Organic Syntheses

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.

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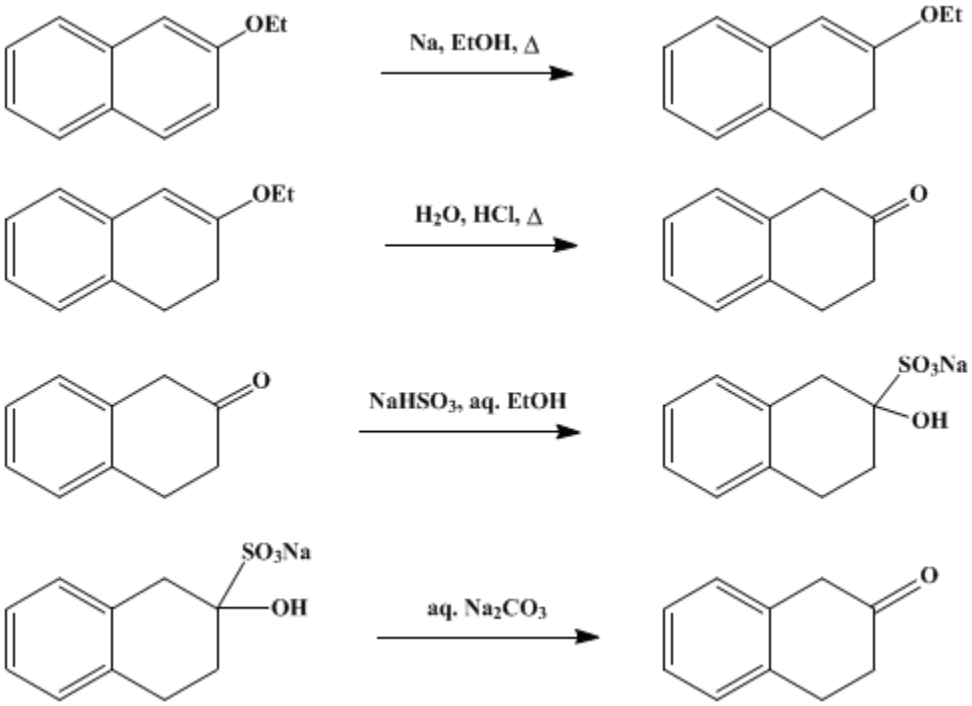
β-TETRALONE

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



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1. Procedure

A. *Reduction and hydrolysis.* A solution of 129 g. (0.75 mole) of β-naphthyl ethyl ether in 1.5 l. of 95% ethanol is prepared in a 5-l. three-necked flask fitted with a mechanical stirrer, a bulb condenser topped by a Friedrichs condenser, and a Y-tube to allow for the introduction of nitrogen and sodium. The apparatus is flushed thoroughly with nitrogen, the nitrogen flow is reduced, and 225 g. (9.8 g. atoms) of sodium is added in small portions (Note 1), with efficient stirring, at a rate sufficient to maintain vigorous boiling. The hydrogen liberated passes through the condensers and a delivery tube into a hood or directly out a window. When approximately two-thirds of the sodium has been introduced, an additional 375 ml. of 95% ethanol is added to reduce the viscosity of the reaction mixture. Approximately 1.5 hours is required for the addition of the sodium. Near the end of this period, the rate of the reaction decreases and heat is supplied by means of an electric heating mantle to maintain the reflux temperature (Note 2).

After all the sodium has dissolved, the hydrogen is thoroughly swept from the system with nitrogen and the heating is discontinued. The Y-tube is replaced by a separatory funnel, and 750 ml. of water is added cautiously (Note 3), with stirring, followed by 1.5 l. of concentrated hydrochloric acid (Note 3). The acidic mixture containing precipitated sodium chloride is heated, with stirring, at the reflux temperature for 30 minutes, and then allowed to cool.

The mixture is extracted with ten 175-ml. portions of benzene or 1:1 benzene-ether mixture (Note 4). The combined extract is washed with 75-ml. portions of water until the washings are neutral to litmus. The organic solvent is removed by distillation on a steam bath. The crude oily residue is converted directly (Note 5) to the β-tetralone bisulfite addition product.

B. *Bisulfite addition product of β-tetralone.* To a solution of 325 g. (3.12 moles) of sodium bisulfite (commercial purified grade) in 565 ml. of water is added 175 ml. of 95% ethanol. The mixture is allowed to stand overnight, and the precipitated sodium bisulfite is removed by filtration. The filtrate is added to the crude β-tetralone, and the mixture is shaken vigorously. Within a few minutes the addition product separates as a voluminous precipitate. The mixture is kept cold for several hours, shaken periodically, and then filtered with the aid of suction. The precipitate is washed well, first with 125 ml. of 95% ethanol, then four times with 125-ml. portions of ether (Note 6). The colorless addition product is air-dried (Note 5) and is stored in air-tight containers. The yield is 113–131 g. (60–70% based on β-naphthyl ethyl ether) (Note 7).

C. *Regeneration of β-tetralone.* Fifty grams (0.20 mole) of β-tetralone bisulfite addition product is suspended in 250 ml. of water, and 75 g. (0.6 mole) of sodium carbonate monohydrate is added. At this point the pH of the solution is approximately 10. The mixture is extracted with five 100-ml. portions of ether (Note 8). The combined extract is washed with 100 ml. of 10% hydrochloric acid, then with 100-ml. portions of water until the washings are neutral to litmus, and is dried over anhydrous magnesium sulfate. The ether is removed by distillation, and the residue is distilled from a Claisen flask under reduced pressure, preferably in a nitrogen atmosphere. The pure β-tetralone is obtained as a colorless distillate; b.p. 70–71°/0.25 mm. (92–94°/1.8 mm., 114–116°/4.5 mm.); n_D^{20} 1.5594. The yield is 17–21 g. (40–50% based on β-naphthyl ethyl ether).

2. Notes

1. The sodium is cut into pieces about 2 in. by 0.5 in. by 0.5 in. and is kept under benzene until used.
2. The concentrated sodium ethoxide solution must be kept hot throughout the process; otherwise a voluminous precipitate separates and the mixture congeals.
3. Both the hydrolysis of the sodium ethoxide and the subsequent neutralization are very exothermic. The water and the acid may be added fast enough to maintain vigorous refluxing, but care must be exercised to keep the reaction under control. When the neutralization is complete, the refluxing subsides, and at this point the excess hydrochloric acid may be added rapidly.
4. Ether is somewhat miscible with the reaction mixture, but the benzene-ether mixture, or benzene alone, is satisfactory.
5. In this step the β-tetralone is separated from starting material and other neutral substances in the reaction mixture. β-Tetralone is sensitive to air oxidation; therefore it should not be stored in the free state. The bisulfite addition product is stable, and the dry material can be stored indefinitely without deterioration.
6. In order to obtain a product of high quality, the washing must be thorough. This is accomplished best by suspending the precipitate in the wash solvent and mixing well before filtering.
7. The yield of the bisulfite addition product is subject to variation owing to coprecipitation of sodium bisulfite.
8. The ether extract and the water layer may be tested for the presence of β-tetralone or the bisulfite addition product by the tetralone blue test.
Tetralone blue test. A few drops of the organic solvent layer or the aqueous phase is shaken in a test tube with 2 ml. of 95% ethanol, and 10 drops of 25% sodium hydroxide solution is poured down the side of the tube. In the presence of air a deep blue color appears at the interface within 1 minute.

3. Discussion

β-Tetralone has been prepared by a variety of methods, but the only practical procedures are ones involving reduction of β-naphthyl methyl ether with sodium and alcohol[2] or with sodium and liquid ammonia,[3] high-pressure catalytic hydrogenation of β-naphthol,[4] catalytic oxidation of 2-tetralol by hydrogen transfer with ethylene,[5] or the condensation of ethylene with phenylacetyl chloride in the presence of aluminum chloride.[6]

The procedure described here is an adaptation[7] of the method of Cornforth, Cornforth, and Robinson.[2]

References and Notes

1. Smith College, Northampton, Massachusetts.
2. Cornforth, Cornforth, and Robinson, *J. Chem. Soc.*, **1942**, 689.
3. Birch, *J. Chem. Soc.*, **1944**, 430.
4. Stork and Foreman, *J. Am. Chem. Soc.*, **68**, 2172 (1946).
5. Adkins, Rossow, and Carnahan, *J. Am. Chem. Soc.*, **70**, 4247 (1948).
6. Burckhalter and Campbell, *J. Org. Chem.*, **26**, 4232 (1961).
7. Soffer, Stewart, Cavagnol, Gellerson, and Bowler, *J. Am. Chem. Soc.*, **72**, 3704 (1950).

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

nitrogen (7727-37-9)

β-naphthol (135-19-3)

sodium bisulfite (7631-90-5)

β-naphthyl methyl ether (93-04-9)

aluminum chloride (3495-54-3)

sodium (13966-32-0)

sodium ethoxide (141-52-6)

ethylene (9002-88-4)

magnesium sulfate (7487-88-9)

phenylacetyl chloride (103-80-0)

β-naphthyl ethyl ether (93-18-5)

tetralone (529-34-0)

sodium carbonate monohydrate (5968-11-6)

β-Tetralone,
2(1H)-Naphthalenone, 3,4-dihydro- (530-93-8)

β-tetralone bisulfite

2-tetralol (530-91-6)