



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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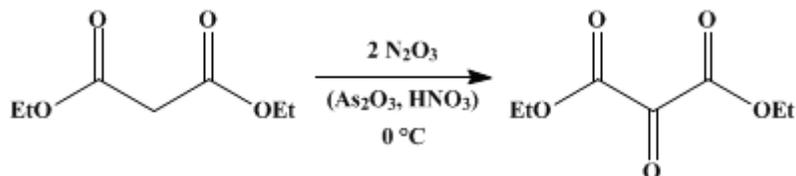
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.266 (1941); Vol. 4, p.27 (1925).

ETHYL OXOMALONATE

[Mesoxalic acid, ethyl ester]



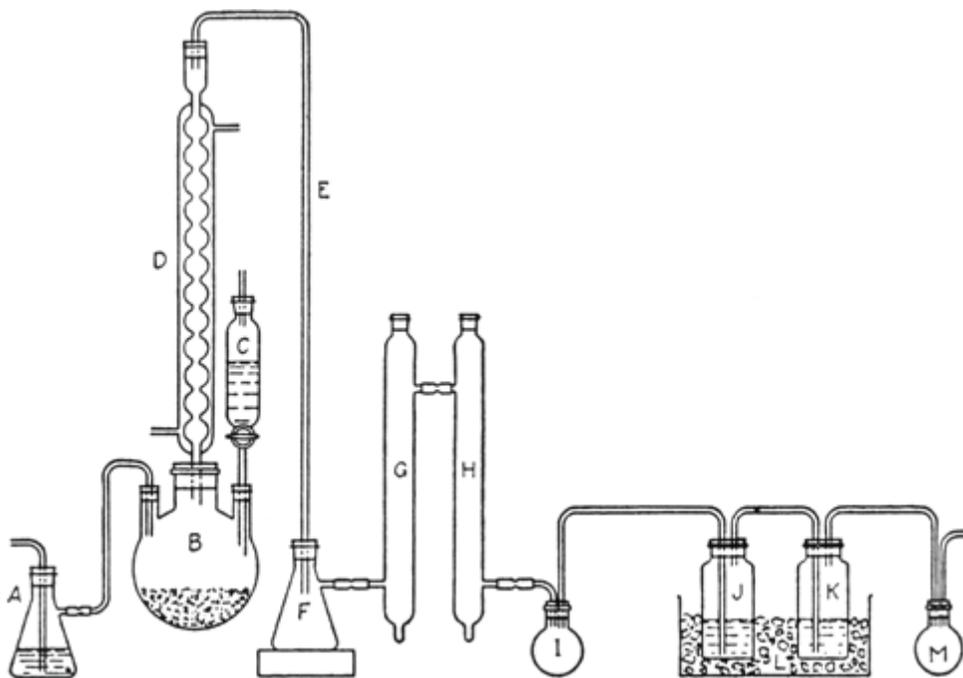
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1. Procedure

(A) *Apparatus*.¹—The apparatus is assembled according to Fig. 15. A is a 500-cc. Pyrex filter flask. B is a 2-l. three-necked, round-bottomed flask; into one of the side necks is fitted a 300-cc. dropping funnel C

Fig. 15.



(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-bottomed 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-bottomed 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. (1.25 moles) 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 (Note 5).

(B) *Ethyl Oxomalonate*.—A rapid stream of nitrous anhydride is passed into the cold ethyl malonate, which becomes dark green in color. There should be an increase in weight of about 200 g. in absorption bottle J in two to three hours (Note 6).

The liquid is left in the freezing mixture for several hours, then gradually allowed to come to room temperature (Note 7). Red gases are slowly evolved. After standing for two days or more at room temperature, the liquid is transferred to a distilling flask provided with a capillary air intake, and the delivery tube connected with a water-cooled condenser and receiver. The distillation is performed under reduced pressure, by the use of a water pump. Considerable nitric oxide is evolved before the pressure drops to about 70 mm. (Note 8).

The first fraction consists mainly of water, a little ethyl acetate, and some ethyl oxomalonate which recombines with the water to form ethyl mesoxalate. When the pressure has dropped to 45 mm. and the temperature has risen to 110°, the receiver is changed (Note 9). The main product, ethyl oxomalonate, now distils at 110–135°/45–50 mm. If the oxidation has been complete, very little residue is left (Note 10). Redistillation gives a golden-yellow liquid boiling between 103–108°/15 mm. The yield is 160–165 g. (74–76 per cent of the theoretical amount).

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. The yield of ethyl oxomalonate is decreased if the nitrous anhydride is not dried.
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. This work was assisted by a grant, to the submitters of the apparatus, from the Cyrus M. Warren fund of the American Academy of Arts and Sciences.
6. 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.

Considerable gas escapes from J and is taken up by K. If large quantities of [ethyl oxomalonate](#) are being prepared, J is removed when it has gained 200 g.; K is connected in the position previously occupied by J; and a bottle with fresh [ethyl malonate](#) is used to back up K.

7. If the temperature is raised too rapidly, the liberation of gases causes the mixture to boil too vigorously.

8. A motor pump is not recommended because the [nitric oxide](#) is apt to cause corrosion. If the pressure is reduced too much at first, a residue of [ethyl isonitrosomalonnate](#) may remain.

9. The remainder of the distillation must be conducted with extreme care. As soon as the [ethyl oxomalonate](#) has partly distilled over and the temperature has risen somewhat, the remaining isonitroso compound begins to decompose and sometimes liberates gases so rapidly that the thermometer and capillary tube may be blown out of the flask. If the manometer is watched closely, and at the first sign of liberation of gas, as evinced by a sudden increase in pressure, a wet towel is placed around the flask, the reaction can be slowed down.

10. In case any considerable amount of residue remains above 135° at 45 mm., it is heated at ordinary pressure to a higher temperature until no more [nitric oxide](#) is given off, then distilled as before.

11. 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° (Elizabeth Gilman and T. B. Johnson, private communication).

3. Discussion

[Ethyl oxomalonate](#) can be prepared by the action of [nitric acid](#) on [sucrose](#) under carefully controlled conditions;² by heating an aqueous solution of [dihydroxyacetone](#) with [cupric acetate](#);³ and by the oxidation of [ethyl malonate](#) by means of oxides of nitrogen⁴ or [selenium dioxide](#).⁵

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 326](#)
- [Org. Syn. Coll. Vol. 3, 609](#)
- [Org. Syn. Coll. Vol. 3, 771](#)
- [Org. Syn. Coll. Vol. 9, 314](#)

References and Notes

1. The apparatus for this preparation was submitted by B. B. Corson and R. K. Hazen.
2. Chattaway and Harris, *J. Chem. Soc.* **121**, 2704 (1922).
3. Evans and Waring, *J. Am. Chem. Soc.* **48**, 2680 (1926).
4. Bouveault and Wahl, *Compt. rend.* **137**, 196 (1903); Schmitt, *ibid.* **140**, 1400 (1905); Curtiss, *Am. Chem. J.* **33**, 603 (1905); *ibid.* **35**, 477 (1906); Meyer, *Bull. soc. chim. (4)* **9**, 423 (1911).
5. Astin, Newman, and Riley, *J. Chem. Soc.* **1933**, 393; Müller, *Ber.* **66**, 1668 (1933).

Appendix

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

oxides of nitrogen

arsenious oxide

vaseline

calcium chloride (10043-52-4)

ethyl acetate (141-78-6)

chloroform (67-66-3)

nitric acid (7697-37-2)

oxygen (7782-44-7)

sucrose

selenium dioxide (7446-08-4)

nitrogen dioxide (10102-44-0)

cupric acetate (142-71-2)

Ethyl oxomalonate,
Mesoxalic acid, ethyl ester,
ethyl mesoxalate

ethyl malonate (1071-46-1)

nitrous anhydride

nitric oxide

nitrogen tetroxide

ethyl isonitrosomaltonate

ethyl dihydroxymalonate

dihydroxyacetone