



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.

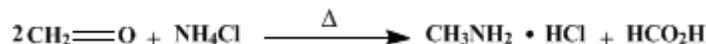
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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METHYLAMINE HYDROCHLORIDE



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1. Procedure

In a 5-l. round-bottomed flask, fitted with a stopper holding a condenser set for downward distillation and a thermometer which will extend well into the liquid, are placed 4 kg. (3711 cc., 47–53 moles) of technical [formaldehyde](#) (35–40 per cent; sp. gr. 1.078 at 20°) (see [Note 1 on p. 378](#)) and 2 kg. (37 moles) of technical [ammonium chloride](#). The mixture is heated on the steam bath until no more distillate comes over and then over a flame until the temperature of the solution reaches 104°. The temperature is held at this point until no more distillate comes over (four to six hours). The distillate, which consists of [methylal](#), [methyl formate](#), and water, may be treated as described in ([Note 1](#)).

The contents of the reaction flask are cooled to room temperature ([Note 2](#)), and the [ammonium chloride](#) which separates is filtered off and centrifuged ([Note 3](#)). The mother liquor is concentrated on the steam bath under reduced pressure to 2500 cc., and again cooled to room temperature, whereupon a second crop of [ammonium chloride](#) is obtained. The total recovery of [ammonium chloride](#) up to this point amounts to 780–815 g.

The mother liquor is again concentrated under reduced pressure until crystals begin to form on the surface of the solution (1400–1500 cc.). It is then cooled to room temperature, and a first crop of [methylamine hydrochloride](#), containing some [ammonium chloride](#), is obtained by filtering the cold solution and centrifuging the crystals ([Note 3](#)). At this point 625–660 g. of crude product is obtained. The mother liquor is now concentrated under reduced pressure to about 1000 cc. and cooled; a second crop of [methylamine hydrochloride](#) (170–190 g.) is then filtered off and centrifuged. This crop of crystals is washed with 250 cc. of cold [chloroform](#), filtered, and centrifuged, in order to remove most of the [dimethylamine hydrochloride](#) which is present; after the washing with [chloroform](#) the product weighs 140–150 g. The original mother liquor is then evaporated under reduced pressure, as far as possible, by heating on a steam bath, and the thick sirupy solution (about 350 cc.) which remains is poured into a beaker and allowed to cool, with occasional stirring, in order to prevent the formation of a solid cake ([Note 2](#)). The thick paste so obtained is centrifuged, and the crystals (170–190 g.) are washed with 250 cc. of cold [chloroform](#); the solution is filtered and the crystals are centrifuged, thus yielding 55–65 g. of product. There is no advantage in further concentrating the mother liquor.

The total yield of crude centrifuged [methylamine hydrochloride](#) is 830–850 g. This product contains, as impurities, water, [ammonium chloride](#), and some [dimethylamine hydrochloride](#). In order to obtain a pure product, the crude [methylamine hydrochloride](#) is recrystallized from absolute [alcohol](#) ([Note 4](#)). The crude salt is placed in a 5-l. round-bottomed flask fitted with a reflux condenser protected at the top with a calcium chloride tube; 2 l. of absolute [alcohol](#) is added and the mixture heated to boiling. After about one-half hour the undissolved material is allowed to settle and the clear solution is poured off. When the alcoholic solution is cooled, [methylamine hydrochloride](#) crystallizes out. It is filtered off and centrifuged, and the alcohol used for another extraction. The process is repeated until the alcohol dissolves no more of the product (about five extractions are necessary). In the flask 100–150 g. of [ammonium chloride](#) remains, making the total recovery of [ammonium chloride](#) 850–950 g. The yield of recrystallized [methylamine hydrochloride](#) is 600–750 g. (45–51 per cent of the theoretical amount, based on the [ammonium chloride](#) used up in the process) ([Note 5](#)) and ([Note 6](#)).

2. Notes

1. [Methylal](#) and [sodium formate](#) may be obtained from the first distillate of the main reaction mixture. The crude distillate is placed in a flask fitted with a reflux condenser, and to it is added a solution of 200

g. of sodium hydroxide in 300 cc. of water. The methyl formate is hydrolyzed to sodium formate. The methylal layer is separated, dried over calcium chloride, and distilled. In this way 240–260 g. of methylal, boiling at 37–42°, is obtained. By evaporating the watery portion to dryness, a residue of about 280 g. of crude sodium formate is obtained.

2. The methylamine hydrochloride solutions should be cooled rapidly in order to bring the salt down in small crystals which may be easily purified.

3. Centrifuging the precipitates is the only satisfactory method of drying, as all the products tend to take up water when allowed to stand in the air.

4. Since ammonium chloride is not absolutely insoluble in 100 per cent ethyl alcohol (100 g. dissolve 0.6 g. at 15°), the methylamine hydrochloride purified in the manner described contains appreciable traces of it. A purer product can be prepared by recrystallizing from *n*-butyl alcohol, in which the solubility of ammonium chloride even at the boiling temperature is negligibly small. Methylamine hydrochloride is somewhat less soluble in this solvent than in ethyl alcohol, but as a rule three extractions carried out at 90–100° with 4–6 parts of fresh butyl alcohol for each extraction result in a substantially complete separation. Since the last traces of the solvent are not readily removed by exposure to air, a solution of the recrystallized material in a small quantity of water should be distilled until free of alcohol, and allowed to crystallize.

An entirely different method for preparing pure methylamine hydrochloride free of ammonium chloride has been described.¹ It is based on the fact that when a mixture of methylamine and ammonia reacts with an insufficient quantity of hydrochloric acid the methylamine is preferentially neutralized and the ammonia left free.

5. The literature² claims a yield of methylamine hydrochloride amounting to 79 per cent of the weight of ammonium chloride used up in the reaction. This figure is probably based on the weight of crude methylamine hydrochloride and not of the recrystallized material.

6. Methylamine can be purified through its benzal derivative, which is distilled and then hydrolyzed by concentrated hydrochloric acid.³ This method has been checked and found satisfactory by one of the editors.

3. Discussion

Methylamine can be prepared by the action of ammonia on methyl iodide,⁴ methyl chloride,⁵ dimethyl sulfate,⁶ methyl *p*-toluenesulfonate⁷ and methyl alcohol with a catalyst and at elevated temperatures;⁸ by the action of bromine and alkali⁹ and of bleaching powder¹⁰ on acetamide; by the action of sodamide on methyl iodide;¹¹ by the reduction of chloropicrin,¹² hydrocyanic or ferrocyanic acid,¹³ hexamethylenetetramine,¹⁴ nitromethane,¹⁵ methyl nitrite,¹⁶ or formaldoxime;¹⁷ from acetyl chloride and sodium azide;¹⁸ and by the action of formaldehyde on ammonium chloride.¹⁹

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

benzal derivative

chloropicrin

hydrocyanic or ferrocyanic acid

ethyl alcohol,
alcohol (64-17-5)

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

Acetamide (60-35-5)

ammonia (7664-41-7)

methyl alcohol (67-56-1)

ammonium chloride (12125-02-9)

sodium hydroxide (1310-73-2)

formaldehyde (50-00-0)

acetyl chloride (75-36-5)

chloroform (67-66-3)

bromine (7726-95-6)

dimethyl sulfate (77-78-1)
methyl chloride (74-87-3)
butyl alcohol,
n-butyl alcohol (71-36-3)
Methyl iodide (74-88-4)
Methylamine hydrochloride (593-51-1)
methylal (109-87-5)
methyl formate (107-31-3)
dimethylamine hydrochloride (506-59-2)
sodium formate
methylamine (74-89-5)
hexamethylenetetramine (100-97-0)
Nitromethane (75-52-5)
methyl nitrite (624-91-9)
sodium azide (26628-22-8)
sodamide (7782-92-5)
Methyl p-toluenesulfonate (80-48-8)