



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.

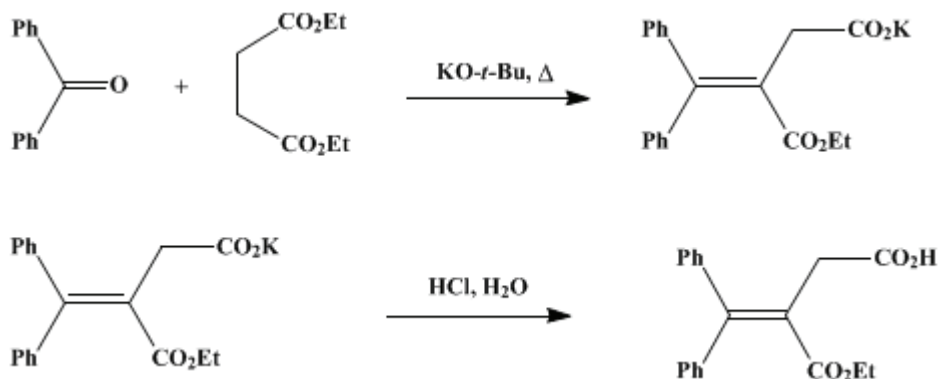
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.132 (1963); Vol. 30, p.18 (1950).

β -CARBETHOXY- γ,γ -DIPHENYLVINYLAACETIC ACID

[Succinic acid, α -benzhydrylidene-, α -ethyl ester]



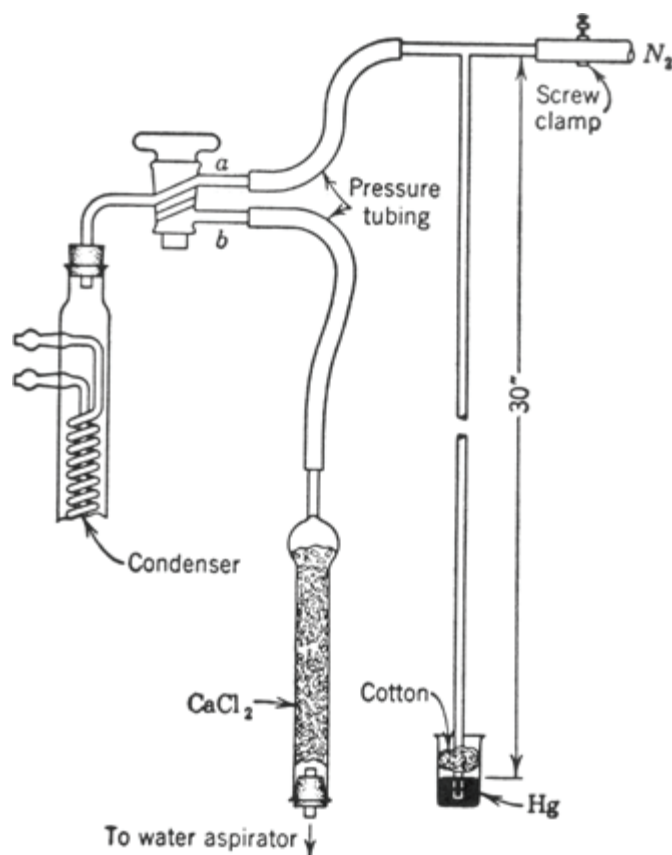
Submitted by William S. Johnson and William P. Schneider¹.
Checked by Arthur C. Cope and Malcolm Chamberlain.

1. Procedure

Caution! See Note 3 concerning the safe handling of potassium.

The reaction is conducted in a 500-ml. round-bottomed flask attached (by a ground-glass joint) to a Pyrex reflux condenser, the top of which is connected to a three-way stopcock leading to (a) a source of nitrogen and a mercury trap and (b) a water aspirator (Fig. 5). The flask and condenser are dried by warming with a free flame while the system is under reduced pressure (stopcock turned to (b) to engage aspirator). Dry nitrogen (Note 1) is then admitted to the apparatus by turning the stopcock slowly to the position indicated in Fig. 5 while nitrogen is bubbling through the mercury trap. The cooled flask is quickly charged with 45 ml. of dry *tert*-butyl alcohol (Note 2) and 2.15 g. (0.055 g. atom) of potassium (Note 3) and is then reconnected to the apparatus. The flow of nitrogen is stopped, the screw clamp is closed, and the mixture is boiled under reflux until the potassium is dissolved (Note 4), hydrogen being liberated through the mercury trap. The solution is then cooled to room temperature while nitrogen is admitted to equalize the pressure. The flask is quickly disconnected just long enough for the addition of 9.11 g. (0.05 mole) of benzophenone (Note 5) and 13.05 g. (0.075 mole) of diethyl succinate (Note 5). The system is then evacuated (until the alcohol begins to boil) and filled with nitrogen. With the stopcock as shown in Fig. 5 and the screw clamp closed, the mixture is refluxed gently for 30 minutes (Note 6). It is then chilled, acidified with about 10 ml. of cold 1:1 hydrochloric acid, and distilled under reduced pressure (water aspirator) until most of the alcohol is removed. Water is added to the residue, which is extracted thoroughly with ether, and the combined extracts are washed with successive portions of 1*N* ammonium hydroxide until a test portion gives no precipitate on acidification. The combined alkaline solutions are washed once with a fresh portion of ether and then added slowly with stirring to an excess of cold dilute hydrochloric acid. When the addition is complete the mixture should still be acidic to Congo red. The pale tan crystalline half-ester is separated on a suction funnel, washed well with water, and dried. The yield is 14.0–14.5 g. (92–94%), m.p. 120–124°. If a purer material is desired the product may be recrystallized by dissolving it in about 50 ml. of warm benzene, filtering, and adding an equal volume of petroleum ether (b.p. 40–60°). Upon cooling, 13.0–13.4 g. of almost colorless half-ester crystallizes, m.p. 123–124.5°.

Fig. 5. Apparatus for alternately evacuating and introducing nitrogen into the reaction vessel.



2. Notes

1. Ordinary tank **nitrogen** is dried satisfactorily by passage through a train consisting of (a) a trap, (b) a wash bottle containing concentrated sulfuric acid, and (c) a drying tube containing fresh soda lime.
2. Commercial **tert-butyl alcohol** is dried by refluxing with **sodium** (about 3 g. per 100 ml.) until the metal is about two-thirds dissolved, and then distilling. It may be necessary to add fresh **sodium** in order to have free metal present throughout the distillation.
3. The following procedure is recommended for the safe handling of **potassium**. The metal may be cut conveniently under **xylene** (which has been dried over **sodium wire**) contained in a mortar. A beaker or crystallizing dish should *not* be used because it is too fragile. Each scrap obtained in cutting off the outer oxide-coated surface of the metal should be immediately transferred with tweezers to a second deep mortar containing dry **xylene**, where the accumulated residues are decomposed as described below as soon as the cutting operation is completed. In order to weigh the freshly cut metal it may be removed with tweezers, blotted rapidly with a piece of filter paper, and introduced into a tared beaker containing dry **xylene**. The weighed **potassium** is then introduced into the reaction mixture, the proper precautions, such as exclusion of air and moisture and rate of addition being taken, depending on the nature of the reaction involved. **Caution!** It is the small scraps of metal that adhere to the knife or float on top of the **xylene** that are most likely to start a fire.

Danger! **Potassium** residues have been known to explode even under a protective liquid. It is therefore important that all such residues be decomposed *immediately*; under no circumstances should they be stored. The mortar containing the scraps is moved to the rear of the hood and **tert-butyl** (not methyl or ethyl) alcohol is added in small portions from a medicine dropper or beaker at such a rate that the reaction does not become too vigorous. A square sheet of asbestos large enough to cover the mortar should be at hand. If the liquid should catch fire it may be extinguished easily by covering the mortar with the asbestos sheet. There should be no other inflammable material or flames in the hood during this treatment. Sufficient **tert-butyl alcohol** must be employed to ensure *complete* decomposition of all the **potassium**. Small specks of **potassium** usually remain in the first mortar used for the cutting operation; they should be decomposed in the hood by cautious addition of small amounts of **tert-butyl alcohol** as

described above.

4. If the alcohol and apparatus have been properly dried, the dissolution of the [potassium](#) will be slow, requiring more than 4 hours of refluxing.
5. Eastman Kodak Company grade material is satisfactory if dried by redistillation.
6. The potassium salt of the half-ester may precipitate during the period of heating.

3. Discussion

[β-Carboethoxy-γ,γ-diphenylvinylacetic acid](#) has been prepared by the condensation of [benzophenone](#) with [diethyl succinate](#) in the presence of [sodium ethoxide](#)² or [sodium hydride](#).³ The procedure described here is a modification involving the use of [potassium tert-butoxide](#) as the condensing agent.⁴

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 261](#)
- [Org. Syn. Coll. Vol. 4, 398](#)
- [Org. Syn. Coll. Vol. 4, 459](#)
- [Org. Syn. Coll. Vol. 5, 306](#)
- [Org. Syn. Coll. Vol. 5, 567](#)
- [Org. Syn. Coll. Vol. 5, 859](#)
- [Org. Syn. Coll. Vol. 5, 989](#)
- [Org. Syn. Coll. Vol. 5, 1060](#)
- [Org. Syn. Coll. Vol. 6, 51](#)
- [Org. Syn. Coll. Vol. 6, 436](#)
- [Org. Syn. Coll. Vol. 6, 507](#)
- [Org. Syn. Coll. Vol. 7, 149](#)

References and Notes

1. University of Wisconsin, Madison, Wisconsin.
 2. Stobbe, *Ann.*, **308**, 89 (1899).
 3. Daub and Johnson, *J. Am. Chem. Soc.*, **70**, 418 (1948).
 4. Johnson, Petersen, and Schneider, *J. Am. Chem. Soc.*, **69**, 74 (1947).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[petroleum ether](#)

[tert-butyl \(not methyl or ethyl\) alcohol](#)

[hydrochloric acid \(7647-01-0\)](#)

[Benzene \(71-43-2\)](#)

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

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

[nitrogen \(7727-37-9\)](#)

Benzophenone (119-61-9)

sodium,
sodium wire (13966-32-0)

sodium ethoxide (141-52-6)

ammonium hydroxide (1336-21-6)

potassium (7440-09-7)

xylene (106-42-3)

sodium hydride (7646-69-7)

Diethyl succinate (123-25-1)

β -CARBETHOXY- γ,γ -DIPHENYLVINYLAACETIC ACID

Succinic acid, α -benzhydrylidene-, α -ethyl ester (5438-22-2)

tert-butyl alcohol (75-65-0)

potassium tert-butoxide (865-47-4)