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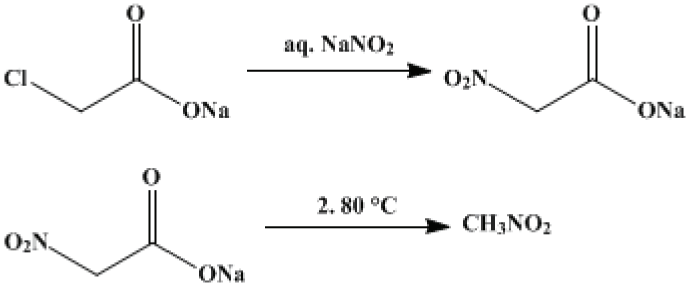
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.003.0083

Organic Syntheses, Coll. Vol. 1, p.401 (1941); Vol. 3, p.83 (1923).

NITROMETHANE

[Methane, nitro-]



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1. Procedure

To a mixture of 500 g. (5.3 moles) of chloroacetic acid and 500 g. of cracked ice, is added, with stirring, just sufficient cold 40 per cent sodium hydroxide solution to make the solution faintly alkaline to phenolphthalein. About 360 cc. is required; the temperature should not rise above 20° (Note 1). The solution is then mixed with 365 g. (5.3 moles) of sodium nitrite dissolved in 500 cc. of water and heated in a 3-l. round-bottomed flask fitted with a two-holed stopper containing a bent tube of large diameter connecting with an efficient condenser (set downward for distillation) and a thermometer dipping into the liquid. The receiver should be so arranged that it can be cooled, if necessary, by a stream of water.

The solution is heated slowly until the first appearance of bubbles of carbon dioxide, which occurs when the temperature has reached about 80°. The flame is then removed and the reaction allowed to proceed by itself (Note 2). If no rise in temperature occurs, heat is very cautiously applied until the temperature rises to 85°, when the flame is again removed (Note 3). At this temperature the exothermic decomposition of the sodium nitroacetate becomes so rapid that the temperature rises almost to 100° without further application of external heat. If heat is applied after the temperature of the liquid reaches 85°, violent frothing will occur, with serious loss of nitromethane. If the reaction becomes too vigorous it may be checked by applying a wet towel to the flask. Nitromethane starts to distil over at about 90°. During the spontaneous heating, about 120 cc. of nitromethane distils over, accompanied by about 170 cc. of water (Note 4). This water is saved for redistillation.

When the mixture ceases to maintain its temperature spontaneously at 95–100°, heat is applied cautiously until the temperature reaches 110°. About 13 cc. of nitromethane and 200 cc. of water distil over. Further distillation gives water which contains too little nitromethane to pay for recovery. At this point enough sodium chloride and sodium carbonate have separated to cause serious bumping.

The water separated from the nitromethane distillates is mixed with one-fourth of its weight of salt, and redistilled, yielding 10–12 cc. of nitromethane and about 100 cc. of water. This water on distillation gives 3–4 cc. of nitromethane and about 45 cc. of water (Note 5).

The total yield of moist product is 125–135 g.; on drying with a little calcium chloride and distilling, 115–125 g. of pure nitromethane, boiling at 98–101°, is obtained (35–38 per cent of the theoretical amount). A small forerun distils over below 98°, and a little dark brown residue remains (Note 6).

2. Notes

1. In making the sodium chloroacetate, the use of sodium hydroxide with proper cooling is much more rapid than the use of sodium carbonate. In the case of sodium hydroxide it is essential to keep the

solution cool in order to prevent the formation of sodium glycolate. If it is preferred to employ sodium carbonate, about 300 g. of the anhydrous material will be required to make the solution slightly alkaline.

2. The thermometer dipping *in the liquid* is absolutely necessary, as the success of the preparation depends on proper temperature control. The vital point of the whole preparation is to remove all external heat as soon as the reaction is well started. This is between 80 and 85°. No frothing ever occurs when this precaution is rigidly adhered to.

3. Several of these distilling sets can be set up and run by one operator, if each lot is started only when the preceding one has reached 85° and external heat has been removed. The corresponding water layers from different sets can be united and distilled at once.

4. It has been recommended[1] that use be made of a gravity separator connected with the adapter in order to separate the nitromethane as fast as it condenses. It was found inadvisable to use such a separator, as the nitromethane is so little heavier than water that a rapid separation is not possible; drops of nitromethane remain suspended and pass over with the water. It is best to allow the distillates to stand in cylinders for at least one-half hour before separating the nitromethane by means of a separatory funnel. During this standing, as much as 2 per cent more of nitromethane sometimes settles out.

5. If the time consumed is an important consideration, it is well to note that the spontaneous heating from 85° to 100° gives three-fourths of all the nitromethane obtained in the preparation. This takes less than one hour. The further heating above 100° and the distillations of the water layers take over two hours, and give only one-fourth of the total yield.

6. It is suggested that improved yields are obtainable when 374 g. of crystalline boric acid is added subsequent to the sodium nitrite and prior to the heating. In this way, carbon dioxide together with some oxides of nitrogen are evolved at about 45°. The reason offered for the higher yields is the destruction of sodium bicarbonate by the boric acid, which thereby prevents alkaline hydrolysis of the sodium chloroacetate (C. L. Tseng, private communication; [2]).

The yield is somewhat improved by using 625 g. of chloroacetic acid and about 450 cc. of 40 per cent sodium hydroxide solution instead of the 500 g. and 360 cc., respectively, now specified (H. Adkins, private communication; [2]).

3. Discussion

Nitromethane can be prepared by the action of dimethyl sulfate on potassium nitrite,[3] or of methyl *p*-toluenesulfonate[4] or methyl chloride[5] on sodium nitrite; and from potassium nitrite and potassium chloroacetate,[2] or, preferably, the corresponding sodium salts.[6] Nitromethane is now commercially available as a product of the vapor-phase nitration of the lower paraffin hydrocarbons.[7]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 413

References and Notes

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

oxides of nitrogen

calcium chloride (10043-52-4)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

sodium nitrite (7632-00-0)

carbon dioxide (124-38-9)

dimethyl sulfate (77-78-1)

methyl chloride (74-87-3)

chloroacetic acid (79-11-8)

sodium chloroacetate (3926-62-3)

Nitromethane,
Methane, nitro- (75-52-5)

phenolphthalein (77-09-8)

sodium nitroacetate

sodium glycolate (2836-32-0)

boric acid (10043-35-3)

potassium nitrite (7758-09-0)

potassium chloroacetate

Methyl p-toluenesulfonate (80-48-8)