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.

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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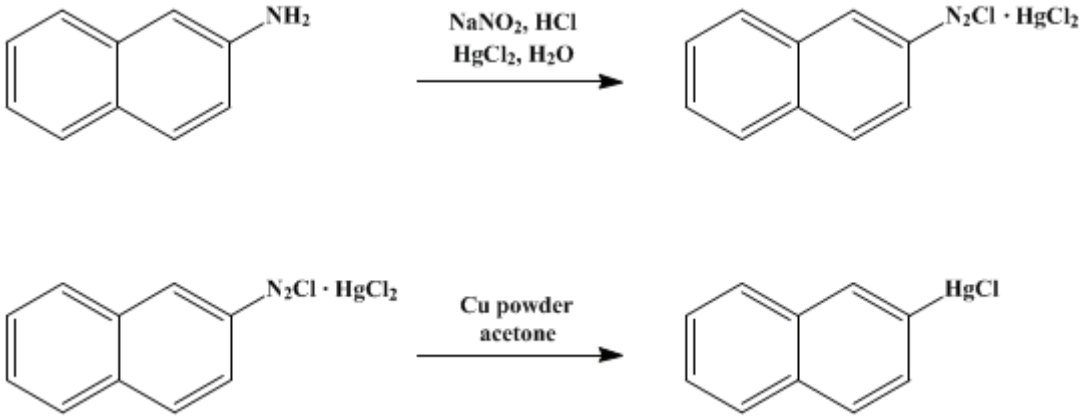
β-NAPHTHYLMERCURIC CHLORIDE

[[Naphthalene, 2-(chloromercuri)-]]



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1. Procedure

To 450 cc. of concentrated hydrochloric acid (sp. gr. 1.19) and 500 cc. of water, in a 4-l. (1-gal.) earthenware crock equipped with an efficient stirrer, is added 143 g. (1 mole) of β-naphthylamine. The suspension of the amine hydrochloride is cooled by the addition of 500 g. of cracked ice. When the temperature reaches 5°, solid sodium nitrite (about 69 g.) is added until starch-iodide paper shows an excess. During the diazotization about 600 g. of cracked ice is introduced at such a rate as to keep the temperature at 5°. The cold solution of the diazonium salt is filtered to remove a small amount of precipitate and returned to the crock. A solution of 271 g. (1 mole) of mercuric chloride in 300 cc. of concentrated hydrochloric acid is mixed with 300 g. of ice and added slowly to the rapidly stirred solution. A heavy precipitate of the yellow addition compound of β-naphthalenediazonium chloride and mercuric chloride separates. Stirring is continued for a half hour, after which the precipitate is collected on a 20-cm. Büchner funnel, sucked as dry as possible, and washed with two 400-cc. portions of water and two 150-cc. portions of acetone (Note 1). The solid is air-dried at about 20° (Note 2) to constant weight. The yield is 380–390 g. (82–84 per cent of the theoretical amount) (Note 3).

In a 2-l. round-bottomed Pyrex flask equipped with a stirrer are placed 139 g. (0.3 mole) of the addition compound, 700 cc. of acetone (Note 4), and 38 g. (0.6 gram atom) of copper powder (Note 5). The mixture is cooled at once to about 20°, stirred for one hour, and then allowed to stand overnight. The insoluble material is collected on a Büchner funnel (Note 6). The solid mixture is extracted with about 3 l. of boiling commercial xylene and filtered through a hot funnel. On cooling the filtrate, crystals of β-naphthylmercuric chloride separate (Note 7). The yield of product which melts at 266–267° is 52–64 g. (40–49 per cent of the theoretical amount based on the amine used) (Note 8) and (Note 9).

2. Notes

1. The washing with large amounts of solvents is necessary to remove small amounts of highly colored impurities. The product is practically insoluble in the cold wash liquids.
2. The double salt *explodes violently* if heated. For preparation of the organic mercury compounds the double salt need not be completely dry.
3. It is unsafe to store the addition complexes of mercuric chloride and diazonium chlorides in a closed vessel. The complex salt should be used as soon as possible and, if it is to be kept for any length of time, should be placed in a large open dish or a loosely covered container.

In one of a number of preparations, a batch of about 960 g. of the addition compound from benzenediazonium chloride was air-dried and placed in a large bottle with a screw cap. About four hours later the entire complex decomposed with considerable violence. At the time no heat or strong light was near the bottle. (Henry Gilman, private communication.)
4. The acetone employed boiled at 55–57°. The use of methyl or ethyl alcohol decreases the yield slightly.
5. The copper powder is prepared from zinc dust and an excess of copper sulfate solution maintained below 70°.
6. The acetone filtrate contains only a trace of the product.
7. The mother liquor from these crystals may be used again to extract the original crude residue, since the product is practically insoluble in cold xylene.
8. If hydrobromic acid and mercuric bromide are used, the product is β-naphthylmercuric bromide.
9. In a similar way, aniline, the three toluidinmnmes, and the aminophenols can be converted into the corresponding chloromercuric compounds in about 40 per cent yields.

3. Discussion

β-Naphthylmercuric chloride has been prepared by the action of mercuric chloride in amyl alcohol on mercury di-β-naphthyl;[1] from β-naphthalenesulfinic acid and mercuric chloride;[2] from β-naphthylboric acid and mercuric chloride;[3] and by the procedure described above.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 381

References and Notes

1. Michaelis, Ber. **27**, 251 (1894).
2. Whitmore and Howe, "Organic Compounds of Mercury," by Frank C. Whitmore, The Chemical Catalog Company, New York, 1921, p. 203.
3. König and Scharrnbeck, J. prakt. Chem. (2) **128**, 168 (1930).

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

mercury compounds

aminophenols

Mercury di-β-naphthyl

β-Naphthylmercuric chloride

methyl or ethyl alcohol

β-naphthylmercuric bromide

toluidinmnmes

β-naphthylboric acid

hydrochloric acid (7647-01-0)

aniline (62-53-3)

HYDROBROMIC ACID (10035-10-6)

copper sulfate (7758-98-7)

benzenediazonium chloride

sodium nitrite (7632-00-0)

copper powder (7440-50-8)

acetone (67-64-1)

zinc (7440-66-6)

mercuric chloride (7487-94-7)

xylene (106-42-3)

amyl alcohol (71-41-0)

β-naphthalenediazonium chloride

Naphthalene, 2-(chloromercuri)- (39966-41-1)

mercuric bromide (7789-47-1)

β-naphthalenesulfinic acid

β-naphthylamine (91-59-8)