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.

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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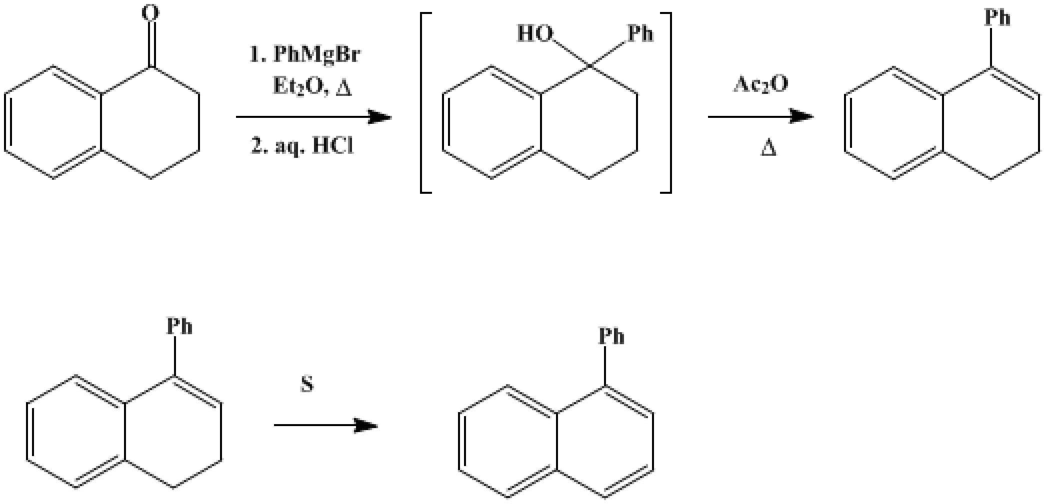
1-PHENYLNAPHTHALENE

[Naphthalene, 1-phenyl-]



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1. Procedure

A. 1-*Phenyldialin.* A solution of phenylmagnesium bromide is prepared in the usual manner[1] from 11 g. (0.45 gram atom) of magnesium, 75 g. (0.48 mole) of bromobenzene, and 175 ml. of ether. As soon as the metal has reacted, a solution of 58.4 g. (0.4 mole) of α-tetralone in 60 ml. of ether is added from a dropping funnel as rapidly as possible so that vigorous refluxing is maintained; about 30 minutes is required. The reaction mixture is then heated under reflux for an additional 30 minutes and allowed to stand for 1 hour. The magnesium complex is decomposed by about 250 g. of ice and 40 ml. of concentrated hydrochloric acid. The ether layer is separated and distilled with steam to remove impurities (Note 1); about 6 hours is necessary, and approximately 4.5 l. of distillate is collected. The heavy residual oil is separated from the water, and 80 ml. of ether and 10 g. of calcium chloride are added. After 4–5 minutes, the calcium chloride is removed by filtration, and the ether is driven off by distillation on a steam bath. Twenty milliliters of acetic anhydride is then added, and the flask and contents are heated in a steam bath (Note 2) for 20–25 minutes. The mixture is finally distilled under reduced pressure through a 15-in. Widmer column (Note 3). The fraction which boils at 135–140°/2 mm. is collected; the yield is 35–40 g. (42–48%).

B. 1-*Phenylnaphthalene.* A mixture of 6 g. (0.18 mole) of powdered sulfur and 35 g. (0.17 mole) of 1-phenyldialin in a 200-ml. Claisen flask having a modified side arm is heated for 30 minutes in a metal bath the temperature of which is 250–270° (Note 4). At the end of this time the evolution of hydrogen sulfide will have ceased. The heavy oil (Note 5) is then distilled from the same flask; the yield is 32–33 g. (91–94%); the boiling range of the product is 134–135°/2 mm. or 189–190°/12 mm. (Note 6) and (Note 7)"/>.

2. Notes

1. Steam distillation removes unused bromobenzene, biphenyl, etc.
2. The reaction is best carried out in a 500-ml. Erlenmeyer flask or beaker which can be lowered into the steam pot and held by a cloth wrap.
3. If a fractionating column is not used, several distillations are necessary to secure a product with the boiling range given. When this distillation is done as described, subsequent operations are facilitated,

and a column is not required for the final distillation of the hydrocarbon. Ebullition tubes are desirable in both distillations.

4. The temperature inside the flask should be 250°.
5. Significant amounts of hydrocarbon are lost with each change of flask. For this reason it is advisable to perform the dehydrogenation and distillation in the same flask.
6. Sometimes the hydrocarbon is blue, probably owing to traces of an azulene. The contaminant is easily removed by dissolving the hydrocarbon in an equal volume of hexane or petroleum ether and shaking this solution with an equal volume of 85% syrupy phosphoric acid until the color has been removed. The hydrocarbon is then obtained on evaporation of the solvent; it does not need redistillation.
7. The over-all yield is 40%, based on the α-tetralone.

3. Discussion

1-Phenylnaphthalene has been prepared by the reaction of α-halonaphthalenes with mercury diphenyl[2] or with benzene in the presence of aluminum chloride,[2] and by means of a Grignard synthesis, starting with either bromobenzene, or cyclohexyl chloride and α-tetralone[3,4] or with α-bromonaphthalene and cyclohexanone.[3,5,6,7] A 60% over-all yield has been reported for the Grignard preparation from cyclohexanone.[7] The formation of the hydrocarbon through the diazo reaction[8,9,10,11] appears to be less attractive than the method described. Dehydrogenation of the reduced naphthalene has been accomplished by the use of sulfur,[3] bromine,[5] platinum black, or selenium.[4]

References and Notes

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

petroleum ether

platinum black

mercury diphenyl

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

acetic anhydride (108-24-7)

magnesium (7439-95-4)

Cyclohexanone (108-94-1)

hydrogen sulfide (7783-06-4)

bromine (7726-95-6)

sulfur (7704-34-9)

aluminum chloride (3495-54-3)

phosphoric acid (7664-38-2)

bromobenzene (108-86-1)

Biphenyl (92-52-4)

α-Bromonaphthalene (90-11-9)

Naphthalene (91-20-3)

cyclohexyl chloride (542-18-7)

Phenylmagnesium bromide (100-58-3)

selenium

α-Tetralone (529-34-0)

hexane (110-54-3)

1-Phenylnaphthalene,
Naphthalene, 1-phenyl- (605-02-7)

1-phenyldialin (643-79-8)

Azulene (275-51-4)