



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.

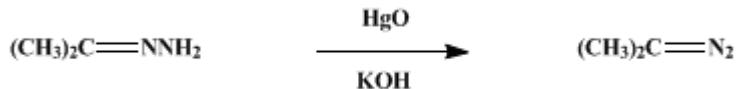
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries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

Organic Syntheses, Coll. Vol. 6, p.392 (1988); Vol. 50, p.27 (1970).

2-DIAZOPROPANE

[Propane, 2-diazo-]



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Checked by G. Swift and W. D. Emmons.

1. Procedure

Caution! 2-Diazopropane is volatile and presumably toxic. All operations should be carried out in an efficient hood behind a protective screen.

A 250-ml., two-necked, round-bottomed flask, placed in a room temperature (*ca.* 20°) water bath, is equipped with a magnetic stirrer, a dropping funnel, and a distillation head carrying a thermometer, and connected *via* an acetone-dry-ice condenser to a receiver cooled to -78° in acetone and dry ice. In the distilling flask are placed 60 g. (0.27 mole) of yellow mercury(II) oxide (Note 1), 100 ml. of diethyl ether (Note 2), and 4.5 ml. of a 3 *M* solution of potassium hydroxide in ethanol (Note 3). The pressure throughout the system is reduced to 250 mm., and with vigorous stirring 15 g. (0.21 mole) of acetone hydrazone (Note 4) is added dropwise through the funnel (Note 5). With continued stirring, the pressure is reduced to 15 mm., and ether and 2-diazopropane co-distill and condense in the receiver (Note 6), yielding 70–90% (Note 7), (Note 8), and (Note 9) of product.

2. Notes

1. Laboratory Reagent yellow mercury(II) oxide purchased from British Drug House was used for most runs. The preparation was not apparently improved by the use of freshly precipitated mercury(II) oxide.
2. The quantity of ether can be varied over a wide range (the submitters have successfully used as little as 60 ml.), and is adjusted to yield the desired concentration of 2-diazopropane in the distillate.
3. A stock solution of potassium hydroxide in ethanol was prepared and stored under nitrogen. Old stocks are brown and contain a dark sediment, but are apparently just as effective as the freshly prepared reagent. Methanolic potassium hydroxide has also been used by the submitters; this remains clear and colorless for long periods but offers no other advantage over the ethanolic solution. In absence of the basic solution, the acetone hydrazone is not oxidized by mercury(II) oxide.
4. *Org. Synth., Coll. Vol. 6*, 161 (1988). Yields are lower if the hydrazone is not freshly redistilled.
5. No special precautions are necessary to keep the reaction mixture cool, since boiling of the ether provides adequate cooling.
6. It is usually unnecessary to dry the distillate, because the water produced in the reaction is largely retained in the distilling flask. That which vaporizes is trapped as ice in the condenser.
7. The solution is *ca.* 2 *M*. Yields were determined by nitrogen evolution on adding acetic acid, or spectrometrically from the visible absorption band at 500 nm, which has $\epsilon \sim 2$ as calculated from the nitrogen evolution. Yields estimated by addition of a standard solution of benzoic acid and titration with alkali were consistently much lower. Both methods underestimate the yield, since decomposition with acid gives tetramethylethylene and some acetone azine in addition to the 2-propyl ester.³ The nitrogen evolution method (and therefore the spectrometric method) probably underestimates the yield by *ca.* 10–20%. the titration method by more than 50%.
8. The entire preparation is very rapid (*ca.* 30 minutes) and is easily adaptable to the preparation of larger amounts of 2-diazopropane. Without difficulty, 2–3 *M* solutions can be obtained (see (Note 2)). The solutions are essentially mercury-free.
9. 2-Diazopropane is an unstable material. The decay is first-order with a half-life of 3 hours at 0°.

3. Discussion

This method⁴ is an adaptation of that given by Staudinger and Gaule.⁵ Highly unstable solutions have been obtained by Applequist and Babad⁵ by use of silver oxide in place of mercury(II) oxide.

Contrary to previous reports,^{5,6,7} 2-diazopropane, as indicated by the present procedure, is neither difficult to prepare nor unduly unstable. The method may be extended to other secondary aliphatic diazo compounds, which have given difficulty in the past.⁸ The success of the method depends on the use of a basic catalyst for the oxidation. The desirability of a basic catalyst has been recognized previously^{9,10} and is well illustrated by the contrast between the two preparations of diphenyldiazomethane^{10,11} (contrast also refs. ⁹ and ¹²). Miller has speculated on the role of the basic catalyst.¹⁰

2-Diazopropane is a potential source of *gem*-dimethyl groups. It undergoes 1,3-dipolar addition to acetylenes,^{13,14} allenes,^{15,16} and olefins,¹⁷ and in all three classes the orientation of addition has been found to be sensitive to steric effects.^{14,16,17} The adducts with acetylenes^{14,18} and allenes^{15,19} give cyclopropenes, and methylenecyclopropanes, respectively, upon photolysis. The adducts with certain acetylenes bearing an α -leaving group, however, are converted photochemically into allenes and conjugated dienes by an ionic mechanism.¹³

References and Notes

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Appendix

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

ethanol (64-17-5)

acetic acid (64-19-7)

ether,
diethyl ether (60-29-7)

silver oxide (20667-12-3)

nitrogen (7727-37-9)

Benzoic acid (65-85-0)

mercury(II) oxide (21908-53-2)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

tetramethylethylene (563-79-1)

Diphenyldiazomethane (883-40-9)

Acetone hydrazone (5281-20-9)

Acetone azine (627-70-3)

2-Diazopropane,
Propane, 2-diazo- (2684-60-8)