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.

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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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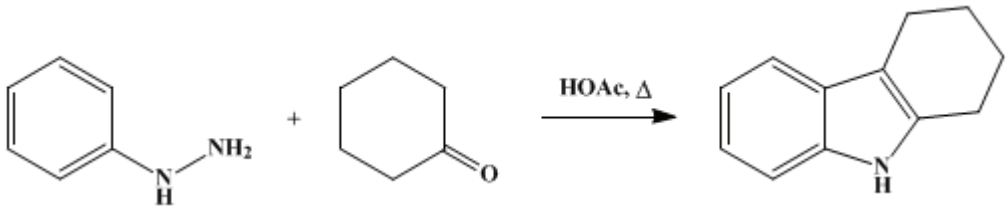
1,2,3,4-TETRAHYDROCARBAZOLE

[Carbazole, 1,2,3,4-tetrahydro-]



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Checked by Charles C. Price, Kenneth N. Campbell, and Robert P. Kane.

1. Procedure

A mixture of 98 g. (1 mole) (Note 1) of cyclohexanone and 360 g. (6 moles) of acetic acid contained in a 1-l. three-necked round-bottomed flask equipped with a reflux condenser, a slip-sealed stirrer, and a dropping funnel is heated under reflux and stirred while 108 g. (1 mole) of phenylhydrazine is added during 1 hour. The mixture is heated under reflux for an additional hour and poured into a 1.5-l. beaker and stirred by hand (Note 2) while it solidifies. It is then cooled to about 5° and filtered with suction, the filtrate being cooled in ice and refiltered through the filter cake. The final filtrate is discarded. The filter cake is washed with 100 ml. of water and finally with 100 ml. of 75% ethanol. Each wash is allowed to soak into the filter cake before it is sucked dry. The crude solid is air-dried overnight (Note 3) and crystallized (Note 4) from 700 ml. of methanol after treatment with decolorizing carbon (Note 5); yield 120–135 g. of 1,2,3,4-tetrahydrocarbazole, m.p. 115–116° (Note 6). The mother liquor is concentrated to one-fourth of its original volume and yields an additional 10 g. of product (total yield 76–85%) (Note 7).

2. Notes

1. Equivalent amounts of cyclohexanone (after suitable compensation for purity) and phenylhydrazine are used. The cyclohexanone was about 90% pure (analyzed by the procedure of Bryant and Smith[2]). Instead of analyzing the ketone, it is safe to assume 90% purity.
2. The stirring should be sufficiently vigorous to prevent the formation of lumps.
3. The crude product requires 50–70 hours of air-drying to attain constant weight (145–155 g., 85–91%). It is preferable to crystallize the partially dried product.
4. The approximate solubility of 1,2,3,4-tetrahydrocarbazole in 100 ml. of methanol at 10°, 35°, and 55° is 5, 12, and 18 g. respectively.
5. A heated funnel is desirable for filtration of the hot solution, for the product separates on slight cooling.
6. The capillary melting point of tetrahydrocarbazole ranges from 113° to 114° with slow heating and from 116° to 118° with fast heating.
7. 1,2-Benzo-3,4-dihydrocarbazole may be prepared by the same general procedure. A solution of 172 ml. (2 moles) of concentrated hydrochloric acid (sp. gr. 1.18) in 500 ml. of water is heated at the reflux temperature and stirred in a 2-l. three-necked round-bottomed flask equipped with a reflux condenser, a slip-sealed stirrer, and a dropping funnel while 108 g. (1 mole) of phenylhydrazine is added during 5 minutes. α-Tetralone (p. 898) (146 g., 1 mole or a correspondingly larger amount of material of 90% purity; see (Note 1)) is added in a period of 1 hour, and the mixture is stirred and heated under reflux for an additional hour. The product is cooled to room temperature with stirring, and the beadlike product is filtered, washed as above, and crystallized from 2.3 l. of methanol after treatment with decolorizing carbon. The first crop amounts to 105–110 g. and the second crop to 75–80 g., making the total yield 82–87%; m.p. 163–164°.

3. Discussion

1,2,3,4-Tetrahydrocarbazole has been prepared from cyclohexanone phenylhydrazone,[3,4,5,6,7,8,9] by the direct reaction of cyclohexanone with phenylhydrazine,[10] by the reaction of 2-chlorocyclohexanone with aniline,[11] by heating 2-phenylcyclohexanone oxime,[12] by the reaction of 2-hydroxycyclohexanone with aniline,[13] by treatment of cyclohexanone phenylhydrazone with a cation-exchange resin,[14] and by the hydrogenation of carbazole.[15] 1,2-Benzo-3,4-dihydrocarbazole has been prepared from the phenylhydrazone of α-tetralone[16] and by the direct reaction of α-tetralone with phenylhydrazine.[10]

References and Notes

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

1,2-Benzo-3,4-dihydrocarbazole

phenylhydrazone of α-tetralone

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

aniline (62-53-3)

Cyclohexanone (108-94-1)

Phenylhydrazine (100-63-0)

decolorizing carbon (7782-42-5)

carbazole (86-74-8)

α-Tetralone (529-34-0)

2-Chlorocyclohexanone (822-87-7)

1,2,3,4-Tetrahydrocarbazole,
Carbazole, 1,2,3,4-tetrahydro- (942-01-8)

tetrahydrocarbazole

2-phenylcyclohexanone oxime

2-hydroxycyclohexanone

cyclohexanone phenylhydrazone