Organic Syntheses

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). 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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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.

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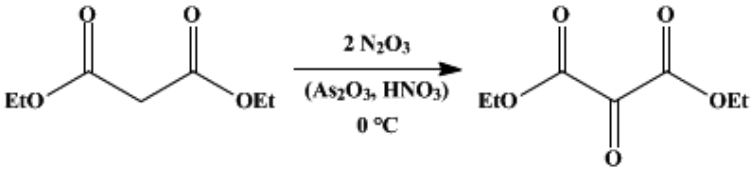
ETHYL OXOMALONATE
[Mesoxalic acid, ethyl ester]



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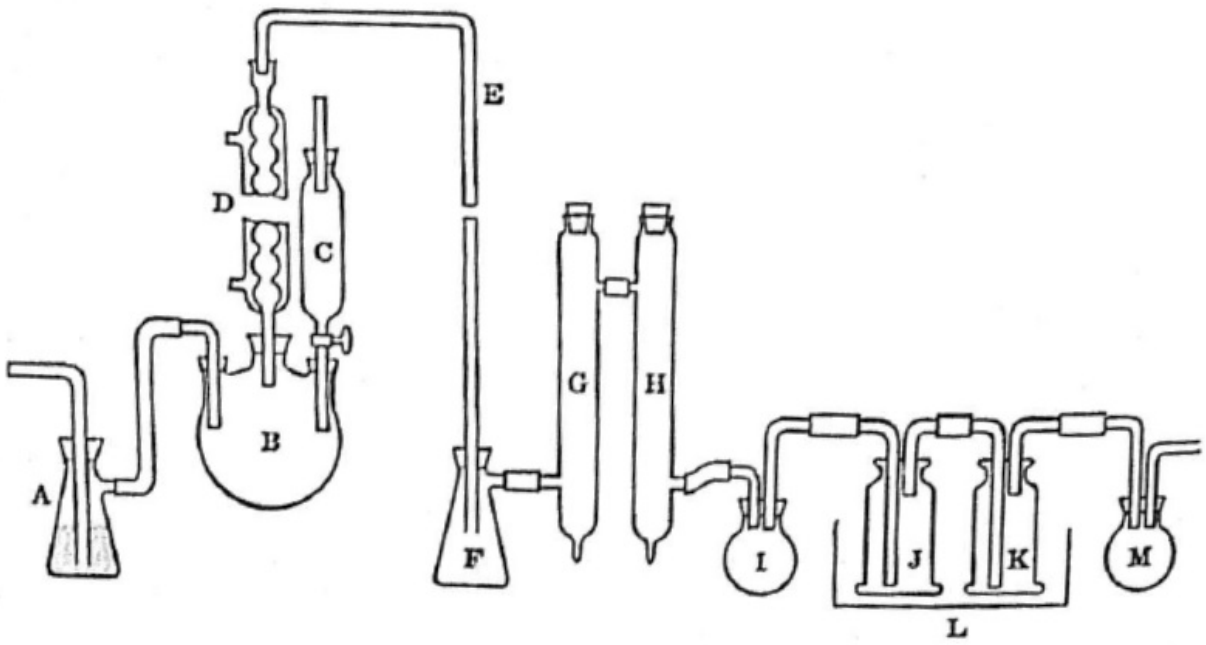
1. Procedure

The apparatus is assembled according to Fig. 3. A is a 500-cc. Pyrex filter flask. B is a 2-l. three-neck round-bottom flask; into one of the side necks is fitted a 300-cc. dropping funnel *C* (Note 1), and the second side neck is closed with a loose-fitting, well-greased rubber stopper, which serves as a safety valve against any sudden increase of pressure in the generator.



A long (75-cm.) water-cooled bulb condenser *D* is connected to the middle neck of the generator flask *B*. The large bore glass tube *E* connects the top of the condenser *D* with trap

F, a 500-cc. filter flask, which is connected by means of a short rubber tube to the drying towers *G* and *H* (Note 2). These towers are conveniently made from glass condenser jackets; the bottom ends are sealed and the top ends closed with rubber stoppers (Note 3). Tower *H* is connected to "sight flask" *I*, a 500-cc. round-bottom flask. This in turn is connected to the absorption vessels *J* and *K* (500-cc. gas washing bottles), which are immersed in an ice-salt bath contained in dish *L*. Absorption bottle *K* is connected to "sight flask" *M*, a 500-cc. round-bottom flask similar to *I*. By means of the sight flasks *I* and *M* the efficiency of absorption can be judged by the depth of color. Flask *I* also serves to catch any liquid sucked back from the absorption vessels.

Before finally assembling the apparatus, the various units are charged as follows: *A* is one-third filled with water to serve as a bubble counter. Generator *B* is about one-quarter filled with dry arsenious oxide, pea size or powdered. Drying towers *G* and *H* are filled with anhydrous calcium chloride. (It is well to place a wad of glass wool in front of the entrance and exit tubes.) In each of the two absorption bottles *J* and *K* is placed 200 g. of ethyl malonate. Dish *L* is filled with an ice-salt freezing mixture.

When assembled as indicated, the apparatus is ready for operation. Concentrated nitric acid is run, in small portions, into generator *B* from dropping funnel *C*. After the action has started, the nitric acid must be forced into flask *B* by applying a small air pressure at the top of dropping funnel *C* and then opening the stopcock. Later on, when the gas generation slackens, flask *B* is heated with a smoky flame. The evolution of gas is maintained at a steady rate by increasing the heat until finally all the arsenious oxide has dissolved and the frothing has ceased. During the whole operation a slow stream of compressed air (Note 4) is passed through the apparatus from "bubble counter" *A*. The stream of air is insufficient if any colorless gas, which turns brown on coming in contact with the air, leaves the apparatus at *M*. When the arsenious oxide is exhausted, as shown by a slackening in gas evolution, the old generator is removed and a fresh one put in its place. (If the generator is first allowed to cool somewhat, this change can be accomplished without much discomfort.) The moist oxides of nitrogen, in passing up through the condenser *D*, lose most of their moisture and the gas on passing down through tube *E* should deposit very little water in trap *F*. The gas is then thoroughly dried in the towers *G* and *H*. When the calcium chloride in *G* becomes wet (after several runs) the tower is refilled; at the same time *G* and *H* are interchanged. After passing through the drying towers and through flask *I*, the gas is absorbed by the cold ethyl malonate in vessels *J* and *K*. The ethyl malonate becomes dark green in color. There should be an increase in weight of about 200 g. in absorption bottle *J* in two or three hours (Note 5).

The rest of the directions are the same as in the original article by Dox (see *Org. Synth.* **1925**, *4*, 27).

2. Notes

1. All the stoppers in this apparatus are of rubber, well greased with Vaseline.
2. All rubber connections of this apparatus must be of thick tubing, well greased inside.
3. Ordinary gas-drying towers may also be used for *G* and *H*.

4. The reaction between arsenious oxide and concentrated nitric acid yields a mixture of nitric oxide and nitrogen dioxide. It also contains some nitrogen tetroxide and perhaps trioxide, the amount in equilibrium depending upon the temperature of the gas. The compressed air forced in via flask *A* insures an excess of oxygen, and thus complete oxidation. Only a slow stream is necessary, two to three bubbles per second.

5. A complete run should if possible be made without stopping. However, if the preparation must be stopped before completion, the absorption vessels should be disconnected, weighed, and protected against moisture by calcium chloride tubes. They lose weight on standing owing to decomposition of the intermediate compound.

6. Upon adding the calculated amount of water to ethyl oxomalonate, decolorization takes place immediately with evolution of heat, and on cooling a solid mass of ethyl dihydroxymalonate results. After recrystallization from chloroform the product melts at 56–57°. (Communicated by Elizabeth Gilman and T. B. Johnson.)

7. This work was assisted by a grant from the Cyrus M. Warren Fund of the American Academy of Arts and Sciences.
