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.

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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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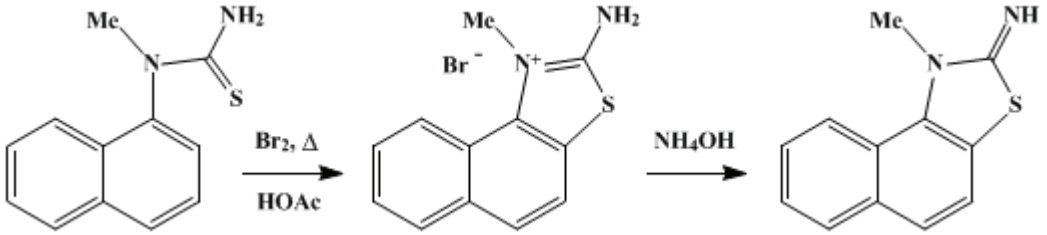
1-METHYL-2-IMINO-β-NAPHTHOTHIAZOLINE

[Naphtho[1,2]thiazole, 1-methyl-1,2-dihydro-2-imino-]



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1. Procedure

In a 1-l. three-necked flask fitted with a thermometer, a dropping funnel, and a mechanical stirrer are placed 65 g. (0.3 mole) of 1-methyl-1-(1-naphthyl)-2-thiourea (p. 609) (Note 1) and 400 ml. of glacial acetic acid (Note 2). To the mechanically stirred suspension, maintained at 18–20° by cooling in a water bath, is added dropwise over a 30-minute period 48 g. (0.3 mole) of bromine in 50 ml. of glacial acetic acid. The light-yellow addition product is stirred an additional 15 minutes at 18–20°. After the thermometer is replaced by an outlet tube (Note 3), the mixture is heated in a water bath maintained at 80–85° (Note 4) for 3 hours. Hydrogen bromide is evolved copiously with the formation of a white, crystalline hydrobromide. When the mixture is cool, it is filtered and the precipitate is washed on the filter with 50 ml. of acetone and then with two 250- to 300-ml. portions of dry ether. One hundred milliliters of concentrated ammonia is then added with stirring to the salt suspended in 700 ml. of warm water (60–65°). The imine base first separates as an oil (Note 5); after the mixture has been stirred and warmed on the steam bath for 10 minutes, it is extracted with 500 ml. of chloroform and filtered by suction through a Norit filter pad 5–6 mm. thick. The bottom layer is separated, washed with 350 ml. of water, and dried by stirring with 40 g. of potassium carbonate. The residual oil, after removal of the solvent on the steam bath under reduced pressure, is poured into an evaporating dish and stirred while cooling. The brownish-colored crystals (Note 6) are dried at 80–85°; they melt at 97–99° and weigh 58–62 g. (90–97%). If desired, the naphthothiazoline (Note 7) can be crystallized from petroleum ether (60–90°) using 75 ml. per gram of product. The recovery of the almost colorless (cream) crystals is 85%. The recrystallized thiazoline melts at 97–99°.

2. Notes

1. The thiazoline was obtained in the best yields and with the lightest color from freshly prepared 1-methyl-1-(1-naphthyl)-2-thiourea. The air-dried thiourea loses hydrogen sulfide and ammonia after several days' storage.
2. The use of glacial acetic acid for cyclization is essential; in chloroform, the bromo-addition product does not lose hydrogen bromide.
3. A gas-absorption trap can be used to absorb the hydrogen bromide evolved.
4. The temperature of the water bath is easily maintained at 80–85° by heating it on a steam bath.
5. The oil solidifies on cooling. The crystalline product can be separated by filtration and recrystallized from 50% aqueous ethanol or petroleum ether (60–90°).
6. This product is satisfactory for synthetic purposes.
7. This type of reaction can be used successfully for the preparation of other naphthothiazolines and naphthoselenazolines. The submitter has prepared 2-imino-1-methylnaphtho [1,2] selenazoline, m.p. 94–95°, and 2-imino-1-ethylnaphtho [1,2] selenazoline, m.p. 82–84°, by similar methods.

3. Discussion

The preparation of this compound is not described in the literature.

References and Notes

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

petroleum ether

1-Methyl-2-imino-β-naphthothiazoline

Naphtho[1,2]thiazole, 1-methyl-1,2-dihydro-2-imino-

naphthothiazoline

naphthothiazolines

naphthoselenazolines

2-imino-1-methylnaphtho [1,2] selenazoline

2-imino-1-ethylnaphtho [1,2] selenazoline

ethanol (64-17-5)

potassium carbonate (584-08-7)

acetic acid (64-19-7)

ammonia (7664-41-7)

ether (60-29-7)

chloroform (67-66-3)

hydrogen sulfide (7783-06-4)

hydrogen bromide, hydrobromide (10035-10-6)

bromine (7726-95-6)

acetone (67-64-1)

thiourea (62-56-6)

1-methyl-1-(1-naphthyl)-2-thiourea (53663-34-6)

thiazoline