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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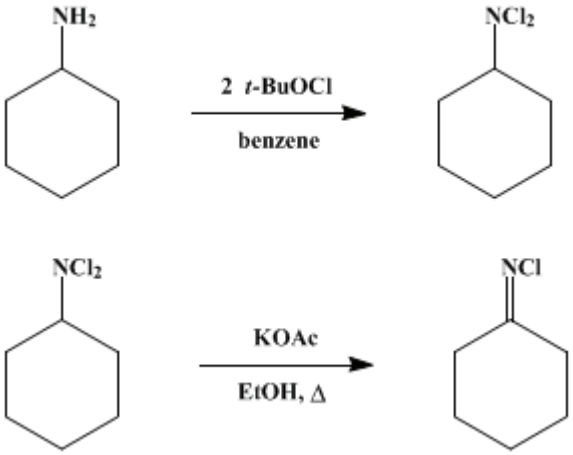
Organic Syntheses, Coll. Vol. 5, p.208 (1973); Vol. 45, p.16 (1965).

N-CHLOROCYCLOHEXYLIDENEIMINE

[Cyclohexanimine, N-chloro-]



Submitted by G. H. Alt[1] and W. S. Knowles[2].
Checked by P. M. Burke and Peter Yates.

1. Procedure

A. *N,N-Dichlorocyclohexylamine* (Note 1). In a 300-ml. three-necked flask fitted with stirrer, addition funnel, thermometer, and calcium chloride tube are placed 9.92 g. (0.10 mole) of cyclohexylamine (Note 2) and 50 ml. of dry benzene (Note 3), and the mixture is cooled to 0–5° by an ice bath. A solution of 24 g. (0.22 mole) of *t*-butyl hypochlorite[3]. [4] in 50 ml. of dry benzene is added dropwise at such a rate that the temperature of the mixture does not exceed 10°. The mixture is allowed to come to room temperature and is then stirred for 1 hour, giving a solution of N,N-dichlorocyclohexylamine suitable for use in the next step.

B. *N-Chlorocyclohexylideneimine*. In a 500-ml. three-necked flask fitted with stirrer, addition funnel, thermometer, and reflux condenser fitted with a calcium chloride tube are placed 15 g. (0.15 mole) of potassium acetate (Note 4) and 100 ml. of absolute ethanol. The mixture is heated to reflux temperature, and, when the potassium acetate has dissolved, the N,N-dichlorocyclohexylamine solution is added at such a rate as to maintain reflux (Note 5). The reaction mixture is heated under reflux for an additional 3 hours, during which time potassium chloride precipitates. The mixture is cooled to room temperature, 200 ml. of ether and 100 ml. of water are added, and the resulting mixture is transferred to a 1-l. separatory funnel. The aqueous layer is separated and discarded. The ethereal layer is washed with three 100-ml. portions of water, three 50-ml. portions of 2*N* hydrochloric acid, and an additional three 100-ml. portions of water, the washings being discarded. The ethereal solution is dried over anhydrous calcium sulfate, and the solvent is removed at room temperature with a rotary evaporator and water aspirator. The residue is transferred to a 25-ml. distilling flask and fractionally distilled at reduced pressure through a short, vacuum-jacketed Vigreux column equipped with a Claisen type still head and a condenser through which ice water is circulated (Note 6). N-Chlorocyclohexylideneimine, b.p. 53–54° (3 mm.) (*Caution! (Note 7)*), n^{25}D 1.506, is obtained in 48–69% yield (6.3–9.1 g.) (Note 8).

2. Notes

1. This method is essentially that of Baumgarten and Petersen.[5]
2. Eastman Organic Chemicals cyclohexylamine, white label grade, was redistilled prior to use.
3. Dried by azeotropic distillation; the first 10% of distillate is discarded.
4. Baker and Adamson, reagent grade.
5. The checkers found it preferable to maintain some external heating; otherwise the rate of addition had

to be very rapid to maintain reflux.
6. Ice water is essential, and cooling of the receiver is recommended; otherwise considerable losses by evaporation occur.
7. The pot temperature should not be allowed to rise above 70° (the submitters used a hot-water bath at 75°), as a fume-off which may proceed with explosive violence is likely to occur. A nitrogen bubbler may be used to eliminate bumping. The distillation should be carried out behind a safety shield.
8. The compound decomposes slowly even under refrigeration and should be used within 24 hours of preparation. Analytically pure material, b.p. 36° (1.5 mm.), may be obtained by redistillation.

3. Discussion

N-Chlorocyclohexylideneimine has been prepared by the treatment of N,N-dichlorocyclohexylamine with triethylamine,[6] potassium hydroxide,[6] or potassium acetate[7] and by reaction of chloramine with cyclohexanone[8] or *N*-cyclohexylideneaniline.[9]

4. Merits of the Preparation

This method, which is an adaptation of that of Alt and Knowles,[7] obviates the need to isolate the N,N-dichlorocyclohexylamine.

N-Chlorocyclohexylideneimine is of theoretical interest, being isoelectronic with the oxime tosylate. On treatment with 1 mole of base the imine undergoes a Neber-type rearrangement to the α-amino ketone[7] and has been shown to be an intermediate in the rearrangement of N,N-dichlorocyclohexylamine to 2-aminocyclohexanone.[5,7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 909

References and Notes

1. Agricultural Research Laboratory, Monsanto Chemical Company, St. Louis, Missouri.
2. Research Department, Organic Division, Monsanto Chemical Company, St. Louis, Missouri.
3. H. M. Teeter and E. W. Bell, *Org. Syntheses.*, Coll. Vol. **4**, 125 (1963). *Caution!* See Warning, this volume, p. 183
4. M. J. Mintz and C. Walling, this volume, p. 184.
5. H. E. Baumgarten and J. M. Petersen, *J. Am. Chem. Soc.*, **82**, 459 (1960); see this volume, p. 909.
6. S. L. Reid and D. B. Sharp, *J. Org. Chem.*, **26**, 2567 (1961).
7. G. H. Alt and W. S. Knowles, *J. Org. Chem.*, **25**, 2047 (1960).
8. B. Rudner (to W. R. Grace and Co.), U.S. Patent 2,894,028 (1959) [*C.A.*, **53**, 19924 (1959)].
9. E. Schmitz, *Angew. Chem.*, **73**, 23 (1961).

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

Cyclohexanone (108-94-1)

calcium sulfate (7778-18-9)

potassium hydroxide (1310-58-3)

potassium chloride (7447-40-7)

potassium acetate (127-08-2)

cyclohexylamine (108-91-8)

chloramine (10599-90-3)

triethylamine (121-44-8)

N-CHLOROCYCLOHEXYLIDENEIMINE,
Cyclohexanimine, N-chloro- (6681-70-5)

N,N-dichlorocyclohexylamine

oxime tosylate

2-aminocyclohexanone

N-cyclohexylideneaniline

t-BUTYL HYPOCHLORITE (507-40-4)