



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.

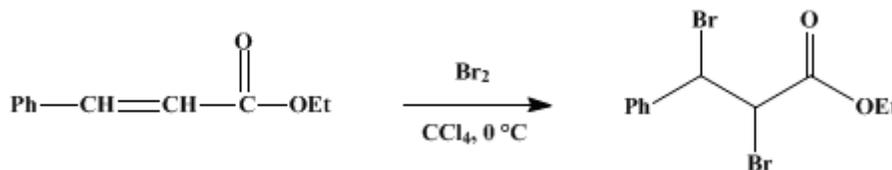
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.270 (1943); Vol. 12, p.36 (1932).

ETHYL α,β -DIBROMO- β -PHENYLPROPIONATE

[Hydrocinnamic acid, α,β -dibromo-, ethyl ester]



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Checked by Henry Gilman and G. F. Wright.

1. Procedure

In a 1-l. round-bottomed flask, provided with a two-holed stopper fitted with a dropping funnel and air-vent, is placed 176.2 g. (1 mole) of [ethyl cinnamate](#) (*Org. Syn. Coll. Vol. I, 1941, 252*) dissolved in 100 cc. of [carbon tetrachloride](#) (*Note 1*). The flask is placed in ice, and 159.8 g. (51.2 cc., 1 mole) of [bromine](#) is added in small quantities with frequent stirring (*Note 2*).

After standing for one hour, the solution is poured into a large dish and the [carbon tetrachloride](#) and unused [bromine](#) allowed to evaporate spontaneously (*Note 3*). The dibromo ester separates in large crystals which form a solid cake in the bottom of the dish (*Note 4*). This cake is broken up and spread in a thin layer on a large Büchner funnel and subjected to suction until all traces of [bromine](#) have disappeared. The white crystals are then dried by pressing between large filter papers. The yield of crude dibromo ester is 280–285 g. (83–85 per cent of the theoretical amount). It melts at 65–71°.

If pure ester is desired, it may be obtained by recrystallizing from petroleum ether (b.p. 70–90°); the yield is 80–85 g. of ester melting at 74–75° from 100 g. of crude product.

2. Notes

1. [Carbon tetrachloride](#) is used instead of [ether](#), which produces a very disagreeable lachrymator.
2. The [bromine](#) disappears rapidly at first, but more slowly at the end of the reaction. No [hydrogen bromide](#) is evolved. The time of addition is about twenty to twenty-five minutes.
3. This process is rather slow; it may be accelerated by inverting over the dish a large funnel which is connected to a suction pump. In this manner the crystalline cake separates in about two hours.
4. If the reaction is carried out carefully, practically no mother liquor is left. However, if such liquor should remain it will yield, on evaporation, crystals which are impure and must be recrystallized before use.

3. Discussion

[Ethyl \$\alpha,\beta\$ -dibromo- \$\beta\$ -phenylpropionate](#) is prepared by adding [bromine](#) to [ethyl cinnamate](#).¹

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 515](#)
- [Org. Syn. Coll. Vol. 7, 172](#)

References and Notes

1. [Anschütz and Kinnicutt, Ber. 11, 1220 \(1878\); Aronstein and Hollemann, ibid. 22, 1181 \(1889\);](#)

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

petroleum ether

ether (60-29-7)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

Ethyl cinnamate (103-36-6)

Ethyl α,β -dibromo- β -phenylpropionate,
Hydrocinnamic acid, α,β -dibromo-, ethyl ester (5464-70-0)