



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.

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.

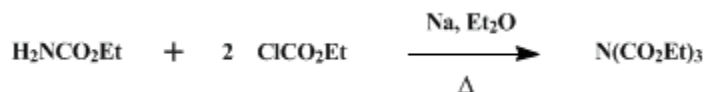
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

*Organic Syntheses, Coll. Vol. 3, p.415 (1955); Vol. 24, p.60 (1944).*

## ETHYL N-TRICARBOXYLATE

[N-Tricarboxylic ester]



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### 1. Procedure

In a 12-l. round-bottomed flask equipped with stirrer, dropping funnel, and efficient reflux condenser are placed 450 g. (5 moles) of **urethan** (m.p. 46–48°), 7.5 l. of dry **ether**, and 218 g. of **sodium** wire (**Note 1**) and (**Note 2**). The mixture is warmed, and evolution of **hydrogen** accompanied by formation of sodium compound soon begins; after 2–3 hours the greater part of the metal will have been replaced by a gelatinous white precipitate. The stirrer is now started and the mixture warmed under reflux for an additional 2 hours. The flask is then cooled externally with running water, and 1050 g. (9.6 moles) of **ethyl chlorocarbonate** is added slowly over a period of 2 hours. The gelatinous precipitate becomes powdery, and the remainder of the **sodium** dissolves. After all the ester has been added, the mixture is stirred overnight at room temperature and then filtered (**Note 3**). The white residue is washed with 1 l. of **ether**, and the **ether** is removed from the combined solutions by evaporation on a steam bath (**Note 4**). The residual oil is distilled; after a fore-run containing some **urethan**, the product distils at 143–147° /12 mm. The yield is 575–640 g. (51–57%). On redistillation, all the product boils at 146–147° /12 mm.

### 2. Notes

1. Since water is usually present, it is advisable to distil the **urethan** before use, discarding the first 10%.
2. **Sodium** wire is not essential. The reaction will proceed just as well with **sodium** cut into pieces the size of a small pea. It is important that the **sodium** be cut into *small* pieces; otherwise a protective coating forms on the surface of the metal, preventing further reaction.
3. The **sodium chloride** is very finely divided and quickly clogs the pores of the filter paper. The mixture should be allowed to stand for a time before filtration to allow the salt to settle; the clear supernatant liquor can then be filtered rapidly.
4. Care should be taken in disposing of this residue; it invariably contains some unreacted **sodium**.

### 3. Discussion

Ethyl N-tricarboxylate has been prepared from **urethan** by reaction with **sodium** and chlorocarbonic ester<sup>1</sup> as well as from the **potassium salt of ethyl imidodicarboxylate**.<sup>2</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 3, 404](#)

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### References and Notes

1. Diels, *Ber.*, **36**, 740 (1903).
  2. Diels, *Ber.*, **36**, 742 (1903).
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

Ethyl N-tricarboxylate

chlorocarbonic ester

[ether](#) (60-29-7)

[hydrogen](#) (1333-74-0)

[sodium chloride](#) (7647-14-5)

[sodium](#) (13966-32-0)

[ethyl chlorocarbonate](#) (541-41-3)

[urethan](#) (51-79-6)

[potassium salt of ethyl imidodicarboxylate](#)