



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.

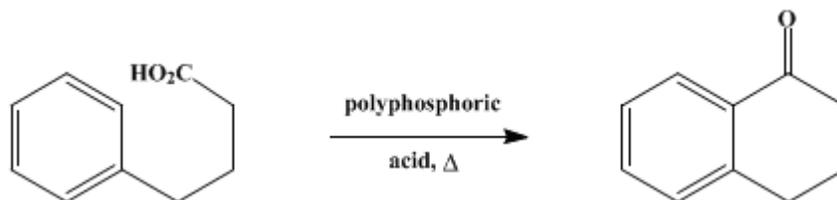
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.798 (1955); Vol. 20, p.94 (1940).

α -TETRALONE

[1(2H)-Naphthalenone, 3,4-dihydro-]



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1. Procedure

In a 600-ml. beaker, 80 g. of polyphosphoric acid (Note 1) is warmed on a steam bath to 90°. There is then added in one lot, with manual stirring, 22.0 g. (0.134 mole) of molten γ -phenylbutyric acid (Note 2), previously warmed to 65–70°. The mixture is removed from the steam bath and is stirred steadily by hand for 3 minutes; during this time a temperature of 90° or slightly higher is maintained by the heat of the reaction. An additional 70 g. of polyphosphoric acid is then added, and the mixture is again warmed on a steam bath for 4 minutes while being stirred vigorously by hand. The resulting solution is allowed to cool to 60°, and is hydrolyzed by addition to 200 g. of ice and water.

When the hydrolysis is complete, as indicated by the disappearance of orange, viscous material and the appearance in its stead of yellow oil, the aqueous mixture is transferred to a 500-ml. separatory funnel and extracted with two portions of ether, 200 ml. and 100 ml., respectively. The extracts are combined and washed successively with 200 ml. of water, two 100-ml. portions of 5% sodium hydroxide solution (Note 3), 200 ml. of water, 100 ml. of 3% aqueous acetic acid, 100 ml. of 5% sodium bicarbonate solution, and 100 ml. of water. The ether solution is dried over anhydrous magnesium sulfate. The ether is removed either by evaporation on a steam bath or by distillation from a 50-ml. flask into which the solution is introduced continuously, as fast as the solvent is distilled, by means of a dropping funnel reaching below the side arm of the distilling head. The flask is fitted with a 6-in. Vigreux column, and the residual oil is distilled under reduced pressure. There is obtained 14.8–16.9 g. (75–86%) of colorless oil, b.p. 90–91°/0.5–0.7 mm. or 94–95°/2.1–2.3 mm. (Note 4).

2. Notes

1. Polyphosphoric acid obtained from the Victor Chemical Company, Chicago, was used.
2. γ -Phenylbutyric acid was obtained by catalytic reduction (palladium-charcoal) of β -benzoylpropionic acid and was purified by distillation; the yield of material, b.p. 133–135°/1.0–1.3 mm., was 96%.
3. The amount of unchanged γ -phenylbutyric acid obtained by acidification of the alkaline solution is negligible. When only 72 g. of polyphosphoric acid in one lot was employed in the reaction, there was recovered 1.5 g. of γ -phenylbutyric acid, and the yield of α -tetralone was 15.9 g. (81%).
4. The submitters have used polyphosphoric acid in the cyclization of hydrocinnamic acid, 2-bromo-5-methoxyhydrocinnamic acid, and *o*-benzoylbenzoic acid.

3. Discussion

Other methods of preparation have been reviewed in earlier volumes.^{1,2} The method consisting of air oxidation of tetralin^{2,3,4,5,6} has in some cases been aided by the use of copper oxide⁴ or sulfate,⁵ and has been said to yield a product which is contaminated with α -tetralol.⁷ The ketone has also been prepared from γ -phenylbutyric acid by cyclization with phosphoric acid-phosphoric anhydride⁸ and with hydrofluoric acid,⁹ and from γ -phenylbutyryl chloride by the action of aluminum chloride.¹⁰ The method described is essentially that of Snyder and Werber.¹¹

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 569
- Org. Syn. Coll. Vol. 3, 223
- Org. Syn. Coll. Vol. 3, 312
- Org. Syn. Coll. Vol. 4, 898

References and Notes

1. *Org. Syntheses*, **15**, 77 (1935).
2. *Org. Syntheses*, **20**, 97 (1940).
3. Hock and Susemihl, *Ber.*, **66**, 61 (1933).
4. Brown, Widiger, and Letang, *J. Am. Chem. Soc.*, **61**, 2601 (1939).
5. U. S. pat. 2,462,103 [*C. A.*, **43**, 3848 (1949)].
6. Medvedev and Pod'yapol'skaya, *J. Phys. Chem. U.S.S.R.*, **13**, 719 (1939).
7. Mentzer and Billet, *Bull. soc. chim. France*, **1948**, 835; Beyerman, *Rec. trav. chim.*, **72**, 550 (1953).
8. Birch, Jaeger, and Robinson, *J. Chem. Soc.*, **1945**, 582.
9. Fieser and Herschberg, *J. Am. Chem. Soc.*, **61**, 1272 (1939).
10. Johnson and Glenn, *J. Am. Chem. Soc.*, **71**, 1092 (1949).
11. Snyder and Werber, *J. Am. Chem. Soc.*, **72**, 2962 (1950).

Appendix

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

polyphosphoric acid

acetic acid (64-19-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

hydrofluoric acid (7664-39-3)

aluminum chloride (3495-54-3)

copper oxide (1317-38-0)

Hydrocinnamic acid (501-52-0)

Tetralin (119-64-2)

magnesium sulfate (7487-88-9)

β -Benzoylpropionic acid (2051-95-8)

γ -Phenylbutyric acid (1821-12-1)

α -Tetralone,
1(2H)-Naphthalenone, 3,4-dihydro- (529-34-0)

γ -phenylbutyryl chloride

α -tetralol (529-33-9)

phosphoric acid-phosphoric anhydride (2466-09-3)

o-benzoylbenzoic acid (85-52-9)

2-bromo-5-methoxyhydrocinnamic acid