alcohol was the principal product. Several methods proposed for the dehydration of diacetone alcohol were investigated. That of Hibbert[2] (using a very small quantity of iodine) is superior to the action of either concentrated sulfuric acid or aluminum phosphate.

METHYLAMINE HYDROCHLORIDE

$$2HCHO + NH_4Cl \rightarrow CH_3NH_2 \cdot HCl + HCO_2H$$

Submitted by C. S. Marvel and R. L. Jenkins.
Checked by J. B. Conant and F. C. Whidden.

1. Procedure

In a 5-l. round-buttoned 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) (Notes 5 and 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 rap-

idly in order to bring the
easily purified.

3. Centrifuging the pre
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stand in the air.

4. Since ammonium ch
cent ethyl alcohol (100 g
hydrochloride purified in
traces of it. A purer prod
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the boiling temperature is
ride is somewhat less solul
as a rule three extraction
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plete separation. Since t
removed by exposure to
in a small quantity of wa
and allowed to crystallize.

An entirely different n
drochloride free of ammo
based on the fact that wh
reacts with an insufficient
mine is preferentially neu

5. The literature[2] clai
amounting to 79 per cent
in the reaction. This figu
methylamine hydrochlorid

6. Methylamine can
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acid.[3] This method has
of the editors.

3. M

Methylamine can be p
iodide,[4] methyl chloride,

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[1] Sharp and Solomon, J. C
[2] Werner, J. Chem. Soc. 11
[3] Sommelet, Compt. rend.
[4] Hofmann, Ann. 79, 16 (1
[5] Vincent and Chappuis, B
[6] Ephrian and Gurewitsch,
Soc. **117**, 236 (1920).

idly 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 literature[2] 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. Methods of Preparation

Methylamine can be prepared by the action of ammonia on methyl iodide,[4] methyl chloride,[5] dimethyl sulfate,[6] methyl *p*-toluenesulfo-

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[1] Sharp and Solomon, J. Chem. Soc. 1477 (1931).

[2] Werner, J. Chem. Soc. **111**, 850 (1917).

[3] Sommelet, Compt. rend. **178**, 217 (1924).

[4] Hofmann, Ann. **79**, 16 (1851).

[5] Vincent and Chappuis, Bull. soc. chim. **45**, 499 (1886).

[6] Ephrian and Gurewitsch, Ber. **43**, 139 (1910); Denham and Knapp, J. Chem. Soc. **117**, 236 (1920).

nate[7] and methyl alcohol with a catalyst and at elevated temperatures;[8] by the action of bromine and alkali[9] and of bleaching powder[10] 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]

[7] Rodionov, Bull. soc. chim. (4) **45,** 109 (1929).

[8] Davis and Elderfield, J. Am. Chem. Soc. **50,** 1786 (1928); E. I. du Pont de Nemours and Co., U. S. pat. 2,017,051 [C. A. **29,** 8001 (1935)].

[9] Hofmann, Ber. **15,** 765 (1882); François, Compt. rend. **147,** 430, 680, 983 (1908).

[10] Bader and Nightingale, U. S. pat. 1,489,380 [C. A. **18,** 1836 (1924)].

[11] Chablay, Compt. rend. **156,** 328 (1913).

[12] Geisse, Ann. **109,** 282 (1859); Wallach and Boehringer, Ann. **184,** 51 (1877); Frankland, Challenger, and Nicholls, J. Chem. Soc. **115,** 159 (1919).

[13] Mendius, Ann. **121,** 139 (1862); Debus, Ann. **128,** 201 (1863); Denham, Z. physik. Chem. **72,** 674 (1910); Riedel, Ger. pat. 264,528 [Frdl. **11,** 110 (1912–14)]; Dreyfus, U. S. pat. 2,072,247 [C. A. **31,** 2619 (1937)].

[14] Meister, Lucius, and Brüning, Ger. pat. 73,812 [Frdl. **3,** 15 (1890–4)]; Trillat and Fayollat, Bull. soc. chim. (3) **11,** 23 (1894); Kundsen, Ger. pat. 143,197 [Frdl. **7,** 24 (1902–4)]; Meister, Lucius, and Brüning, Ger. pat. 148,054 [Frdl. **7,** 26 (1902–4)]; Isono, J. Pharm. Soc. Japan No. 397, 209 (1915) [C. A. **9,** 2232 (1915)].

[15] Pierron, Bull. soc. chim. (3) **21,** 783 (1899); Mailhe and Murat, ibid. (4) **7,** 954 (1910); Zerewitinov and Ostromisslensky, Ber. **44,** 2403 (1911).

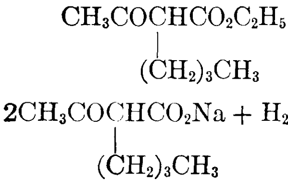
[16] Gaudion, Bull. soc. chim. (4) **7,** 824 (1910) and Ann. chim. phys. (8) **25,** 136 (1912).

[17] Takaki and Ueda, J. Pharm. Soc. Japan **58,** 276 (1938) [C. A. **32,** 5376 (1938)].

[18] Naegeli, Grüntuch and Lendorff, Helv. Chim. Acta **12,** 227 (1929).

[19] Brochet and Cambier, Bull. soc. chim. (3) **13,** 534 (1895); François, Compt. rend. **147,** 429 (1908); Werner, J. Chem. Soc. **111,** 848 (1917); Jones and Wheatley, J. Am. Chem. Soc. **40,** 1411 (1918); Wietzel and Köhler, Ger. pat. 468,895 [C. A. **23,** 846 (1929)].

METH



$CH_3COCHCO_2C_2H_5$ / $(CH_2)_3CH_3$

$2CH_3COCHCO_2Na + H_2$ / $(CH_2)_3CH_3$

Submi
Check

In a 12-l. round-bott
stirrer, is placed 5 l. of a
moles). To this is adde
925 g.) obtained (p. 248)
ture is stirred at room t
the monosubstituted ac
passes into solution. T
unsaponified material sep
ous layer is separated (
with a stopper fitted wi
tube leading to a conde

Through the separat
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than the amount requir
in the saponification of
oxide ceases to be vigor
boiling, and from one-t
tilled. The distillate is
(Note 2) and redistilled

In the distillate the
the latter is distilled un
layer in this distillate is
tilled. This procedure is
of ketone is obtained in
fraction is washed four
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* Commercially available