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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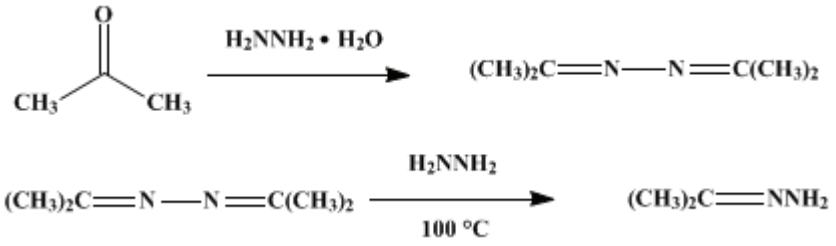
ACETONE HYDRAZONE

[2-Propanone, hydrazone]



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1. Procedure

Caution! Hydrazine is toxic and should be handled in a hood. Anhydrous hydrazine is extremely reactive with oxidizing agents (including air) and should always be prepared and used behind a protective screen.

A. *Acetone azine*. A 500-ml., round-bottomed flask containing 145 g. (183 ml., 2.50 moles) of acetone (Note 1) is fitted with a mechanical stirrer (Note 2) and a dropping funnel and cooled in an ice bath. With vigorous stirring, 65.5 g. (1.31 moles) of 100% hydrazine hydrate (Note 1) is added at such a rate that the temperature is maintained below 35°. The addition takes 20–30 minutes. The mixture is stirred for an additional 10–15 minutes before 50 g. of potassium hydroxide pellets is added with vigorous stirring and continued cooling (Note 3). The upper liquid layer is separated and allowed to stand over 25 g. of potassium hydroxide pellets for 30 minutes, with occasional swirling (Note 4). After filtration, the liquid is further dried with two successive 12.5-g. portions of potassium hydroxide. Distillation gives 120–126 g. (86–90%) of almost colorless acetone azine, b.p. 128–131°, n_D^{22} 1.4538 (Note 5).

B. *Acetone hydrazone*. Anhydrous hydrazine is prepared by heating under reflux 100% hydrazine hydrate with an equal weight of sodium hydroxide pellets for 2 hours, followed by distillation in a slow stream of nitrogen introduced through a capillary leak. *(Caution! Distillation in air can lead to explosion.)* The distillate boils at 114–116° and the yield is 95–97% (Note 6).

A mixture of 112 g. (1.00 mole) of acetone azine and 32 g. (1.0 mole) of anhydrous hydrazine is placed in a 300-ml. round-bottomed flask fitted with a reflux air condenser and drying tube, and kept at 100° for 12–16 hours. *(Caution! This reaction and the subsequent distillation should be carried out behind a protective screen.)* The crude product is then distilled rapidly through a water-cooled condenser, and the colorless fraction boiling at 122–126° is collected, n_D^{22} 1.4607 (Note 7), yielding 111–127 g. (77–88%, (Note 7) and (Note 8)) of essentially pure acetone hydrazone (Note 9).

2. Notes

1. The acetone and hydrazine hydrate were good-quality commercial products purified before use.
2. A Hershberg stirrer made of Nichrome wire is most efficient for aiding dissolution of the potassium hydroxide added after azine formation is complete.
3. The dissolution of the potassium hydroxide is strongly exothermic. A small proportion may remain undissolved.
4. A lower, aqueous phase may form at this stage, but the product is easily decanted from it.
5. The distillation gives a small forerun, b.p. 120–128°, containing hydrazine and acetone hydrazone. There is virtually no distillation residue. The submitters carried out the preparation of both acetone

azine and acetone hydrazone on a fourfold scale with comparable results.
6. The purity is 95–98% by this method.[3] The purity is lower (85–95%) by an alternative procedure[4] which requires separation of the hydrazine and alkaline phases above 60°; with the latter method the submitters found that a frequent problem was the solidification of the lower phase in the separating funnel, and in one case *a very serious fire* occurred during the transfer of the hot (*ca.* 100°) mixture to the separating funnel.
7. The forerun contains hydrazine; material boiling above 126° contains much acetone azine. With a slow rate of distillation, disproportionation occurs and the yield of acetone hydrazone is reduced. If the forerun and material boiling above 126° are combined and reheated at 100° for 12–16 hours, they give more acetone hydrazone on redistillation. With further repetitions of this procedure, the yield is almost quantitative.
8. The highest yields were obtained in cases where the anhydrous hydrazine was treated with barium oxide for several hours before use.
9. The hydrazone should be used as soon as possible. If it is stored, care must be taken to exclude moisture, which catalyzes disproportionation to hydrazine and acetone azine.[5,6,7] Even in the absence of moisture it disproportionates slowly at room temperature and so should be redistilled immediately before use. Old samples can be regenerated fairly satisfactorily by reheating them for 12–16 hours at 100° before redistillation, but there is always some irreversible decomposition to high-boiling products during storage.

3. Discussion

The procedure for acetone azine is essentially that of Curtius and Thun.[5] The method for acetone hydrazone is adapted from that of Staudinger and Gaule.[8] The hydrazone has been prepared directly from acetone and hydrazine, but this is much less satisfactory.[6]

Acetone hydrazone is produced in good yield by the method described, but an inferior product is obtained without the precautions noted. The compound is used for the preparation of 2-diazopropane.[8,9,10]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 161

References and Notes

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

sodium hydroxide pellets (1310-73-2)

barium oxide

nitrogen (7727-37-9)

acetone (67-64-1)

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

hydrazine hydrate (7803-57-8)

hydrazine (302-01-2)

Acetone hydrazone,
2-Propanone, hydrazone (5281-20-9)

Acetone azine (627-70-3)

2-Diazopropane (2684-60-8)