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for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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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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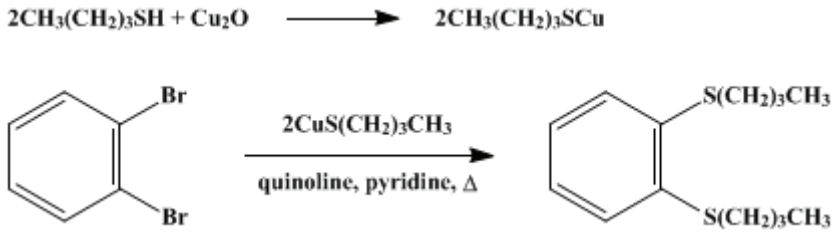
1,2-BIS(*n*-BUTYLTHIO)BENZENE

[Benzene, *o*-bis(butylthio)-]



Submitted by Roger Adams[1], Walter Reifschneider[2], and Aldo Ferretti[3].
Checked by William E. Parham, Wayland E. Noland, and James R. Throckmorton.

1. Procedure

A. *Cuprous n-butylmercaptide*. A mixture of 42.9 g. (0.30 mole) of freshly prepared cuprous oxide (Note 1), 61.3 g. (0.68 mole)of 1-butanethiol, and 750 ml. of 95% ethanol is heated under reflux with mechanical stirring (Note 2) until the orange or red color of the cuprous oxide is completely changed to the white color of the cuprous *n*-butylmercaptide (Note 3). The product is collected by filtration, washed several times with 95% ethanol, and dried in a vacuum. The yield is 91.6 g., essentially quantitative (Note 4).

B. *1,2-Bis(n-butylthio)benzene*. In a 1-l., round-bottomed, three-necked flask fitted with a reflux condenser, a mechanical stirrer, and a thermometer which reaches into the reaction mixture is placed a solution of 59.0 g. (0.25 mole) of *o*-dibromobenzene in a mixture of 250 ml. of quinoline and 80 ml. of pyridine. To this solution is added 84.0 g. (0.55 mole) of cuprous *n*-butylmercaptide, and the mixture is stirred and heated under reflux (Note 5) for 3.5 hours (Note 6). Heating is stopped and the reaction mixture is allowed to cool to about 100°. It is then poured into a stirred mixture of 1500 g. of ice and 400 ml. of concentrated hydrochloric acid; occasional stirring is continued for about 2 hours. The aqueous part is then decanted from the dark brown, gummy residue and is extracted twice with 400 ml. portions of ether. The ether extract is added to the residue, and the resulting mixture is stirred for about 5 minutes. The ether solution is then decanted from the residue and is filtered. The residue is extracted twice more with 400-ml. portions of ether (Note 7). The combined ether extract is washed twice with 100-ml. portions of 10% hydrochloric acid, once with water, and twice with 100-ml. portions of concentrated ammonia (Note 8). After a final wash with water, the ether solution is dried over anhydrous potassium carbonate. The potassium carbonate is collected on a filter, and the ether is removed from the filtrate by distillation. The remaining brown oil is distilled in vacuum, giving a pale orange oil, b.p. 123–124°/0.3 mm., n_D^{25} 1.5684. The yield is 46.5–56.0 g. (73–87%) (Note 9).

2. Notes

1. Cuprous oxide was prepared according to the procedure of King.[4] A good grade of commercial cuprous oxide may also be used, but the time required to complete the conversion into mercaptide may be considerably longer (see (Note 3)).
2. It is not necessary to carry out the reaction under nitrogen, but it is advisable to close the condenser with a cotton plug or with a capillary tube to limit the entrance of air.
3. When freshly prepared cuprous oxide is used, a period of about 12 hours is generally sufficient. For commercial grade cuprous oxide the time required varies between 8 and 150 hours, depending on the reactivity of the cuprous oxide.
4. The checkers obtained a yield of 97%. The submitters and checkers have found that both larger and smaller runs can be carried out without difficulty or reduction in yield.
5. The pot temperature should rise during the reaction from about 150° at the beginning of reflux to about 170° at the end of the reaction time. Pot temperatures lower than 150° and higher than 180° result

in lower yields.
6. Approximately 10 minutes after the mixture starts to boil a homogeneous solution is obtained.
7. If the last ether extract is not almost colorless, one more extraction of the residue with ether should be carried out.
8. If the ammonia layer is dark blue at the second extraction, extraction with ammonia should be continued until only a pale blue extract results.
9. The present procedure has also been used by the submitters to prepare the following thioethers: 1,4-bis-(*n*-butylthio)benzene, pale yellow oil, b.p. 142°/0.5 mm., n_D^{20} 1.5726, from *p*-dibromobenzene and cuprous *n*-butylmercaptide (yield 68–74%); 1,2-bis(phenylthio)benzene, white crystals, m.p. 42.5–44.5°, b.p. 190°/1 mm., from *o*-dibromobenzene and cuprous phenylmercaptide (see below) (yield 79–83%), or from *o*-dichlorobenzene (see below) and cuprous phenylmercaptide (yield 58–71%); 1,4-bis (phenylthio)benzene, white crystals, m.p. 82–83°, from *p*-dibromobenzene and cuprous phenylmercaptide (yield 80–84%), or from *p*-dichlorobenzene (see below) and cuprous phenylmercaptide (yield 59–72%).[5] The same method can be applied to the preparation of many other thioethers.
Cuprous phenylmercaptide is prepared from cuprous oxide and benzenethiol according to the procedure given for cuprous *n*-butylmercaptide. A heating period of only 2 hours (when freshly prepared cuprous oxide is used), however, is required to obtain the yellow compound. Chloro compounds can be used instead of bromo compounds for the reaction with cuprous phenylmercaptide. However, a higher reaction temperature (210–220°) and a longer reaction time (24 hours) is required. The necessary pot temperature is obtained by using a mixture of 350 ml. of quinoline and 8 ml. of pyridine as solvents. It is also advantageous to use a larger excess of cuprous phenylmercaptide (121 g., 0.69 mole).
Aromatic chloro compounds cannot be used for reactions with aliphatic cuprous mercaptides.

3. Discussion

1,2-Bis(*n*-butylthio)benzene and 1,4-bis(*n*-butylthio)benzene have been prepared from the corresponding dibromobenzene and cuprous *n*-butylmercaptide, using a mixture of quinoline and pyridine as solvent.[6,5] 1,2-Bis(phenylthio)benzene and 1,4-bis(phenylthio)benzene have been prepared from the corresponding dichloro- or dibromobenzenes and cuprous phenylmercaptide, using a mixture of quinoline and pyridine as solvent.[6] 1,4-Bis(phenylthio)benzene has also been prepared from *p*-dibromobenzene or *p*-bromophenyl phenyl sulfide and lead phenylmercaptide[7] and from diazotized 4-aminophenyl phenyl sulfide and sodium phenylmercaptide.[8]

4. Merits of Preparation

As indicated (Note 9), the present procedure can be adapted for the preparation of a wide range of aryl and vinyl sulfides.[5] This, in combination with the cleavage reaction described for the preparation of 1,2-dimercaptobenzene (p. 419), provides a convenient and general method for the preparation of aryl mercaptans.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 419

References and Notes

1. University of Illionis, Urbana, Illinois.
2. Agricultural Chemical Research, The Dow Chemical Co., Midland, Michigan.
3. Via Martiri Triestini, 12, Milan, Italy.
4. A. King, "Inorganic Preparations," D. Van Nostrand Co., Inc., Princeton, New Jersey, 1936, p. 39.
5. R. Adams and A. Ferretti, *J. Am. Chem. Soc.*, **81**, 4927 (1959).
6. R. Adams, W. Reifschneider, and M. D. Nair, *Croat. Chem. Acta*, **29**, 277 (1957).
7. E. Bourgeois and A. Fouassin, *Bull. Soc. Chim. France*, [4] **9**, 938 (1911); *Rec. Trav. Chim.*, **30**,

431 (1911).
8. G. Leandri and M. Pallotti, *Ann. Chim. (Rome)*, **46**, 1069 (1956).

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

ethanol (64-17-5)

potassium carbonate (584-08-7)

hydrochloric acid (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

nitrogen (7727-37-9)

pyridine (110-86-1)

cuprous oxide

Quinoline (91-22-5)

Benzenethiol (108-98-5)

1-butanethiol (109-79-5)

1,2-bis(phenylthio)benzene

phenylmercaptide (139-66-2)

1,4-bis(phenylthio)benzene

dibromobenzene,
o-dibromobenzene (583-53-9)

4-aminophenyl phenyl sulfide (1135-14-4)

1,2-Dimercaptobenzene (17534-15-5)

cuprous phenylmercaptide (34012-88-9)

o-dichlorobenzene (95-50-1)

p-dibromobenzene (106-37-6)

p-dichlorobenzene (106-46-7)

1,2-BIS(n-BUTYLTHIO)BENZENE,
Benzene, o-bis(butylthio)- (53663-38-0)

cuprous n-butylmercaptide

1,4-bis-(n-butylthio)benzene,
1,4-bis(n-butylthio)benzene

p-bromophenyl phenyl sulfide

lead phenylmercaptide

sodium phenylmercaptide

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