



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.

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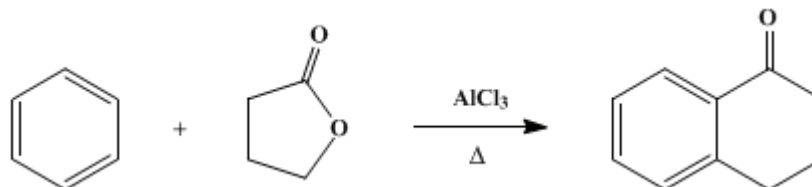
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.898 (1963); Vol. 35, p.95 (1955).

α -TETRALONE

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

[I. METHOD A]



Submitted by Cecil E. Olson and Alfred R. Bader¹.

Checked by James Cason, Gerhard J. Fonken, and William G. Dauben.

1. Procedure

A 3-l. three-necked flask is fitted with a mercury-sealed stirrer, an efficient condenser capped by a drying tube filled with calcium chloride, and a wide-bore rubber tube leading to a 1-l. Erlenmeyer flask. One liter of dry, thiophene-free benzene and 104 g. (1.21 moles) of γ -butyrolactone (Note 1) are placed in the 3-l. flask. Six hundred grams (4.5 moles) of reagent grade anhydrous aluminum chloride (Note 2) is placed in the Erlenmeyer flask and is added to the stirred reaction mixture during a period of 2 hours. The mixture becomes dark brown, refluxes gently, and evolves hydrogen chloride. After addition of all the catalyst, the mixture is heated on a steam bath with continued stirring for 16 hours. It is then cooled to room temperature and poured onto 3 kg. of crushed ice drenched with 500 ml. of concentrated hydrochloric acid. The lower aqueous layer is separated and extracted with about 500 ml. of toluene. The brown, organic, upper layer and the toluene extract are combined, washed successively with water, 20% potassium hydroxide solution, and water, and distilled under reduced pressure to remove benzene, toluene, and traces of water. Distillation of the residue in a Claisen flask (Note 3) yields 160–170 g. (91–96%) of α -tetralone, b.p. 75–85°/0.3 mm., n_D^{25} 1.565–1.568 (Note 4) and (Note 5). There is a residue consisting of 130–150 g. of red-purple viscous oil.

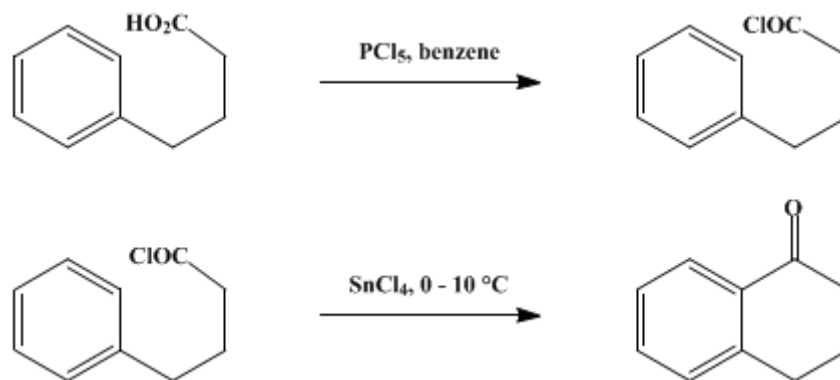
2. Notes

1. A commercial grade of butyrolactone supplied by the General Aniline and Film Corporation, 230 Park Avenue, New York 17, New York, was used by the submitters. The checkers used material from Eastern Chemical Corporation, 34 Spring Street, Newark 2, New Jersey, which was distilled before use, b.p. 208–210°.
2. The checkers found technical grade aluminum chloride, containing a little ferric chloride, equally satisfactory. After 150–200 g. of aluminum chloride is added there is usually a rather sudden and vigorous evolution of hydrogen chloride accompanied by refluxing. It is advisable to interrupt addition of aluminum chloride at this point until the mixture is refluxing smoothly.
3. The checkers distilled the product through a 0.5-meter packed column with heated jacket and partial reflux head. The yield was 148–155 g. (85–88%), b.p. 143–145°/20 mm., n_D^{25} 1.5669–1.5671. There was a fore-run of 10–15 g. and an after-run of about 8 g., b.p. 145–180°/20 mm.
4. The submitters state that varying the amounts of aluminum chloride varied the yields as shown in the table.

AlCl ₃ , g.	α -Tetralone, g.	Yield, %
400	119	68
500	151	86
600	165	94
700	166	95

5. Replacing the butyrolactone with 120 g. (1.20 moles) of γ -valerolactone in an otherwise identical procedure yields 150–160 g. (79–84%) of 4-methyl-1-tetralone, b.p. 108–110°/1 mm.

[II. METHOD B]



Submitted by G. Dana Johnson²

Checked by James Cason, William G. Dauben, Bradford H. Walker, and Charles E. Stehr.

1. Procedure

In a dry 2-l. three-necked round-bottomed flask, fitted with a gas-tight stirrer and a reflux condenser carrying at the top a calcium chloride drying tube connected to a gas-absorption trap (a good hood is preferable), are placed 98.5 g. (0.6 mole) of γ -phenylbutyric acid³ and 200 ml. of dry thiophene-free benzene (Note 1). After the solution has been cooled, with stirring, for a few minutes in an ice bath, 125 g. (0.6 mole) of phosphorus pentachloride is added during 5 minutes (Note 2). After the ice bath is removed the contents of the flask are heated during 20 minutes (vigorous evolution of hydrogen chloride) to the boiling point by means of a water bath, and refluxing is continued for about 5 minutes. As stirring is continued the flask is cooled in an ice-salt bath until the internal temperature (Note 3) reaches about -10° . With continued efficient cooling, there is added during 30–40 minutes a solution of 150 ml. (1.28 moles) of anhydrous stannic chloride in 150 ml. of dry thiophene-free benzene (Note 1), as the temperature is maintained below 15° . The reaction is highly exothermic, and hydrogen chloride is rapidly evolved. Stirring is continued for 1 hour at $0-10^\circ$, at the end of which time the thermometer is replaced by the condenser and the complex is decomposed by careful addition of 300 g. of ice followed by 250 ml. of concentrated hydrochloric acid. This two-phase mixture is heated to reflux, with vigorous stirring, on a water bath for about 25 minutes or until hydrogen chloride is no longer evolved (Note 4).

The cooled reaction mixture is separated in a separatory funnel, and the aqueous phase is extracted with three 50-ml. portions of benzene. These extracts are combined with each other but kept separate from the original organic phase; each wash solution is used first with the original organic phase, then the extracts. The washes are 150 ml. of water (Note 4), 100 ml. of 10% sodium carbonate solution, 100 ml. of water, and finally 50 ml. of saturated sodium chloride solution (Note 5). Solvent is distilled from the combined extracts, and the residue is distilled at reduced pressure in a Claisen flask. The yield of α -tetralone, b.p. 135–137°/15 mm., n_D^{25} 1.5671–1.5672, is 75–80 g. (85–91%).

2. Notes

1. A total of 350 ml. of dry benzene is required. It may be dried by allowing it to stand for a few days with about 1 g. of sodium wire, or by slowly distilling about 20% of a lot of benzene and cooling the residue with protection from atmospheric moisture by use of a calcium chloride tube.
2. It is convenient to weigh the phosphorus pentachloride in an Erlenmeyer flask which is then attached to a side neck of the three-necked flask by a 6-in. length of wide-bore thin-walled rubber tubing.
3. The condenser is replaced by a thermometer extending into the stirred liquid. The thermometer is inserted through a wide-bore T-tube whose side outlet is protected by a calcium chloride tube.

4. The [stannic chloride](#) complex is decomposed relatively slowly. Addition of 5–10 ml. of [ether](#) facilitates the decomposition. If the decomposition is not completed during the heating period, the wash with water gives a troublesome precipitation of [stannic hydroxide](#). If this occurs the organic phase should either be heated for 30 minutes with, or allowed to stand overnight with, 100 ml. of 6*N* [hydrochloric acid](#).

5. The wash with saturated salt solution usually gives a clean separation and removes most of the water from the organic phase. No additional drying is necessary since the remaining water is removed by azeotropic distillation with [benzene](#).

3. Discussion

Other methods of preparation of [\$\alpha\$ -tetralone](#) have been reviewed in earlier volumes.^{4,5} Further references to the preparation of [\$\alpha\$ -tetralone](#) by the oxidation of [tetralin](#) include the use of [oxygen](#) in the presence of [cobaltous chloride](#) and [acetic acid](#)⁶ and [chromic anhydride](#).^{7,8} Beyerman⁹ and Eastham¹⁰ state that the [\$\alpha\$ -tetralone](#) obtained by the air oxidation of [tetralin](#) contains [\$\alpha\$ -tetralol](#), which cannot be separated readily by fractional distillation. The former recommends removing the [\$\alpha\$ -tetralol](#) by treatment with [chromic acid](#) in [acetic acid](#) below 15°, while the latter investigator suggests that the reaction product be dissolved in an equal volume of 75% [sulfuric acid](#), and the mixture extracted with [hexane](#). The [hexane](#) extract is discarded, the acid layer is then diluted with 2 volumes of water and again extracted with [hexane](#). The [\$\alpha\$ -tetralone](#) recovered from this [hexane](#) extract by washing, concentrating, and distilling melts at 6–7°. Eastham¹⁰ believes that the melting point rather than the refractive index should be used as a test of purity of [\$\alpha\$ -tetralone](#). [\$\alpha\$ -Tetralone](#) also has been obtained from [tetrahydronaphthalene peroxide](#) and [sodium hydroxide](#) or [cupric chloride](#).¹¹

4-Methyl-1-tetralone has been prepared from [\$\gamma\$ -phenylvaleric acid](#) and [sulfuric acid](#)¹² and from [\$\gamma\$ -phenylvaleryl chloride](#) and [aluminum chloride](#).^{13,14}

Method I is based on the procedure of Truce and Olson.¹⁵

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 4, 884](#)
- [Org. Syn. Coll. Vol. 7, 319](#)

References and Notes

1. Pittsburgh Plate Glass Company, Milwaukee, Wisconsin.
 2. Indiana University, Bloomington, Indiana.
 3. *Org. Syntheses Coll. Vol. 2*, 499 (1943).
 4. *Org. Syntheses Coll. Vol. 2*, 569 (1943).
 5. *Org. Syntheses Coll. Vol. 3*, 798 (1955).
 6. Institut français du pétrole des carburants et lubrifiants, French pat. 1,095,348 [*C. A.*, **53**, 1289 (1959)].
 7. Staveley and Smith, *J. Inst. Petroleum*, **42**, 55 (1956).
 8. Nazarov and Burmistrova, *Zhur. Obsheei Khim. (J. Gen. Chem.)*, **20**, 1304 (1950) [*C. A.*, **45**, 1562 (1951)].
 9. Beyerman, *Rec. trav. chim.*, **72**, 550 (1953).
 10. Eastham, Private communication.
 11. Johnson (to Koppers Co., Inc.), U. S. pat. 2,462,103 [*C. A.*, **43**, 3848 (1949)].
 12. Kloetzel, *J. Am. Chem. Soc.*, **62**, 1708 (1940).
 13. Mayer and Stamm, *Ber.*, **56**, 1431 (1923).
 14. v. Braun and Stuckenschmidt, *Ber.*, **56**, 1724 (1923).
 15. Truce and Olson, *J. Am. Chem. Soc.*, **74**, 4721 (1952).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

Benzene (71-43-2)

ether (60-29-7)

sodium hydroxide (1310-73-2)

phosphorus pentachloride (10026-13-8)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

oxygen (7782-44-7)

aluminum chloride (3495-54-3)

potassium hydroxide (1310-58-3)

toluene (108-88-3)

sodium (13966-32-0)

chromic acid (7738-94-5)

cupric chloride (7758-89-6)

ferric chloride (7705-08-0)

γ -butyrolactone,
Butyrolactone (96-48-0)

γ -valerolactone (108-29-2)

chromic anhydride

stannic chloride (7646-78-8)

Tetralin (119-64-2)

γ -Phenylbutyric acid (1821-12-1)

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

hexane (110-54-3)

α -tetralol (529-33-9)

4-methyl-1-tetralone (19832-98-5)

stannic hydroxide

cobaltous chloride

tetrahydronaphthalene peroxide

γ -phenylvaleric acid

γ -phenylvaleryl chloride