



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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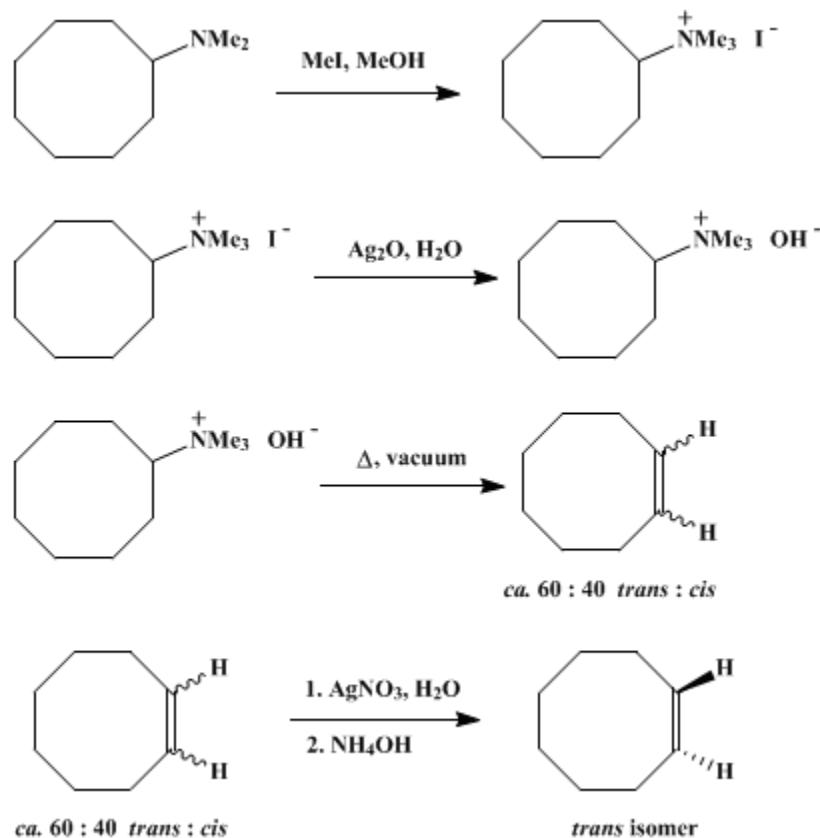
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trans-CYCLOOCTENE



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1. Procedure

A. *N,N,N*-Trimethylcyclooctylammonium iodide. To a 2-l., three-necked, round-bottomed flask equipped with a stirrer, condenser, drying tube, and pressure-equalizing dropping funnel are added 155.3 g. (1 mole) of *N,N*-dimethylcyclooctylamine (Note 1) and 700 ml. of reagent grade methanol. To the stirred solution is added 170.3 g. (1.2 moles) of iodomethane (Note 2) dropwise over a 30-minute period. The flask is cooled intermittently with an ice bath to keep the reaction temperature at approximately 25° (Note 3). After 1 hour the bath is removed and the reaction mixture is allowed to stir at 25° for an additional 3 hours.

The light yellow solution is transferred to a 2-l. round-bottomed flask, and the solvent is removed under reduced pressure (Note 4) with slight warming. The solid product is triturated with 500 ml. of diethyl ether, filtered, and washed with three 200-ml. portions of diethyl ether. The white solid (291–296 g.) is dried under reduced pressure, m.p. 269–270° dec. (Note 5).

B. *N,N,N*-Trimethylcyclooctylammonium hydroxide. To a 1-l. round-bottomed flask equipped with a stirrer are added 100 g. (0.34 mole) of *N,N,N*-trimethylcyclooctylammonium iodide, 76 g. of silver oxide (Note 6), and 350 ml. of distilled water. The suspension is stirred at room temperature for 5 hours and is filtered through a Buchner funnel. The filter cake is washed with four 35-ml. portions of distilled water. The light yellow filtrate is transferred to a 1-l. round-bottomed flask and the volume is reduced to approximately 90 ml. employing a rotary evaporator and a 40° water bath. The viscous *N,N,N*-trimethylcyclooctylammonium hydroxide solution is transferred (Note 7) to a 200-ml. dropping funnel, with a pressure-equalizing side arm, for use in the next step in the synthesis (Note 8).

C. *trans*-**Cyclooctene**. A 500-ml., three-necked, round-bottomed flask is equipped with a nitrogen inlet capillary tube (Note 9), a short (10–20 cm.) unpacked column (Note 10), and a pressure-equalizing dropping funnel. The round-bottomed flask is connected by the unpacked column to a 100-ml. trap cooled in an ice bath. This trap is then connected to a 200-ml. trap cooled in dry ice-acetone (Note 11). The flask is heated in an oil bath to 110–125°, and the apparatus is evacuated to a pressure of *ca.* 10 mm. under a constant sweep of **nitrogen**. The hydroxide solution is added dropwise at approximately the rate of decomposition of the quaternary **ammonium hydroxide** (Note 12).

The combined distillates from the cold traps are allowed to come to room temperature (Note 13) and are placed in a 1-l. separatory funnel with 200 ml. of 5% **hydrochloric acid** solution. The mixture of *cis*- and *trans*-cyclooctenes (Note 14) is extracted with 200 ml. of **n-pentane** and subsequently with two 50-ml. portions of **n-pentane**. The **n-pentane** extracts are combined and washed with 170 ml. of 5% **sodium bicarbonate** solution.

To a 1-l. separatory funnel is added *ca.* 500 ml. of 20% aqueous **silver nitrate** solution (100 g. of Mallinckrodt C.P. crystals to *ca.* 500 ml. of water). The **pentane** solution is added to the separatory funnel in five approximately equal portions, with intermittent shaking until all the **silver nitrate** complex has gone into solution (Note 15).

The **silver nitrate** solution is extracted as described above with three portions of **n-pentane** to remove *cis*-cyclooctene (Note 16). The aqueous **silver nitrate** solution is added slowly to 300 ml. of concentrated **ammonium hydroxide** containing cracked ice. The hydrocarbon that separates is extracted with 300 ml. of **n-pentane** as described above and the **pentane** solution is dried over anhydrous **magnesium sulfate** and the **pentane** distilled through a 23 × 250 mm. column packed with glass beads.

The product is distilled under reduced pressure through a short (8 cm.) Vigreux column (Note 17) and has b.p. 75° (78 mm.), 44° (23 mm.), $n^{25}\text{D} = 1.4741$, $d_4^{25} = 0.8456$. The yield of pure *trans*-cyclooctene is 15.0 – 15.3 g. (40%) (Note 18), (Note 19), (Note 20), (Note 21).

2. Notes

1. Cyclooctylamine was purchased from Aldrich Chemical Co. It was converted to **N,N-dimethylcyclooctylamine** in 74% yield using a procedure analogous to that for β -phenylethyldimethylamine.³
2. Fischer reagent grade **methanol** and Eastman Organic Chemicals **iodomethane** were used.
3. The molar ratio of **iodomethane** to **N,N-dimethylcyclooctylamine** may be reduced if precautions are taken to prevent loss of **iodomethane** due to vaporization.
4. It is convenient to use a rotary evaporator for removal of the solvents.
5. After one recrystallization from an **acetone-methanol** mixture, the compound melts at 273–275° dec. The compound is sufficiently pure for the next step in the synthesis without recrystallization.
6. Mallinckrodt purified **silver oxide powder** was used. The reaction flask should be protected from direct sunlight with a suitable wrapping.
7. The flask may be rinsed with a minimum of water and transferred to the dropping funnel. The total volume of hydroxide solution at this point should not exceed 100 ml.
8. The conversion of the quaternary ammonium iodide to the hydroxide may also be carried out using a strongly basic ion exchange resin.⁴
9. The decomposition should be carried out under a constant sweep of **nitrogen**. The **nitrogen** may be introduced through the pressure-equalizing dropping funnel if that is more convenient.
10. The unpacked column should be wrapped with a heating tape, or Nichrome heating wire, and kept at *ca.* 110° throughout the decomposition.
11. The reaction is stopped and the trap, cooled in dry ice-acetone, is emptied when the reaction is *ca.* one half finished to prevent plugging by ice. Most of the olefinic products are found in the first trap. The second trap contains mostly **trimethylamine** and water.
12. About 3 hours is required to add the hydroxide solution. The rate of addition may be increased, but considerable foaming occurs during the decomposition, and caution should be taken that the hydroxide does not foam over into the traps.
13. This part of the experiment should be carried out in a hood because **trimethylamine** is evolved.
14. The decomposition of **N,N,N-trimethylcyclooctylammonium hydroxide** forms a mixture of *cis*- and

trans-cyclooctenes which contains *ca.* 60% of the *trans*- and 40% of the *cis*-isomer (see (Note 19)). The mixture is separated by extraction of the *trans*-isomer with aqueous silver nitrate.⁵

15. If the pentane solution is added to the silver nitrate solution too rapidly, the *trans*-cyclooctene forms a dark precipitate that is difficult to get into solution. This situation can, however, be remedied by the addition of more silver nitrate solution and continued shaking.

16. The pentane is removed and *ca.* 11 g. of *cis*-cyclooctene is obtained on distillation, b.p. 65° (59 mm.); $n^{25}\text{D} = 1.4684$.

17. Considerable foaming occurs during distillation of *trans*-cyclooctene. The distillation may therefore be facilitated by use of a distilling adapter with a foam trap. The distilling adapter (5225) may be purchased from Ace Glass Incorporated, Vineland, New Jersey. The bath temperature should be kept below 100° owing to the possibility of isomerization to *cis*-olefin and polymerization.⁶ The distillation should be carried out as rapidly as possible because the condensed product evaporates under prolonged exposure to reduced pressure.

18. The submitters carried out this preparation on a 1.0-mole scale and obtained 49–51 g. (45–46%) of *trans*-cyclooctene.

19. The purity of the *trans*-cyclooctene may be determined by infrared spectroscopy⁵ or by gas chromatography using an NMPN (3-nitro-3-methylpimelonitrile) column.⁷ A low injection port temperature is desirable (<200°).

20. *trans*-Cyclooctene is stable for at least 1 year if kept under refrigeration and if a free radical inhibitor is used (*e.g.* di-*t*-butyl-resorcinol). The compound has a very disagreeable odor.

21. Since this procedure was submitted the submitter has found that higher overall yields of *trans*-cyclooctene may be obtained from a stirred suspension of trimethylcyclooctylammonium iodide in anhydrous dimethyl sulfoxide using commercially available (sublimed) potassium *t*-butoxide as the base at 25°. The *cis/trans* ratio under these conditions is 1/4.6 (private communication from R. D. Bach).

3. Discussion

trans-Cyclooctene has been prepared by the Hofmann elimination of N,N,N-trimethylcyclooctylammonium hydroxide,^{5,8} the present method; by the treatment of N,N,N-trimethylcyclooctylammonium bromide with phenyllithium, methylolithium, and potassium amide;⁹ and by the treatment of *trans*-1,2-cyclooctene thiocarbonate with triisoctyl phosphite.¹⁰

This procedure illustrates a general method for preparing olefins by the elimination of an amine and a β-hydrogen atom.¹¹ The present method is more convenient for adaptation to large-scale laboratory preparation than is the Wittig modification, which utilizes liquid ammonia; both methods give essentially the same overall yield of *trans*-cyclooctene.

The preparation of olefins *via* their thiocarbonate¹⁰ is a stereo-specific elimination reaction which may be used to advantage when a mixture of *cis*- and *trans*-olefins is difficult to separate. However, all the reagents required to prepare the thiocarbonate are not readily available.

References and Notes

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

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methanol (67-56-1)

diethyl ether (60-29-7)

sodium bicarbonate (144-55-8)

silver oxide,
silver oxide powder (20667-12-3)

silver nitrate (7761-88-8)

nitrogen (7727-37-9)

ammonium hydroxide (1336-21-6)

iodomethane (74-88-4)

Pentane,
n-PENTANE (109-66-0)

Trimethylamine (75-50-3)

Phenyllithium (591-51-5)

magnesium sulfate (7487-88-9)

acetone-methanol (590-90-9)

potassium amide

β-PHENYLETHYLDIMETHYLAMINE (1126-71-2)

Methylolithium (917-54-4)

dimethyl sulfoxide (67-68-5)

N,N-dimethylcyclooctylamine

N,N,N-trimethylcyclooctylammonium iodide,

trimethylcyclooctylammonium iodide

N,N,N-trimethylcyclooctylammonium hydroxide

Cyclooctylamine (5452-37-9)

3-nitro-3-methylpimelonitrile

N,N,N-trimethylcyclooctylammonium bromide

triisooctyl phosphite

potassium t-butoxide (865-47-4)

cis-cyclooctene (931-87-3)

trans-Cyclooctene (931-89-5)

di-t-butyl-resorcinol

trans-1,2-cyclooctene thiocarbonate

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