



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.

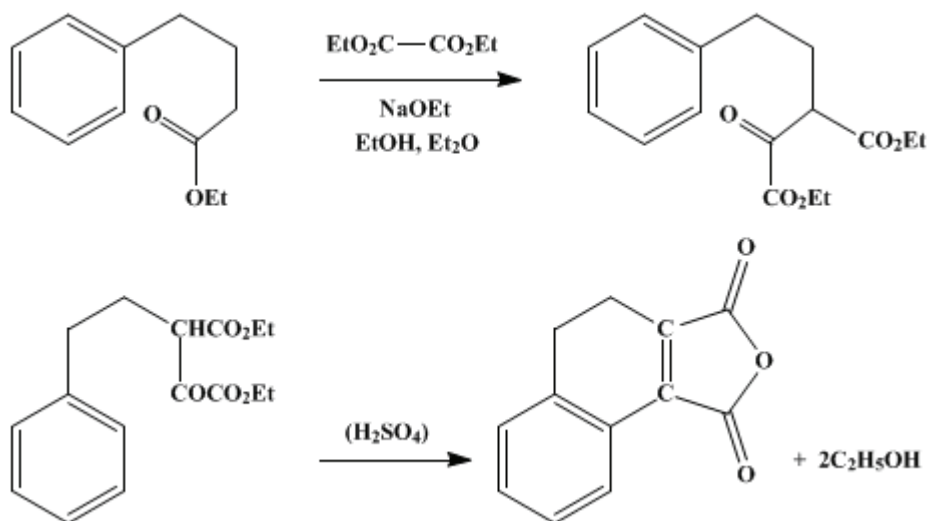
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 2, p.194 (1943); Vol. 18, p.24 (1938).*

## 3,4-DIHYDRO-1,2-NAPHTHALIC ANHYDRIDE

[1,2-Naphthalenedicarboxylic anhydride, 3,4-dihydro-]



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### 1. Procedure

(A) *Ester Condensation*.—In a 1-l. round-bottomed flask, fitted with a reflux condenser equipped with a dropping funnel and a calcium chloride tube, is placed a suspension of 6.1 g. (0.27 mole) of powdered sodium (Note 1) in 150 cc. of absolute ether. A solution of 12.6 g. (0.27 mole) of absolute ethyl alcohol (Note 2) and 50 cc. of absolute ether is added, and the mixture is allowed to stand overnight to complete the reaction. To the suspension of sodium ethoxide, 57 g. (0.39 mole) of ethyl oxalate (Org. Syn. Coll. Vol. I, 1941, 261), diluted with 50 cc. of ether, is added in portions. After the spontaneous reaction subsides, the pale yellow solution is allowed to stand for one-half hour, and 50 g. (0.26 mole) of ethyl  $\gamma$ -phenylbutyrate (Note 3), diluted with 50 cc. of absolute ether is added. The mixture is refluxed gently for twenty-four hours (Note 4).

The deep red solution is cooled in an ice bath and neutralized by the addition, with shaking, of an ice-cold solution of 15 cc. of concentrated sulfuric acid in 200 cc. of water. The ether layer is separated, washed with water, and dried over sodium sulfate. The ether is removed by dropping the solution from a separatory funnel the stem of which extends to the bottom of an evacuated Claisen flask heated on the steam bath. The residue is a pale yellow oil consisting of a mixture of ethyl  $\alpha$ -ethoxalyl- $\gamma$ -phenylbutyrate and unchanged ethyl oxalate (Note 5).

(B) *Cyclization*.—The above oil is poured slowly into 500 cc. of concentrated sulfuric acid, the temperature being kept at 20–25° by cooling in an ice bath. After standing for one and one-half hours at 20–25°, the deep red solution is poured on 3 l. of ice and water. The anhydride, precipitated as a pale yellow solid, is collected and washed thoroughly with water. Dried *in vacuo* at 25°, the material weighs 40–45 g. and melts at 117–122°. Distillation under diminished pressure gives a light yellow product, m.p. 122–124°. The yield is 38–42 g. (73–81 per cent of the theoretical amount). This material is suitable for most purposes. Crystallization from 100 cc. of benzene with the addition of 75 cc. of ligroin (b.p. 60–80°) gives 34–41 g. of pale yellow prisms, m.p. 125–126° (Note 6).

### 2. Notes

1. The powdered sodium for this preparation may be prepared as in Org. Syn. Coll. Vol. I, 1941, 252, or

according to the following procedure for [potassium](#), using [xylene](#) instead of [toluene](#). (With certain other  $\gamma$ -arylbutyric esters it is better to use [potassium](#).) Commercial [potassium](#) is cleaned by melting it under [toluene](#), and 10.4 g. (0.27 mole) of the metal and 150 cc. of dry [toluene](#) are placed in a 1-l. flask. After the liquid is heated to boiling on a hot plate, the flask is removed and closed with a ground-glass stopper carrying a sealed-on stopcock. Apparatus with interchangeable ground joints is essential. After one shake with the stopcock open to relieve superheating, the stopcock is closed, and the flask is shaken quickly and vigorously to powder the metal. The mixture is allowed to cool undisturbed, and [nitrogen](#) is admitted. The stopper is replaced by a distilling head carrying a 500-cc. flask, into which the [toluene](#) can be decanted. The powdered metal is washed several times with absolute [ether](#) and finally covered with [ether](#) (150 cc.) and converted into the ethoxide with 12.6 g. of [alcohol](#) diluted with 150 cc. of [ether](#). Traces of [potassium](#) in the wash liquors are destroyed safely by treatment under reflux with alcohol diluted with [ether](#).

2. The alcohol was dried according to [Org. Syn. Coll. Vol. I, 1941, 251, Note 1](#).

3. [Ethyl  \$\gamma\$ -phenylbutyrate](#) is prepared in 85–88 per cent yields by refluxing for three hours a mixture of 50 g. of  [\$\gamma\$ -phenylbutyric acid](#) (p. 499), 150 cc. of [alcohol](#) dried over lime, and 5 g. of concentrated [sulfuric acid](#). The ester is isolated by distilling 100 cc. of the [alcohol](#) under reduced pressure from a steam bath, diluting the residue with 200 cc. of water, separating, and extracting the aqueous layer twice with 50-cc. portions of [ether](#). The combined ester and [ether](#) layers are dried with [sodium sulfate](#), the [ether](#) removed, and the residue distilled under diminished pressure; the portion boiling at 144–147°/19 mm. is collected.

4. With [potassium ethoxide](#) the reaction is complete in twelve hours.

5. The keto ester decomposes on distillation, even under diminished pressure.

6. For the cyclization of the keto esters from  $\gamma$ -naphthylbutyric esters it is advisable to use 80 per cent [sulfuric acid](#), and to heat the mixture, with stirring, at 70–80° for one-half hour.

### 3. Discussion

The above procedure is a modification<sup>1</sup> of the method of von Auwers and Möller.<sup>2</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 423](#)
- [Org. Syn. Coll. Vol. 3, 300](#)

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### References and Notes

1. Fieser and Hershberg, *J. Am. Chem. Soc.* **57**, 1851 (1935).
  2. von Auwers and Möller, *J. prakt. Chem.* (2) **109**, 137 (1925).
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### Appendix

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

ligroin

ethyl  $\alpha$ -ethoxalyl- $\gamma$ -phenylbutyrate

[ethyl alcohol](#),  
[alcohol](#) (64-17-5)

[sulfuric acid](#) (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

toluene (108-88-3)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

potassium (7440-09-7)

xylene (106-42-3)

Ethyl oxalate

3,4-Dihydro-1,2-naphthalic anhydride,  
1,2-Naphthalenedicarboxylic anhydride, 3,4-dihydro- (37845-14-0)

ethyl  $\gamma$ -phenylbutyrate (10031-93-3)

$\gamma$ -Phenylbutyric acid (1821-12-1)

potassium ethoxide (917-58-8)