



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.

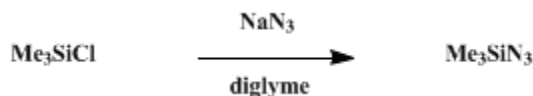
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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TRIMETHYLSILYL AZIDE

[Silane, azidotrimethyl-]



Submitted by L. Birkofer¹ and P. Wegner.

Checked by R. F. Merritt and W. D. Emmons.

1. Procedure

Caution! This reaction should be conducted behind a safety screen in a hood. If the system is not completely dry, the presence of toxic hydrazoic acid is probable.

A 1-l., three-necked flask fitted with a stirrer, reflux condenser equipped with a drying tube, and addition funnel provided with a pressure-equalizer arm is dried in a 100° oven and assembled while warm. The warm apparatus is immediately purged with dry nitrogen, introducing the nitrogen at the top of the addition funnel. The flask is charged with 81 g. (1.2 moles) of sodium azide (Note 1) and 500 ml. of freshly distilled diethylene glycol dimethyl ether (Note 2). A simple distillation apparatus is then dried in the oven and assembled while warm under a slow nitrogen purge. The distillation flask is charged with 112 g. of chlorotrimethylsilane (Note 3), and after a forerun of approximately 2 g. the remaining material is distilled (b.p. 57–58°) directly into the addition funnel of the reaction flask. During this distillation it is convenient to disconnect the nitrogen stream from the top of the addition funnel and introduce it into the distillation flask. After the distillation is complete, the distillation apparatus is disconnected and the nitrogen stream is again introduced at the top of the addition funnel. The chlorotrimethylsilane (108.6 g., 1.000 mole) (Note 4) is then added rapidly to the sodium azide slurry, and this mixture is stirred at 70° for 60 hours. During this period the nitrogen flow is terminated (Note 5).

After the heating period is complete, the nitrogen stream is again initiated, and the mixture is cooled to 30°. The addition funnel and reflux condenser are replaced with two gas-inlet tubes with stopcocks. One inlet tube is connected to the nitrogen source and the other to a standard vacuum trap, of at least 150 ml. capacity. A vacuum (15–20 mm.) is applied to the trap after the latter is cooled to –78°, and the product is then distilled at 30° (15 mm.) into the trap. Slight heating is necessary to maintain 30°, and rapid stirring should be continued throughout. Removal of volatile product is complete within 5 hours under these conditions. The entire system is then slowly pressurized to atmospheric pressure with nitrogen, and the product is redistilled through a 5-cm. Vigreux column. From 121 g. of crude flash distillate are obtained 4.0 g. of forerun and 98 g. (85%) of pure trimethylsilyl azide, b.p. 95–99°. During the distillation the pot temperature is maintained at 135–140° with a thermostated oil bath. The pot residue contains 19 g. of diethylene glycol dimethyl ether with traces of trimethylsilyl azide. The purity of the product cut as established by ¹H NMR (CCl₄) is 98%. A single peak at 13 cps. downfield from tetramethylsilane is observed, the only impurity being siloxane hydrolysis products. Chlorotrimethylsilane is conspicuous by its absence.

2. Notes

1. Sodium azide was obtained from Alpha Inorganics, Inc., Beverly, Massachusetts, and the freshly opened material was used without further purification or drying.
2. Diethylene glycol dimethyl ether from Aldrich Chemical Co. was distilled under a nitrogen atmosphere, and the fraction boiling at 161–162° was used.
3. The chlorotrimethylsilane was obtained from Peninsula Chem-research Corp., Gainesville, Florida.
4. It is undesirable to reweigh the chlorotrimethylsilane in the addition funnel because moisture

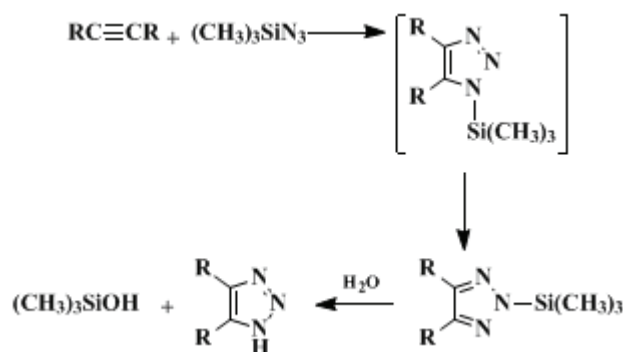
contamination is possible. An excess of sodium azide is used in this preparation, and the exact amount of the silane used is not critical.

5. If the nitrogen flow is maintained during the heating period, the volatile materials will be swept out and the yield will be reduced.

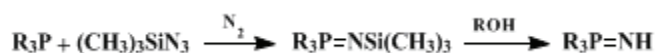
3. Discussion

Trimethylsilyl azide has been prepared by the thermolysis of 1-trimethylsilyl-5-trimethylsilylamino-tetrazole, by reaction of hydrazoic acid with hexamethyl-disilazane, and by reaction of chlorotrimethylsilane with sodium azide.² With a suitable solvent and anhydrous conditions the last procedure is the method of choice and has been extended to other trialkyl and triarylsilyl azides.³

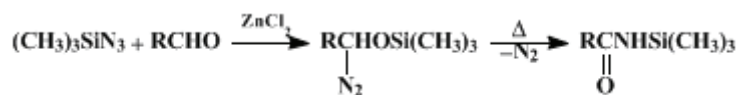
Unlike hydrazoic acid, trimethylsilyl azide is thermally quite stable. Even at 200° it decomposes slowly and without explosive violence. Accordingly, it is a very convenient and safe substitute for hydrazoic acid in many reactions. A notable example is the cycloaddition of hydrazoic acid to acetylenes, a general route to substituted triazoles.⁴ The reaction of trimethylsilyl azide with acetylenes is also a general reaction, from which 2-trimethylsilyl-1,2,3-triazoles may be obtained in good yield.⁵ These adducts are hydrolyzed under mild conditions to the parent alkyl 1,2,3-triazoles.⁵



Another interesting application of trimethylsilyl azide is as a convenient preparation of trialkyl- or triarylophosphinimines, first prepared by Appel and Hauss using chloramine.⁶



This synthesis is quite simple and its success lies in the facile cleavage of the Si-N bond.^{7,8} Trimethylsilyl azide also reacts with aldehydes, giving the stable adducts, 1-trimethylsilyloxyalkyl azides, which on thermolysis yield *N*-trimethylsilyl amides.⁹



This preparation is referenced from:

- Org. Syn. Coll. Vol. 10, 207

References and Notes

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 8. L. Birkofer and S. M. Kim, *Chem. Ber.*, **97**, 2100 (1964).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number);
(Registry Number)

hydrazoic acid

nitrogen (7727-37-9)

sodium azide (26628-22-8)

chloramine (10599-90-3)

diethylene glycol dimethyl ether (111-96-6)

tetramethylsilane (75-76-3)

CHLOROTRIMETHYLSILANE (75-77-4)

siloxane (13597-73-4)

hexamethyl-disilazane (999-97-3)

TRIMETHYLSILYL AZIDE,
Silane, azidotrimethyl- (4648-54-8)

1-trimethylsilyl-5-trimethylsilylaminotetrazole