



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.

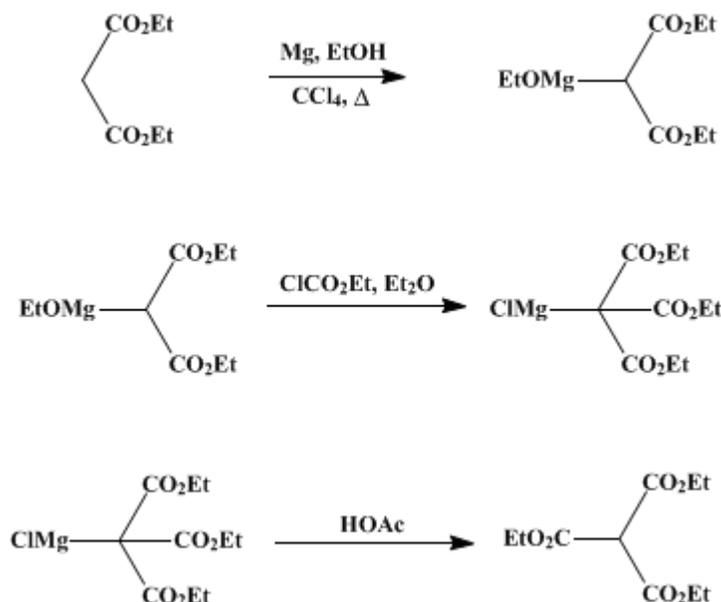
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.594 (1943); Vol. 17, p.86 (1937).

TRICARBETHOXYMETHANE

[Methanetricarboxylic acid, triethyl ester]



Submitted by Hakon Lund and Axel Voigt.

Checked by W. H. Carothers and W. L. McEwen.

1. Procedure

In a 1-l. round-bottomed flask, provided with an efficient and not too narrow reflux condenser, are placed 25 g. (1.03 gram atoms) of **magnesium turnings** (Grignard), 25 cc. of absolute **alcohol** (Note 1), 1 cc. of **carbon tetrachloride** (Note 2), and 30 cc. of a mixture of 160 g. (151 cc., 1 mole) of **ethyl malonate** and 80 cc. of absolute **alcohol**. Provision is made for cooling the flask when necessary in cold water, and the mixture is gently heated until **hydrogen** is evolved. The reaction may become so violent that external cooling is necessary. The **ethyl malonate** is gradually added through the condenser at such a rate that the reaction proceeds vigorously but not beyond control. When the reaction moderates the flask is cooled and 300 cc. of **ether**, dried twenty-four hours with **calcium chloride**, is added through the condenser. On gentle heating the crystals which have separated are dissolved, and **hydrogen** is again evolved for some time without further heating. The reaction is brought to completion on the steam bath. The flask is then removed from the steam bath, and a mixture of 100 cc. of **ethyl chloroformate** (1.05 moles) and 100 cc. of dry **ether** is added through the condenser from a dropping funnel at such a rate that vigorous boiling is maintained throughout the addition (Note 3). The reaction is complete after heating for fifteen minutes on the steam bath.

The viscous magnesium compound formed is cautiously decomposed with dilute **acetic acid** (75 cc. in 300 cc. of water), the flask being cooled under the tap. Two clear layers are formed, and, after separation, the aqueous layer is extracted with 100 cc. of **ether**, the combined ethereal solution is washed with water and dried with **sodium sulfate**, and the **ether** is distilled on the steam bath. The residue is distilled under reduced pressure. After a small fore-run the temperature rapidly rises to 130° at 10 mm. when the pure **tricarbethoxymethane** begins to distil. The yield of material collected over a five-degree interval is 204–215 g. (88–93 per cent of the theoretical amount). The product solidifies at 25°. The melting point of the pure substance is 28–29°.

2. Notes

1. Anhydrous alcohol is preferable, but a good grade of commercial absolute alcohol may be used without appreciably lowering the yield. The submitters used alcohol dehydrated by means of magnesium.¹
2. Carbon tetrachloride (as well as a number of other halogen compounds) greatly accelerates the reaction between magnesium and alcohol. If anhydrous alcohol is used the reaction will start after some time without heating, whereas 99.5 per cent alcohol has to be heated nearly to boiling before the evolution of hydrogen becomes rapid.
3. Towards the end of the reaction the magnesium compound of ethyl methanetricarboxylate separates as a viscous mass which tends to prevent the remaining magnesium malonic ester and ethyl chloroformate from reacting. Vigorous boiling keeps the material from forming a compact mass. If larger runs are made it may be necessary to stir during this part of the process.

3. Discussion

Tricarbethoxymethane has been prepared by the action of ethyl chloroformate upon sodiomalonic ester suspended in benzene,² toluene, or xylene;³ by the distillation of ethyl ethoxalylmalonate;⁴ from ethyl carbonate and malonic ester;⁵ and by the procedure described above.⁶

According to Backer and Lolkelma,³ the aromatic esters of methanetricarboxylic acid and the ethyl ester of that acid are best prepared by the Lund procedure using magnesium; the other aliphatic esters of methanetricarboxylic acid are best prepared using sodium—compare the preparation of the trimethyl ester below—with toluene or xylene as the reaction medium.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 379
- Org. Syn. Coll. Vol. 4, 285

References and Notes

1. Lund and Bjerrum, Ber. **64**, 210 (1931).
 2. Conrad and Guthzeit, Ann. **214**, 32 (1882).
 3. Backer and Lolkelma, Rec. trav. chim. **57**, 1237 (1938).
 4. Bouveault, Bull. soc. chim. (3) **19**, 79 (1898); Scholl and Egerer, Ann. **397**, 353 (1913).
 5. Wallingford, Homeyer, and Jones, J. Am. Chem Soc. **63**, 2056 (1941).
 6. Lund, Ber. **67**, 938 (1934).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

magnesium compound of ethyl methanetricarboxylate

magnesium malonic ester

ethyl ethoxalylmalonate

aromatic esters of methanetricarboxylic acid

aliphatic esters of methanetricarboxylic acid

alcohol (64-17-5)
calcium chloride (10043-52-4)
acetic acid (64-19-7)
Benzene (71-43-2)
ether (60-29-7)
hydrogen (1333-74-0)
magnesium,
magnesium turnings (7439-95-4)
sodium sulfate (7757-82-6)
carbon tetrachloride (56-23-5)
toluene (108-88-3)
sodium (13966-32-0)
xylene (106-42-3)
ethyl malonate (1071-46-1)
ethyl chloroformate (541-41-3)
ethyl carbonate
Tricarbethoxymethane,
Methanetricarboxylic acid, triethyl ester (6279-86-3)