



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

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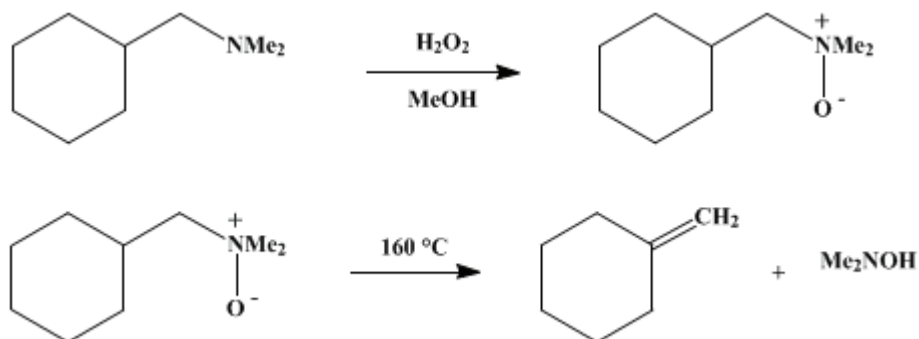
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 4, p.612 (1963); Vol. 39, p.40 (1959).*

## METHYLENECYCLOHEXANE AND N,N-DIMETHYLHYDROXYLAMINE HYDROCHLORIDE

[Cyclohexane, methylene-]

[Hydroxylamine, N,N-dimethyl-, hydrochloride]



Submitted by Arthur C. Cope and Engelbert Ciganek<sup>1</sup>.  
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### 1. Procedure

In a carefully cleaned 500-ml. Erlenmeyer flask, covered with a watch glass, are placed 49.4 g. (0.35 mole) of *N,N*-dimethylcyclohexylmethylamine (Note 1), 39.5 g. (0.35 mole) of 30% hydrogen peroxide, and 45 ml. of methanol. The homogeneous solution is allowed to stand at room temperature for 36 hours. After 2 and 5 hours hydrogen peroxide (39.5-g. portions each time) is added (Note 2), (Note 3). The excess hydrogen peroxide is destroyed by stirring the mixture with a small amount of platinum black (Note 4) until the evolution of oxygen ceases. The solution is filtered into a 500-ml. round-bottomed flask and concentrated at a bath temperature of 50–60° (Note 5), a water aspirator being used initially and an oil pump finally, until the amine oxide hydrate solidifies. A Teflon-covered stirring bar is introduced into the flask, which is then connected by a 20-cm. column to a trap (reversed to avoid plugging) cooled in Dry Ice-acetone. The flask is heated in an oil bath to 90–100°, and the apparatus is evacuated to a pressure of ca. 10 mm. with stirring of the liquefied amine oxide hydrate. When the content of the flask resolidifies, the temperature of the oil bath is raised to 160°. The amine oxide decomposes completely within about 2 hours at this temperature. Water (100 ml.) is added to the contents of the trap. The olefin layer is removed with a pipette and washed with two 5-ml. portions of water, two 5-ml. portions of ice-cold 10% hydrochloric acid (Note 6), (Note 7), and one 5-ml. portion of 5% sodium bicarbonate solution. The olefin is cooled in a Dry Ice-acetone bath and filtered through glass wool (Note 8). Distillation over a small piece of sodium through a semimicro column<sup>2</sup> yields 26.6–29.6 g. (79–88%) of methylenecyclohexane, b.p. 100–102° (Note 9),  $n_D^{25}$  1.4474 (Note 10).

The aqueous layer is combined with the two neutral aqueous extracts and acidified by addition of 45 ml. of concentrated hydrochloric acid. The solution is concentrated under reduced pressure at 60–70° until no more distillate comes over. The residue, which solidifies on cooling, is dried in a vacuum desiccator over potassium hydroxide pellets to yield 30.7–32.7 g. (90–96%) of crude *N,N*-dimethylhydroxylamine hydrochloride, m.p. 103–106° (sealed tube). Crystallization from 40 ml. of isopropyl alcohol gives 26.6–30.7 g. (78–90%) of the pure hydrochloride, m.p. 106–108° (sealed tube).

### 2. Notes

1. The preparation of *N,N*-dimethylcyclohexylmethylamine is described on p.339.
2. Many amines are oxidized much more rapidly than the one used in this preparation, and it is often necessary to cool such reaction mixtures in order to avoid decomposition of the amine oxide or a

vigorous exothermic reaction.

3. The completion of the oxidation should be tested by adding 1 drop of an alcoholic [phenolphthalein](#) solution and 3 drops of water to 1 drop of the oxidation mixture on a porcelain spot plate. Amine oxides give no color with [phenolphthalein](#).

4. Prepared by the procedure of Feulgen, *Ber.*, **54**, 360 (1921), and added as an aqueous suspension.

5. Some amine oxides decompose at slightly elevated temperatures. In these cases, removal of the solvents should be carried out at room temperature. It is convenient to use a rotary evaporator for removal of the solvents.

6. [Methylenecyclohexane](#) does not rearrange to [1-methylcyclohexene](#) under these conditions. In preparations of those olefins which are more sensitive to acid, washing with acid should be omitted.

7. By making the acid extracts strongly alkaline, extracting the basic material with [ether](#), and distilling the [ether](#) extracts, 1.0–2.5 g. (2–5%) of [N,N-dimethylcyclohexylmethylamine](#) containing a small amount of a higher-boiling basic compound of unknown structure may be recovered.

8. The material obtained in this manner is of high purity before distillation; it has the same refractive index as the distilled [methylenecyclohexane](#), and no impurities could be detected by gas chromatographic analysis on two different columns.

9. Most of the material boils at 101–102°; the small fore-run has the same refractive index as the main fraction.

10. [1-Methylcyclohexene](#) is completely absent, as shown by gas chromatography on a column packed with 30% by weight of a 52% solution of [silver nitrate](#) in [tetraethylene glycol](#) (Dow Chemical Company) on 48–100 mesh "firebrick" at 60°. It is estimated that the presence of less than 0.01% of this isomer could have been detected.

### 3. Discussion

The present preparation of [methylenecyclohexane](#) is an example of an amine oxide pyrolysis. This route from amines to olefins in many cases yields pure olefins where the alternative method, the Hofmann exhaustive methylation reaction, is accompanied by some rearrangement to more stable isomeric olefins.

[Methylenecyclohexane](#) has been prepared by treatment of [cyclohexylmethyl iodide](#) with alcoholic [potassium hydroxide](#) solution,<sup>3</sup> by thermal decarboxylation of [cyclohexylideneacetic acid](#) and of [cyclohexane-1-acetic acid](#),<sup>4,5,6</sup> and of [cyclohexane-1,1-diacetic acid](#);<sup>7</sup> by pyrolysis of the xanthate,<sup>8</sup> the acetate,<sup>9,10,11,12,13</sup> and the stearate<sup>14</sup> of [cyclohexanemethanol](#); by the action of [triphenylphosphine-methylene](#) on [cyclohexanone](#);<sup>15</sup> by the pyrolysis of [N,N-dimethylcyclohexylmethylamine methohydroxide](#)<sup>16,17</sup> and of [N,N-dimethylcyclohexylmethylamine N-oxide](#);<sup>16,17</sup> and by treatment of [benzylhexahydrobenzylidimethylammonium bromide](#) with [sodium amide](#) in liquid ammonia.<sup>18</sup>

[N,N-Dimethylhydroxylamine](#) has been prepared by the action of [methylmagnesium iodide](#) on [ethyl nitrate](#).<sup>19</sup>

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### References and Notes

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

platinum black

N,N-dimethylcyclohexylmethylamine methohydroxide

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

methanol (67-56-1)

ether (60-29-7)

sodium bicarbonate (144-55-8)

Cyclohexanone (108-94-1)

silver nitrate (7761-88-8)

oxygen (7782-44-7)

potassium hydroxide,  
potassium hydroxide pellets (1310-58-3)

sodium (13966-32-0)

isopropyl alcohol (67-63-0)

hydrogen peroxide (7722-84-1)

cyclohexanemethanol (100-49-2)

methylmagnesium iodide (917-64-6)

phenolphthalein (77-09-8)

sodium amide (7782-92-5)

ethyl nitrate (625-58-1)

1-methylcyclohexene

N,N-Dimethylcyclohexylmethylamine (16607-80-0)

Methylenecyclohexane,  
Cyclohexane, methylene- (1192-37-6)

N,N-DIMETHYLHYDROXYLAMINE HYDROCHLORIDE,  
Hydroxylamine, N,N-dimethyl-, hydrochloride (16645-06-0)

tetraethylene glycol (112-60-7)

cyclohexylmethyl iodide

cyclohexylideneacetic acid

cyclohexane-1-acetic acid (5292-21-7)

cyclohexane-1,1-diacetic acid (4355-11-7)

triphenylphosphine-methylene

N,N-dimethylcyclohexylmethylamine N-oxide

benzylhexahydrobenzyltrimethylammonium bromide

N,N-Dimethylhydroxylamine (5725-96-2)