



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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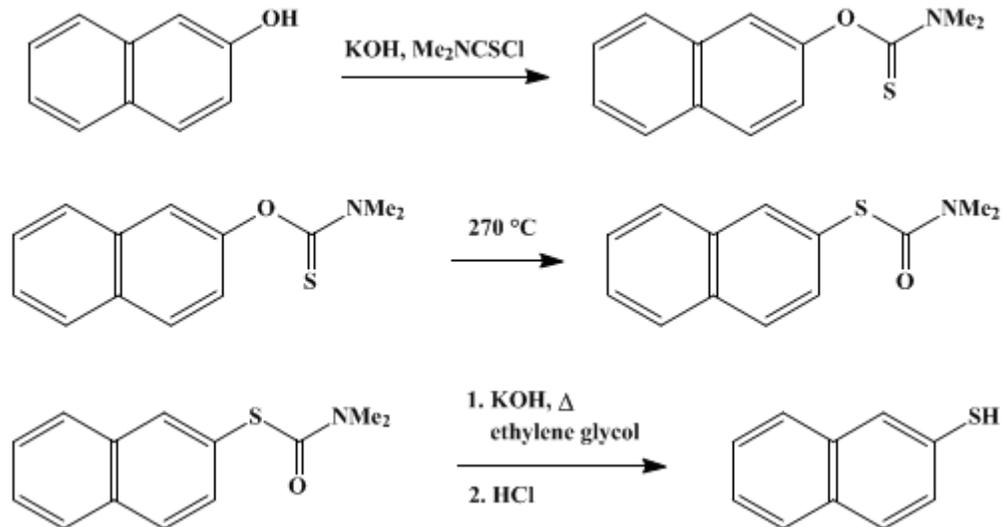
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 6, p.824 (1988); Vol. 51, p.139 (1971).

THIOPHENOLS FROM PHENOLS: 2-NAPHTHALENETHIOL



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1. Procedure

Caution! Benzene has been identified as a carcinogen; OSHA has issued emergency standards on its use. All procedures involving benzene should be carried out in a well-ventilated hood, and glove protection is required.

A. *O*-2-Naphthyl dimethylthiocarbamate. A solution of 21.6 g. (0.150 mole) of 2-naphthol (Note 1) in 100 ml. of water containing 8.4 g. (0.15 mole) of potassium hydroxide is cooled below 10° in a 500-ml., three-necked flask equipped with a stirrer, a thermometer, and a 125-ml. addition funnel. A solution of 24.8 g. (0.201 mole) of *N,N*-dimethylthiocarbamyl chloride (Note 2) in 40 ml. of dry tetrahydrofuran (Note 3) is added over 20–30 minutes to the stirred solution at such a rate that the temperature never exceeds 12° . After the addition is complete, the cooling bath is removed and stirring is continued for 10 minutes. The reaction mixture is made alkaline with 50 ml. of 10% potassium hydroxide and shaken three times with 100-ml. portions of benzene. The organic layers are combined, washed with saturated sodium chloride, and dried by filtration through anhydrous magnesium sulfate. The solvent is removed by distillation, giving the crude product. Crystallization from 75 ml. of absolute methanol yields 23.5–25.2 g. (68–73%) of *O*-2-naphthyl dimethylthiocarbamate, as colorless crystals, m.p. $90\text{--}90.5^\circ$.

B. 2-Naphthalenethiol. A 250-ml. flask, fitted with a diffusion tube³ and swept with nitrogen, is charged with 23.1 g. (0.100 mole) of *O*-2-naphthyl dimethylthiocarbamate (Note 4). The flask is heated at $270\text{--}275^\circ$ for 45 minutes in a salt bath (Note 5). After cooling, a solution of 8.4 g. (0.15 mole) of potassium hydroxide in 10 ml. of water and 75 ml. of ethylene glycol is added to the flask. The diffusion tube is replaced with a condenser, and the mixture is heated at reflux for 1 hour (Note 6). The cooled reaction mixture is poured onto 150 g. of ice. After the ice has melted, the mixture is shaken two times with 150-ml. portions of chloroform. The chloroform layers are discarded, and the aqueous layer is cautiously acidified with concentrated hydrochloric acid (Note 7) and shaken three times with 75-ml. portions of chloroform. The organic layers are combined and dried by filtration through anhydrous magnesium sulfate. The solvent is removed by distillation, yielding 13–15 g. of crude product. Distillation yields 10.3–12.8 g. (71–80%) of pure 2-naphthalenethiol, b.p. $92\text{--}94^\circ$ (0.4 mm.), m.p. $80\text{--}81^\circ$ (Note 8).

2. Notes

1. Practical 2-naphthol, obtained from Matheson, Coleman and Bell, was recrystallized twice from benzene, m.p. 123–124°.
2. *N,N*-Dimethylthiocarbamyl chloride can be prepared as described in *Org. Synth.*, **Coll. Vol. 4**, 310 (1963), or by rapidly adding 740 g. (10.5 moles) of chlorine dissolved in 3 l. of carbon tetrachloride to a stirred, refluxing suspension of 2400 g. (9.982 moles) of tetramethylthiram disulfide (Note 9) in 5 l. of carbon tetrachloride. After the addition is complete, approximately one-half of the solvent is removed by distillation. The reaction mixture is cooled, filtered, removing the precipitated sulfur, and further concentrated. The residue is distilled, yielding 1980 g. (80%) of *N,N*-dimethylthiocarbamyl chloride, b.p. 65–68° (0.2 mm.).
3. See *Org. Synth.*, **Coll. Vol. 5**, 976 (1973) for a warning note regarding the purification of tetrahydrofuran.
4. Crude *O*-2-naphthyl dimethylthiocarbamate should not be used in this step as the yield is markedly decreased.
5. The salt bath is described in *Org. Synth.*, **Coll. Vol. 4**, 498 (1963).
6. The hydrolysis should be performed in a hood because of the vigorous evolution of dimethylamine.
7. The dilute acid solution should be added slowly since foaming results from the evolution of carbon dioxide.
8. Purification can be accomplished by recrystallization from methanol, but the overall yield of pure material is 65–70%.
9. Tetramethylthiram disulfide was obtained from the Pennwalt Corporation.

3. Discussion

The procedure described is a good, general method⁴ for obtaining a thiophenol from the respective phenol. It employs three steps: conversion of a phenol to the *O*-aryl dialkylthiocarbamate by treatment with *N,N*-dialkylthiocarbonyl chloride; pyrolysis of the *O*-aryl dialkylthiocarbamate to the *S*-aryl dialkylthiocarbamate; and hydrolysis of the latter to the aryl mercaptan.

Previous preparations of 2-naphthalenethiol have included reduction of 2 naphthylsulfonyl chloride with zinc and acid^{5,6} or phosphorus and iodine.^{7,8} Alternatively, 2-naphthyldiazonium chloride has been converted to the thiol using potassium ethyl xanthate and sodium carbonate.⁹

References and Notes

1. Department of Chemistry, Ohio State University, Columbus, Ohio 43210.
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Appendix

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

tetramethylthiram disulfide
hydrochloric acid (7647-01-0)
Benzene (71-43-2)
methanol (67-56-1)
chloroform (67-66-3)
sodium chloride (7647-14-5)
sodium carbonate (497-19-8)
PHOSPHORUS (7723-14-0)
carbon tetrachloride (56-23-5)
nitrogen (7727-37-9)
2-naphthol (135-19-3)
sulfur (7704-34-9)
carbon dioxide (124-38-9)
iodine (7553-56-2)
chlorine (7782-50-5)
potassium hydroxide (1310-58-3)
zinc (7440-66-6)
ethylene glycol (107-21-1)
dimethylamine (124-40-3)
potassium ethyl xanthate (140-89-6)
magnesium sulfate (7487-88-9)
2-naphthyldiazonium chloride
Tetrahydrofuran (109-99-9)
N,N-dimethylthiocarbamyl chloride (16420-13-6)
2-Naphthalenethiol (91-60-1)
O-2-naphthyl dimethylthiocarbamate (2951-24-8)

2 naphthylsulfonyl chloride (93-11-8)

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