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.

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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.

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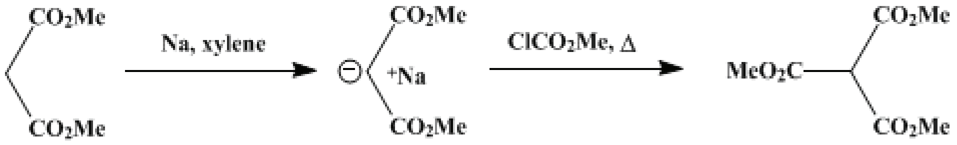
TRICARBOMETHOXYMETHANE

[Methanetricarboxylic acid, trimethyl ester]



Submitted by B. B. Corson and J. L. Sayre.
Checked by Roger Adams and A. E. Knauf.

1. Procedure

In a 2-l. three-necked flask, fitted with an upright condenser, a separatory funnel, and a mercury-sealed stirrer, are placed 400 cc. of dry xylene and 13 g. (0.56 gram atom) of sodium. The flask is heated in an oil bath until the sodium melts, and the mixture is stirred until the sodium is broken up into fine globules. Then 69 g. (0.57 mole) of methyl malonate is added over a period of five to ten minutes (Note 1).

The mixture is cooled while being well stirred, and, when the temperature reaches about 65°, 57 g. (0.6 mole) of methyl chloroformate is added during five to ten minutes. The mixture is then warmed slowly so that the boiling point is reached in about fifteen to twenty minutes. Boiling and stirring are maintained for five hours.

The mixture is cooled to room temperature, the flask is filled two-thirds full with water, and stirring is continued for five minutes. The xylene solution is separated, washed with water, dried over calcium chloride, filtered, and distilled under reduced pressure. After removal of the solvent, the tricarbomethoxymethane distils at 128–142°/18 mm. The yield of crude product is 50–51 g. (50–51 per cent of the theoretical amount). This material becomes semi-solid on cooling.

The crude product is purified by dissolving it in an equal volume of methyl alcohol and then cooling the solution in a freezing mixture until crystallization is complete. The crystals are filtered with suction, and the mother liquors are again cooled in a freezing mixture. If necessary this process is repeated a third time or until no further crop of crystals separates on chilling the mother liquors. The crystals are transferred from the funnel to a beaker, stirred with about 70 cc. of petroleum ether (b.p. 32–45°), filtered, pressed dry, and washed with a little petroleum ether. The yield of fine, snow-white crystals melting at 43–45° is about 40–42 g. (40–42 per cent of the theoretical amount) (Note 2).

2. Notes

1. A brisk evolution of hydrogen occurs, and sodium methyl malonate settles as a pasty mass. Stirring should be vigorous during the addition of the malonic ester and also during the subsequent heating, to avoid caking of the sodium salt.
2. Tricarbomethoxymethane is very soluble, and only by repeated cooling and filtration can a good recovery be obtained. Owing to this excessive solubility the apparent loss on crystallization is high. However, a considerable portion of this material can be recovered from the alcoholic mother liquors.

3. Discussion

The method described is very similar to one published by Adickes, Brunnert, and Lücker[1] for the preparation of the ethyl ester. In other procedures the sodium derivative of methyl malonate was isolated.[2] Compare the "Methods of Preparation" for tricarbethoxymethane on p. 596 above.

References and Notes

1. Adickes, Brunnert, and Lücker, J. prakt. Chem. (2) **130**, 163 (1931).
2. Scholl and Egerer, Ann. **397**, 355 (1913); Philippi, Hanusch, and von Wacek, Ber. **54**, 901 (1921); Backer and Lolkelma, Rec. trav. chim. **57**, 1237 (1938).

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

petroleum ether

sodium derivative of methyl malonate

calcium chloride (10043-52-4)

methyl alcohol (67-56-1)

hydrogen (1333-74-0)

sodium (13966-32-0)

xylene (106-42-3)

Tricarbethoxymethane (6279-86-3)

Tricarbomethoxymethane,
Methanetricarboxylic acid, trimethyl ester (1186-73-8)

methyl malonate

methyl chloroformate (79-22-1)

sodium methyl malonate