Organic Syntheses

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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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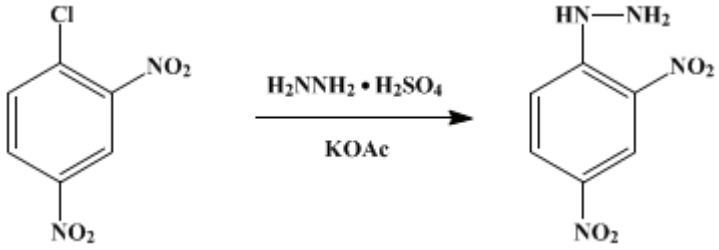
Organic Syntheses, Coll. Vol. 2, p.228 (1943); Vol. 13, p.36 (1933).

2,4-DINITROPHENYLHYDRAZINE

[Hydrazine, (2,4-dinitrophenyl)-]



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1. Procedure

Thirty-five grams (0.27 mole) of hydrazine sulfate (Org. Syn. Coll. Vol. I, **1941**, 309) is suspended in 125 cc. of hot water in a 400-cc. beaker and stirred by hand during the addition of 85 g. (0.87 mole) of potassium acetate (Note 1). The mixture is boiled five minutes and then cooled to about 70°; 75 cc. of alcohol is added, and the solid is filtered with suction and washed with 75 cc. of hot alcohol. The filtered hydrazine solution is saved for the next step.

In a 1-l. flask fitted with a stirrer and reflux condenser, 50.5 g. (0.25 mole) of technical 2,4-dinitrochlorobenzene is dissolved in 250 cc. of alcohol; the hydrazine solution is added, and the mixture is refluxed with stirring for an hour. Most of the product separates during the first ten minutes (Note 2); it is cooled well, filtered, and washed, once with 50 cc. of warm alcohol (60°) to remove unchanged halide and then with 50 cc. of hot water. The solid weighs 30 g. and melts at 190–192° with evolution of gas (Note 3); it is pure enough for most purposes. By distilling half the alcohol from the filtrate a less pure second crop is obtained; this is recrystallized from *n*-butyl alcohol (30 cc. per g.) (Note 4). The total yield is 40–42 g. (81–85 per cent of the theoretical amount) (Note 5)–(Note 10).

2. Notes

1. An equivalent amount of sodium acetate may be substituted for the potassium acetate.
2. Considerable heat is evolved during the separation.
3. The melting point is not sharp; in the capillary tube the sample shrinks about 10° below the melting point.
4. For recrystallization, *n*-butyl alcohol is the best solvent in spite of the large amount required, but tetralin, pyridine, or dioxane (10 cc. per g.) may be used where large quantities are involved. Fortunately, most of the material as prepared does not need further purification.
5. Complete evaporation of the filtrate yields a gummy residue; the amount of dinitrochlorobenzene present is too small to justify recovery.
6. By substituting 10 g. of sodium hydroxide for every 35 g. of potassium acetate and boiling for five minutes without filtering the salt, a 70 per cent yield of dinitrophenylhydrazine results; the quality is not quite so good as that obtained by the use of potassium acetate.
7. A slightly higher yield is obtained by starting with hydrazine hydrate.
8. 2,4-Dinitrophenylhydrazine is used in qualitative organic analysis for preparing solid derivatives of carbonyl compounds.[1], [2]
9. By this procedure 2,6-dinitrophenylhydrazine can be prepared from 2,6-dinitrochlorobenzene; picryl chloride gives 2,4,6-trinitrophenylhydrazine.
10. These directions have been used equally successfully with twice, and with five times, the amounts specified.

3. Discussion

2,4-Dinitrophenylhydrazine has been prepared from hydrazine hydrate and 2,4-dinitrochlorobenzene[3], [2] or 2,4-dinitrobromobenzene,[4] and from the same halogen compounds and hydrazine acetate.[1]

References and Notes

1. Allen, J. Am. Chem. Soc. **52**, 2955 (1930).
2. Brady and Elsmie, Analyst **51**, 77 (1926); Brady, J. Chem. Sec. **1931**, 757.
3. Purgotti, Gazz. chim. ital. **24** (I) 555 (1894).
4. Curtius and Dedichen, J. prakt. chem. (2) **50**, 258 (1894).

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

alcohol (64-17-5)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

n-butyl alcohol (71-36-3)

pyridine (110-86-1)

hydrazine hydrate (7803-57-8)

2,4-dinitrochlorobenzene (97-00-7)

dinitrochlorobenzene

2,4-Dinitrophenylhydrazine,
Hydrazine, (2,4-dinitrophenyl)- (119-26-6)

Hydrazine sulfate (10034-93-2)

Tetralin (119-64-2)

dioxane (123-91-1)

potassium acetate (127-08-2)

dinitrophenylhydrazine

2,6-dinitrophenylhydrazine

2,6-dinitrochlorobenzene (606-21-3)

picryl chloride (88-88-0)

2,4,6-trinitrophenylhydrazine (653-49-6)

2,4-dinitrobromobenzene (584-48-5)

hydrazine acetate (7335-65-1)