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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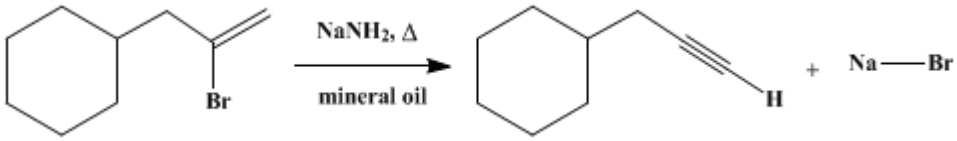
3-CYCLOHEXYLPROPINE

[Propyne, 3-cyclohexyl-]



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1. Procedure

A mixture of 120 g. (3.1 moles) of sodamide (Note 1) and 200 cc. of purified mineral oil (Note 2) is ground together in a mortar until the amide is finely pulverized (Note 3). This suspension is transferred to a 2-l. round-bottomed, three-necked flask fitted with a reflux condenser holding a calcium chloride tube, a 500-cc. separatory funnel, and an efficient mechanical stirrer through a mercury seal. The mortar and pestle are rinsed with an additional 250 cc. of the oil which is then added to the reaction flask. This is heated in an oil bath maintained at 160–165°, the stirrer is started, and 203 g. (1 mole) of cyclohexylbromopropene (p. 186) is dropped in during one and one-half hours. Ammonia is evolved, and this is allowed to pass through the condenser and is collected in water.

After all the cyclohexylbromopropene has been run in, heating is continued for about two hours, the mixture is cooled and 500 cc. of ether is added. This mixture is poured on 1.5 kg. of cracked ice in a 5-l. flask and then acidified with 280 cc. of concentrated hydrochloric acid. The ether layer is separated, dried over calcium chloride, and transferred to a 1-l. modified Claisen flask (p. 130) for distillation. The ether is distilled at ordinary pressure and then the cyclohexylpropine under diminished pressure. The product boiling up to 115°/20 mm. is collected and fractionated. The cyclohexylpropine boils at 58–63°/20 mm. The higher-boiling material is chiefly unchanged cyclohexylbromopropene which may be used again in a subsequent run. The yield of cyclohexylpropine is 80 g. (66 per cent of the theoretical amount not taking into consideration the recovered cyclohexylbromopropene which amounts to about 10 g.) (Note 4). The pure compound boils at 61–63°/24 mm.

2. Notes

1. The sodamide must be free from sodium hydroxide and may be conveniently weighed under the 250 cc. of purified mineral oil which is used to rinse out the mortar. Care must be exercised in the use of old sodamide as it sometimes contains an explosive compound that might cause trouble. The nature of this explosive compound is not definitely known; however, it appears to be associated with the development of a lemon yellow color. Should any part of the sodamide develop this color it is recommended that the whole be destroyed at once.
Directions for preparing sodamide are to be found in Org. Syn. **20**, 86.
2. Any clean, high-boiling petroleum oil may be used. None of it should boil below 250°.
3. It is essential that the sodamide be very finely divided. The state of subdivision of the sodamide particles seriously affects the yield of product. A mechanical grinder was used by the original authors, who obtained better yields than those reported here.
4. By a similar procedure[1] decine may be made from 2-bromodecene in 68 per cent yield, b.p. 80–82°/22 mm., and 4-phenylbutine from 4-phenyl-2-bromobutene in 60 per cent yield, b.p. 95–99°/17 mm.

3. Discussion

3-Cyclohexylpropine can be prepared by heating 3-cyclohexyl-1-bromopropene with alcoholic potassium hydroxide[1] or by the action of sodamide on 3-cyclohexyl-2-bromopropene[2]

References and Notes

1. Rességuier, Bull. soc. chim. (4) **7**, 433 (1910); Johnson and McEwen, J. Am Chem. Soc. **48**, 469 (1926).
2. Bourguel, Ann. chim. (10) **3**, 231 (1925).

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

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

sodium hydroxide (1310-73-2)

potassium hydroxide (1310-58-3)

3-Cyclohexyl-2-bromopropene (53608-85-8)

cyclohexylbromopropene

4-phenyl-2-bromobutene

2-bromodecene

3-CYCLOHEXYLPROPINE,
Propyne, 3-cyclohexyl-,
cyclohexylpropine (17715-00-3)

decine (764-93-2)

4-phenylbutine (16520-62-0)

3-cyclohexyl-1-bromopropene

sodamide (7782-92-5)