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for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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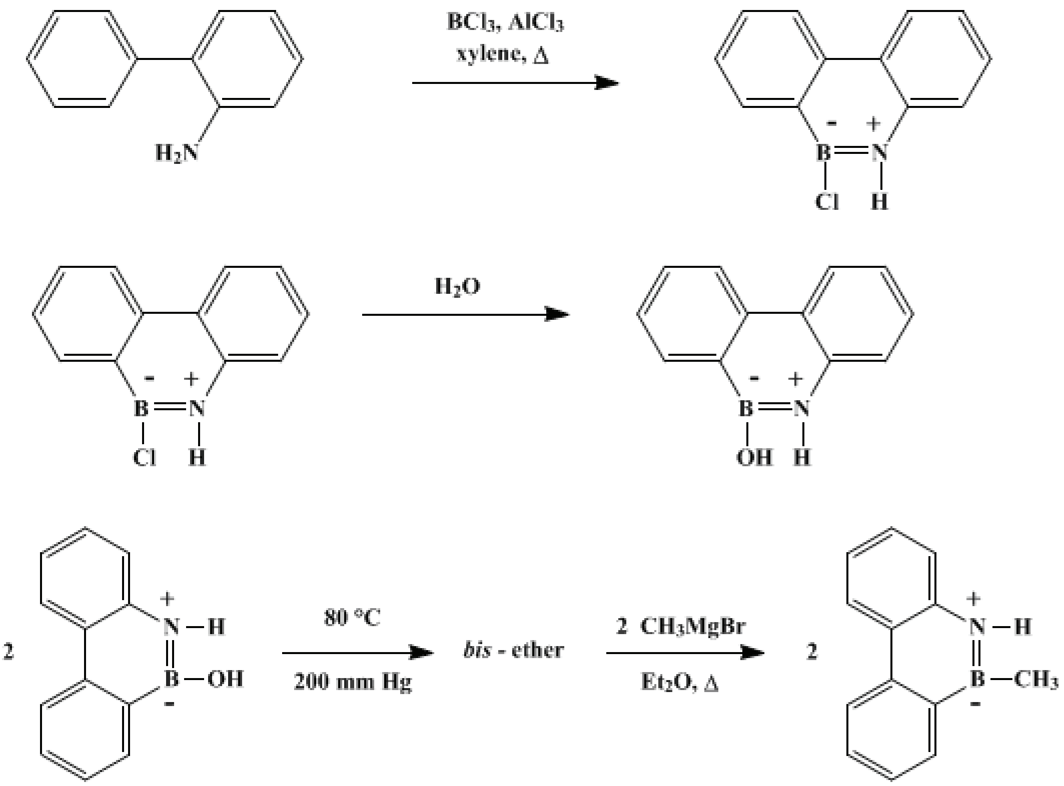
10-METHYL-10,9-BORAZAROPHENANTHRENE

[Dibenz[c,e][1,2]azaborine, 5,6-dihydro-6-methyl-]



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Checked by Jack A. Snyder and B. C. McKusick.

1. Procedure

A. *Bis(10,9-borazarophenanthryl) ether*. *Caution! All the operations involving boron trichloride should be carried out in a good hood.*

A solution of 250 g. (1.48 moles) of 2-aminobiphenyl (Note 1) in 2.0 l. of dry xylene (Note 2) is placed in a 5-l. four-necked flask equipped with a 500-ml. pressure-equalized dropping funnel, a reflux condenser fitted with a drying tube loosely packed with calcium chloride, a thermometer, and a mechanical stirrer. A solution of 250 g. (174 ml., 2.14 moles) of boron trichloride in 250 ml. of very cold xylene is placed in the dropping funnel (Note 3).

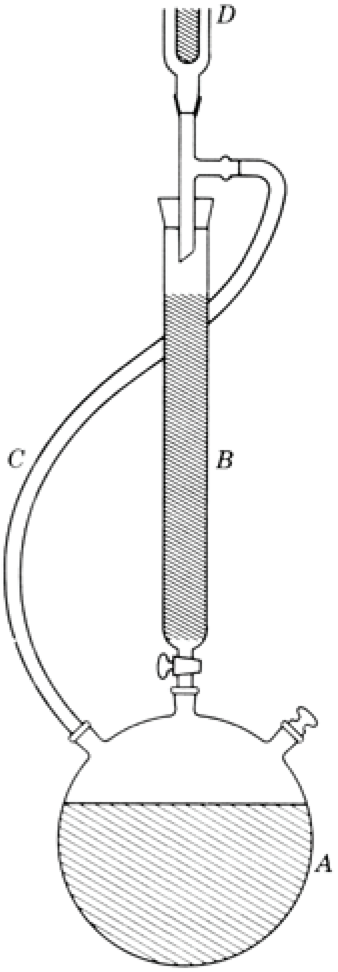
The boron trichloride solution is added dropwise to the stirred amine solution over a period of 30 minutes; a thick precipitate forms as the first third of the solution is added, but it gradually dissolves, and the reaction mixture is a clear, dark amber solution at the end of the addition. The mixture is heated under reflux for 1 hour; the temperature of the mixture gradually rises from 110° to 140° as hydrogen chloride and boron chloride are evolved (Note 4). The mixture is cooled to about 100°, the dropping funnel is replaced by a powder funnel, and 15 g. of anhydrous aluminum chloride is cautiously added. The funnel is replaced by a well-greased stopper (Note 5), and the mixture is heated under reflux for 2 hours. The mixture is cooled slightly, and an additional 5 g. of aluminum chloride is added. The reaction mixture is heated under reflux at least 16 hours, and then the reflux condenser is replaced by a Claisen head leading to a water condenser and receiver. About 80% of the solvent (1.6–1.7 l.) is distilled with vigorous stirring.

A dropping funnel with a pressure-equalizing arm is inserted in place of the stopper, and 2.5 l. of distilled water is added from it with vigorous stirring. The reaction with water is extremely exothermic at first, and the first 30 ml. of water is added not faster than 1 drop per second. The mixture is steam-distilled with heating and vigorous stirring until the head temperature reaches 100°. A fresh receiver is attached, and the distillation is continued until the distillate no longer smells of xylene; this is usually after about 300 ml. of distillate has been collected in the receiving vessel (Note 6). If necessary, water is added from time to time to maintain the liquid level in the flask. The flask is cooled to room temperature with vigorous stirring (Note 7), and crystalline 10-hydroxy-10,9-borazarophenanthrene separates. The solid is collected by suction filtration, washed with about 750 ml. of water, and dried overnight at 75–80° in an oven under reduced pressure (200 mm. or below). Dehydration to bis(10,9-borazarophenanthryl) ether usually takes place during the drying. The ether, a tan solid, weighs 221–250 g. (80–91%) (Note 8).

B. *10-Methyl-10,9-borazarophenanthrene*. The tan bis(10,9-borazarophenanthryl) ether from the previous step is transferred to a dry, 5-l., four-necked flask equipped with a mechanical stirrer, a nitrogen inlet, a 1-l. pressure-equalized dropping funnel, a thermometer, and a very efficient reflux condenser with a drying tube packed with silica gel at the top (Note 9). A 3.2-l. portion of anhydrous ether is placed in the flask, and the mechanical stirrer is started. The flask is cooled in an ice bath, and 700 ml. (2.1 moles) of 3*M* methylmagnesium bromide solution in ether (Note 10) is added dropwise through the funnel during 1 hour. The reaction mixture is heated under reflux overnight. The mixture is cautiously and slowly poured into 1 l. of ice water and then cautiously acidified with 385 ml. (10% excess) of 6*N* hydrochloric acid. The ether layer is separated, and the water layer is extracted with five 400-ml. portions of ether. The combined ether fractions are washed with 200 ml. of saturated sodium bicarbonate solution; the sodium bicarbonate solution is washed with 300 ml. of ether, which is added to the other ether fractions.

The combined ether fractions are dried over 50 g. of magnesium sulfate, the ether is removed at reduced pressure, and the residue is dried overnight at 60° (10 mm.). The resulting slightly oily, crystalline, brown solid is a mixture of 10-methyl-10,9-borazarophenanthrene, bis(10,9-borazarophenanthryl) ether, and tars; weight about 220 g.; m.p. 92–98°. The methyl derivative is isolated by continuous chromatography over about 500 g. of Merck basic alumina (chromatography grade) in the apparatus shown in Fig. 1 (Note 11). The crude product is placed on top of the alumina, 4 l. of petroleum ether (b.p. 30–60°) is poured into the flask, and the extractor is operated for 30–35 hours. 10-Methyl-10,9-borazarophenanthrene gradually crystallizes as fine needles on the walls of the flask.

Fig. 1. *A*, 5-l. three-necked flask with electric heating mantle; *B*, alumina column 45 cm. × 3.8 cm. (Merck basic alumina); *C*, polyethylene tubing; *D*, condenser (see (Note 11)).



The flask is cooled to room temperature, all solvents are allowed to drain from the column, and 120–150 g. of colorless product, m.p. 99–101°, is separated by filtration and washed with petroleum ether. A second crop, weight 25–40 g.,m.p. 98.5–101.0°, is obtained by concentrating the combined filtrates to about 250 ml. and cooling the concentrate to room temperature. The crops of 10-methyl-10,9-borazarophenanthrene are combined; weight 155–182 g. (54–65% based on 2-aminobiphenyl). The product is sufficiently pure for many purposes. A purer product, m.p. 103–104°,[2] may be obtained by recrystallization from petroleum ether (b.p. 35°) (Note 12).

2. Notes

1. A technical grade of 2-aminobiphenyl obtainable from Columbia Organic Chemicals Co. is satisfactory. This black material contains the carcinogenic 4-isomer; it should therefore be handled carefully to avoid contact with the skin. Purification of the amine by vacuum distillation removes the black impurities but does not improve either the yield or the quality of the final product.
2. The xylene is dried over sodium wire or sodium-lead alloy before use.
3. Boron trichloride boils at 13°. To prepare the solution, the submitters poured liquid boron trichloride into a tared beaker containing dry xylene until the weight increased by 250 g. The beaker was in a methanol-ice bath.
The checkers placed 250 ml. of dry xylene in a 500-ml. round-bottomed flask marked with a line corresponding to a volume of 424 ml. and with a gas inlet above the line. A cold finger containing a mixture of dry ice and methanol was attached to the flask, which was immersed in the same mixture. Gaseous boron trichloride (Matheson Co.) was passed in until the flask was filled to the 424-ml. line, and the cold solution was transferred to the dropping funnel.
4. During the most vigorous evolution of gas it is advisable to replace the drying tube by a tube leading

to the back of the hood or to a gas absorption trap.

5. Unless the stopper is well greased, the aluminum chloride will cement it to the flask.

6. The purpose of the steam distillation is to remove all the xylene. If the crystals are collected prematurely, the last traces of xylene are hard to remove.

7. If the mixture is not vigorously stirred while cooling, an intractable cake forms at the bottom of the flask.

8. The product may be bis(10,9-borazarophenanthryl) ether, 10-hydroxy-10,9-borazarophenanthrene, or a mixture. The melting point of either product varies widely with the method of determination. The checkers placed analytical samples in a bath at 125° with the temperature rising 9–12° per minute and observed m.p. 154–159° for the ether, m.p. 133° (with frothing) for the hydroxy compound. The infrared spectrum of the hydroxy compound has a band at 2.83 μ that is lacking in the spectrum of the ether. According to the submitters, either the ether or the hydroxy compound can be used in step B. The checkers used only the ether.

The tan product is almost pure. Extraction with petroleum ether (b.p. 60–70°) in a Soxhlet gives white crystals.

9. A West condenser and a Friedrich condenser in tandem are recommended.

10. The methylmagnesium bromide solution is obtainable from Arapahoe Chemicals, Inc., Boulder, Colorado.

11. This procedure may prove useful in other cases where impurities are strongly adsorbed on alumina; it avoids the use of enormous volumes of solvent. The heating mantle is controlled by a Variac, set so that the liquid level remains constant. The plastic tubing should not be of Tygon®, since this is attacked by the solvent; polyethylene tubing is suitable. An efficient condenser is essential; the use of a West condenser and a Friedrich condenser in tandem is recommended. A similar but more complicated apparatus is described by Meier and Fletschinger.[3]

12. Some unreacted bis(10,9-borazarophenanthryl) ether can be recovered from the column by extraction with methanol.

3. Discussion

10-Chloro-10,9-borazarophenanthrene has been obtained only by Friedel-Crafts cyclization of the adduct from 2-aminobiphenyl and boron trichloride;[2] the procedure described here is an improvement on the original process,[2] in which no solvent was used.

10-Methyl-10,9-borazarophenanthrene has been obtained by the action of methylmagnesium halides on 10-chloro-10,9-borazarophenanthrene[2] or bis(10,9-borazarophenanthryl) ether.[4] The former preparation was satisfactory when pure 2-aminobiphenyl was available, but existing grades lead to products containing intractable impurities, presumably derived from the 4-isomer. These impurities are eliminated during the hydrolysis to 10-hydroxy-10,9-borazarophenanthrene.

4. Merits of the Preparation

10,9-Borazarophenanthrene was the first representative of a new class of heteroaromatic compounds containing boron atoms in six-membered aromatic rings.[4] These compounds are of a different order of stability from previously known types of organoboron compounds, being chemically similar to "normal" aromatics, and their discovery has opened up a new field of aromatic chemistry. The procedure indicated here has been used to prepare a large number of related aromatic systems.

The cyclization can be carried out with halogenated amines, and substitution products of the new ring systems can also be obtained in the conventional way, by nitration, etc. Similar compounds can be prepared directly by using arylboron dichlorides in place of boron trichloride in the procedure indicated above. The parent borazarene derivatives, with hydrogen attached to boron, can be made from the B-hydroxy compounds with lithium aluminum hydride in the presence of aluminum chloride.[4,5] N-Alkyl derivatives can be made either by using N-alkyl derivatives of the aminobiphenyls as starting materials, or by N-alkylation of the unsubstituted compounds via their N-lithio derivatives.[5] Apart from their inherent interest, compounds of this type can serve as intermediates in various syntheses. Thus benzocinnolines and 2,2'-dihydroxybiphenyls can be obtained from derivatives of 2-aminobiphenyl.[5,6,7]

References and Notes

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6. M. J. S. Dewar and P. M. Maitlis, *J. Am. Chem. Soc.*, **83**, 187 (1961).
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Appendix
Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

alumina

petroleum ether

10-Methyl-10,9-borazarophenanthrene

Dibenz[c,e][1,2]azaborine, 5,6-dihydro-6-methyl-

Bis(10,9-borazarophenanthryl) ether

10-hydroxy-10,9-borazarophenanthrene

sodium-lead alloy

10-Chloro-10,9-borazarophenanthrene

10,9-Borazarophenanthrene

hydrogen chloride,
hydrochloric acid (7647-01-0)

methanol (67-56-1)

ether (60-29-7)

hydrogen (1333-74-0)

sodium bicarbonate (144-55-8)

aluminum chloride (3495-54-3)

sodium (13966-32-0)

xylene (106-42-3)

magnesium sulfate (7487-88-9)

boron (7440-42-8)

methylmagnesium bromide (75-16-1)

lithium aluminum hydride (16853-85-3)

boron trichloride (10294-34-5)

2-aminobiphenyl (90-41-5)

boron chloride (20583-55-5)