



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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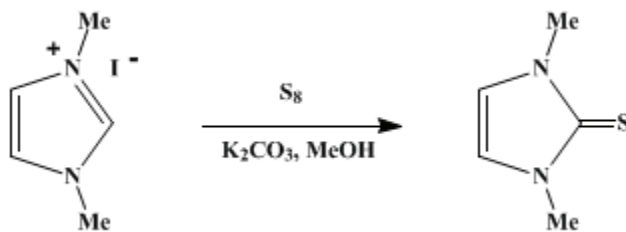
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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1,3-DIMETHYLIMIDAZOLE-2-THIONE

[2*H*-Imidazole-2-thione, 1,3-dihydro-1,3-dimethyl-]



Submitted by Brian L. Benac¹, Edward M. Burgess², and Anthony J. Arduengo, III³.
Checked by David R. Brittelli, Joseph Buriak, Jr., and Bruce E. Smart.

1. Procedure

In a dry, 500-mL, round-bottomed flask, equipped with a magnetic stirrer and a drying tube are placed 44.8 g (0.20 mol) of 1,3-dimethylimidazolium iodide (Note 1), 35.0 g (0.25 mol) of anhydrous potassium carbonate, 6.5 g (0.20 mol) of sulfur (Note 2), and 300 mL of methanol (Note 3). The mixture is stirred for 40 hr at room temperature. The cloudy yellow mixture is filtered through a pad of Celite (Note 4) and the filter cake is washed with 80 mL of dichloromethane. The combined mother liquor and wash is evaporated to dryness on a rotary evaporator. The orange residue is dissolved in 500 mL of hot water and the hot solution is filtered to remove insoluble impurities. The aqueous filtrate is reheated and the product crystallizes on cooling. The white needles are collected by filtration, washed with 50 mL of cold water and air dried for 1 hr. The mother liquor is concentrated to yield a second crop of crystals to give a total of 15–16 g (58–62%) of pure 1,3-dimethylimidazole-2-thione, mp 182–183.5°C (Note 5).

2. Notes

- The imidazolium iodide salt is conveniently prepared by the following procedure. A 500-mL, three-necked, round-bottomed flask equipped with a dropping funnel, thermometer, water-cooled condenser, and magnetic stirrer is charged with 200 mL of anhydrous methylene chloride and 82.1 g (1.0 mol) of 1-methylimidazole (from the Aldrich Chemical Company, Inc.). The solution is cooled and maintained at 5°C while 143.0 g (1.01 mol) of iodomethane in 75 mL of anhydrous methylene chloride is added dropwise over a 30-min period. When the addition is completed, the cooling bath is removed and the reaction mixture is stirred for 30 min at room temperature. Methylene chloride is removed on a rotary evaporator to yield 213.6–216.7 g (95–97%) of 1,3-dimethylimidazolium iodide, mp 81–83°C, ¹H NMR (*d*₆-DMSO) δ: 3.89 (s, 6 H), 7.73 (s, 2 H), 9.16 (s, 1 H). The submitters report the following spectral data: ¹H NMR (*d*₆-DMSO) δ: 4.08 (s, 6 H), 7.75 (s, 2 H), 9.86 (s, 1 H); ¹³C NMR (*d*₆-DMSO) δ: 36.10 (s), 123.04 (s), 136.69 (s). The submitters report that the bromide and methyl sulfate salts of the 1,3-dimethylimidazolium cation gave similar yields in the thione synthesis.
- Lac (precipitated) sulfur gives the best results. The checkers found that with sublimed sulfur (Fisher Scientific Company, laboratory grade) the yield of thione product is 12.5–12.8 g (49–50%). Lac sulfur is prepared by boiling a suspension of 33 g of calcium oxide and 50 g of sublimed sulfur (Fisher Scientific Company) in 200 mL of water for 30 min, then filtering the hot solution and acidifying the clear filtrate to pH 5 with hydrochloric acid. The precipitated sulfur is collected, washed with water, and dried in a vacuum desiccator.
- ACS-grade methanol from the Fisher Scientific Company was used without further purification. The submitters report that attempts to use ethanol or water as solvents were unsuccessful.
- The reaction mixture has a distinct odor of sulfur and should be handled in a hood. The product is odorless.
- The submitters report a melting point of 182–184°C for material that was recrystallized from water or sublimed under reduced pressure. The product shows the following ¹H NMR spectrum (CDCl₃) δ: 3.58 (s, 6 H), 6.71 (s, 2 H). The submitters report the following spectral data: ¹H NMR (CDCl₃) δ: 3.6 (s, 6

H), 6.68 (s, 2 H); ^{13}C NMR (d_6 -DMSO) δ : 34.34 (s), 117.82 (s), 161.87 (s); IR (CHCl_3) cm^{-1} : 2940 (C-H), 1450, and 1380.

3. Discussion

1,3-Dimethylimidazole-2-thione was first reported by Ansell, Forkey, and Moore,⁴ who studied the X-ray crystal structure of this thione. No detailed synthesis of the thione has appeared in the chemical literature. This unusual thione has been used as a precursor to unusual thione ylides,^{5,6} tricoordinate sulfuranes⁷ and as a desulfurizing agent for a thiirane.⁶ The thione also has remarkable antioxidant properties.⁸ Compared to tetramethylthiourea, 1,3-dimethylimidazole-2-thione is remarkably resistant to desulfurization.

This procedure has been used to synthesize a variety of 1,3-dialkylimidazole 2-thiones. Other imidazole-2-chalcogenones (Se, Te) can be synthesized by similar procedures.

References and Notes

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6. Janulis, E. P., Jr.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1983**, *105*, 3563.
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Appendix

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

ethanol (64-17-5)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

methanol (67-56-1)

sulfur (7704-34-9)

calcium oxide

iodomethane (74-88-4)

methylene chloride,
dichloromethane (75-09-2)

thiirane (420-12-2)

1,3-Dimethylimidazole-2-thione,
2H-Imidazole-2-thione, 1,3-dihydro-1,3-dimethyl-,
1, 3-dimethylimidazole-2-thione (6596-81-2)

1,3-dimethylimidazolium iodide (4333-62-4)

1-methylimidazole (616-47-7)

tetramethylthiourea (2782-91-4)