



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.

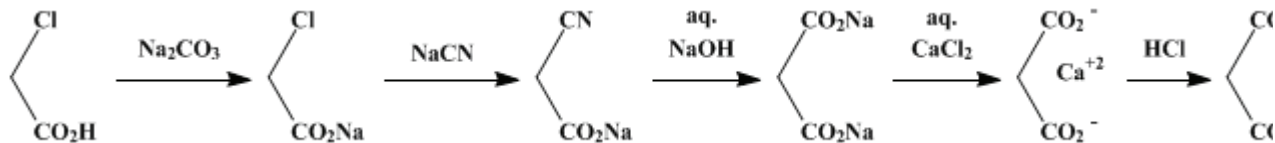
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 2, p.376 (1943); Vol. 18, p.50 (1938).*

## MALONIC ACID



Submitted by Nathan Weiner

Checked by C. R. Noller and M. E. Synerholm.

### 1. Procedure

In a 5-l. round-bottomed flask, 500 g. (5.3 moles) of [chloroacetic acid](#) ([Note 1](#)) is dissolved in 700 cc. of water. The solution is warmed to 50°, neutralized with 290 g. (2.7 moles) of anhydrous [sodium carbonate](#), and again cooled to room temperature. Meanwhile, 294 g. (6 moles) of [sodium cyanide](#) (97 per cent) is dissolved in 750 cc. of water warmed to 55°; the solution is cooled to room temperature and then added to the [sodium chloroacetate](#) solution, with rapid mixing of the two solutions and cooling under the water tap. When the solutions are completely mixed, cooling is stopped and the temperature allowed to rise. When it reaches 95°, the solution is cooled by adding 200 cc. of ice water, and this is repeated, if necessary, until the temperature no longer rises ([Note 2](#)). The solution is then heated on the steam bath for one hour to ensure completion of the reaction.

At the end of this time, the solution is cooled to room temperature and 240 g. (6 moles) of solid u.s.p. [sodium hydroxide](#) is slowly dissolved in it. When solution is complete, the reaction mixture is again heated on the steam bath under a hood. When the temperature reaches 60–70°, evolution of [ammonia](#) begins and becomes more vigorous with rise in temperature. Most of the [ammonia](#) is evolved in forty-five minutes, but the solution is heated for at least three hours, and the last traces of [ammonia](#) are removed by bubbling steam through the hot solution for forty-five to sixty minutes more.

A solution of 600 g. of anhydrous [calcium chloride](#) in 1.8 l. of water warmed to 40° is added slowly with rapid mixing to the hot [sodium malonate](#) solution. A cheese-like precipitate of [calcium malonate](#) is formed immediately and becomes coarsely crystalline on standing for twenty-four hours. After the supernatant solution is decanted, the [calcium malonate](#) is washed by decantation four or five times with 500-cc. portions of cold water. It is then transferred to a filter, sucked as dry as possible, and dried in the air, or at 45–50°, to constant weight. The yield is 800–900 g.

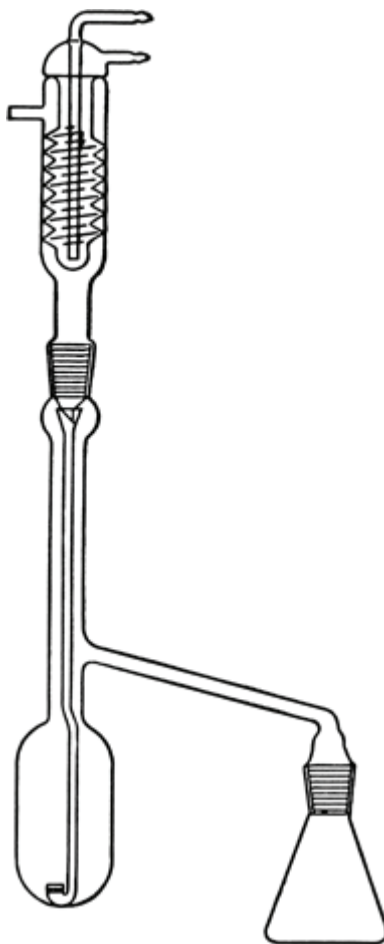
The dry [calcium malonate](#) is placed in a 3-l. round-bottomed flask with sufficient (750–1000 cc.) alcohol-free [ether](#) ([Note 3](#)) to make a paste which can be stirred. The flask is surrounded by an ice bath, and the well-stirred salt is treated with 1 cc. of 12 *N* [hydrochloric acid](#) for each gram of salt. After the acid has been added slowly through a dropping funnel, the solution is transferred to a continuous extractor ([Note 4](#)) and extracted with [ether](#) until no more [malonic acid](#) is obtained. The product, as obtained from the undried [ether](#) solution by concentration, filtration, and drying in the air, melts at 130° or higher and is sufficiently pure for most purposes. The yield is 415–440 g. (75–80 per cent of the theoretical amount).

### 2. Notes

1. A freshly distilled product boiling over a 3° range was used.
2. If the reaction between the cyanide and the chloroacetate becomes too vigorous, [hydrogen cyanide](#) is liberated and partly changed to a brown material, and a corresponding quantity of glycolate is formed. If the temperature of the reaction mixture is allowed to go above 95° spontaneously, the liquid may boil so vigorously and suddenly as to escape from the flask despite the large extra volume provided.
3. [Ether](#) is used to avoid unnecessarily increasing the volume of aqueous solution to be extracted. This [ether](#) may be used for further extraction. It is necessary to use alcohol-free [ether](#) to avoid esterifying the [malonic acid](#) during the protracted extraction period.

4. A convenient type of extractor used in this preparation was made as follows by modifying that described by J. Friedrichs:<sup>1</sup> A 20-cm. calcium chloride tower, or other narrow-necked cylinder with a volume of about 1.3 l., was used as an extraction chamber. The mantle-tube, conducting the ether vapors to an Allihn condenser, was made of 25-mm. tubing and was about 50 cm. long. The goose-neck to the extraction flask, of 14-mm. tubing, was sealed to the mantle-tube about 8 cm. from the bottom end. The inner tube was of 14-mm. tubing, about 65 cm. long, flanged at the top to a diameter of about 20 mm. A Witt filter plate of the proper diameter may be sealed into the bottom of the tube to make the ether pass up through the water in a stream of fine bubbles, or this can also be accomplished by sealing off the bottom of the tube and piercing it with 3–6 pinholes. The mantle-tube was fitted to the chamber by a properly bored rubber stopper, the condenser to the top of the mantle-tube, and the 500-cc. extraction flask to the goose-neck by charred cork stoppers. With this apparatus 395–400 g. of malonic acid was extracted in seventy-two hours, the ether being changed every twenty-four hours, and the final traces were extracted after an additional twenty-four hours. The extractor as described by Friedrichs is shown in Fig. 12.

Fig. 12



### 3. Discussion

Malonic acid has been prepared by the hydrolysis of malononitrile with concentrated hydrochloric acid;<sup>2</sup> by the hydration of carbon suboxide;<sup>3</sup> and from an alkali cyanide and ethyl bromoacetate,<sup>4</sup> ethyl chloroacetate,<sup>5</sup> or chloroacetic acid<sup>6</sup> followed by hydrolysis. The preparation using sodium cyanide and chloroacetic acid is the most convenient and economical.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 436

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## References and Notes

1. Friedrichs, Chem. Fabrik **1**, 91 (1928).
  2. Henry, Compt. rend. **102**, 1396 (1886).
  3. Diels and Wolf, Ber. **39**, 696 (1906).
  4. Franchimont, *ibid.* **7**, 216 (1874).
  5. Kolbe, Ann. **131**, 349 (1864); Müller, *ibid.* **131**, 352 (1864); Petriev, J. Russ. Phys.-Chem. Soc. **10**, 64 (1878).
  6. v. Miller, J. prakt. Chem. (2) **19**, 326 (1879); Grimaux and Tcherniak, Bull. soc. chim. (2) **31**, 338 (1879); Bourgoïn, *ibid.* (2) **33**, 574 (1880); Conrad, Ann. **204**, 126 (1880).
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## Appendix

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

carbon suboxide

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium cyanide (143-33-9)

hydrogen cyanide (74-90-8)

sodium carbonate (497-19-8)

chloroacetic acid (79-11-8)

sodium chloroacetate (3926-62-3)

Ethyl chloroacetate (105-39-5)

Malonic acid (141-82-2)

sodium malonate (141-95-7)

calcium malonate

Malononitrile (109-77-3)

Ethyl bromoacetate (105-36-2)

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