to about 100° in an oven<sup>2</sup> or at 145–150° in an oil bath;<sup>3</sup> by treatment with concentrated sulfuric acid;<sup>4</sup> and by the use of an organic compound like carbon tetrachloride to distil off the water.<sup>5</sup> A preliminary trial of the concentrated sulfuric acid method showed it to be less suitable than the other methods. The weakness of the method involving the direct application of heat has been chiefly a lack of standardization.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 246
- Org. Syn. Coll. Vol. 1, 261
- Org. Syn. Coll. Vol. 1, 366
- Org. Syn. Coll. Vol. 2, 414
- Org. Syn. Coll. Vol. 2, 416
- Org. Syn. Coll. Vol. 3, 203
- Org. Syn. Coll. Vol. 3, 381

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## References and Notes

1. Johnson and Partington, J. Chem. Soc. 1510 (1930).
  2. Villiers, Bull. soc. chim. (2) **33**, 415 (1880); Rising and Stieglitz, J. Am. Chem. Soc. **40**, 726 (1918).
  3. Peter, Bull. soc. chim. (2) **38**, 406 (1882).
  4. Maumené, Jahresber. 371 (1864); Villiers, Bull. soc. chim. (2) **33**, 415 (1880); Lescoeur, Ann. chim. (6) **19**, 58 (1890); Fisher, Proc. Chem. Soc. **8**, 186 (1892).
  5. Hultman, Davis, and Clarke, J. Am. Chem. Soc. **43**, 368 (1921); Johnson and Partington, J. Chem. Soc. 1510 (1930).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

carbon tetrachloride (56-23-5)

Oxalic acid,  
OXALIC ACID (ANHYDROUS) (144-62-7)

toluene (108-88-3)