



# ORGANIC SYNTHESSES

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METHODS FOR THE PREPARATION  
OF ORGANIC CHEMICALS

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Preparations appear in the alphabetical order of common names of the compounds. For convenience in surveying the literature concerning any preparation through *Chemical Abstracts* subject indexes, the *Chemical Abstracts* indexing name for each compound is given as a subtitle if it differs from the common name used as the title.

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Chemists are invited to submit for publication in *Organic Syntheses* procedures for the preparation of compounds which are of general interest, as well as procedures which illustrate synthetic methods of general utility. It is fundamental to the usefulness of *Organic Syntheses* that submitted procedures represent optimum conditions, and the procedures should have been checked carefully by the submitters, not only for yield and physical properties of the products but also for any hazards that may be involved. Full details of all manipulations should be described, and the **range** of yields should be reported rather than the maximum yield obtainable by an operator who has had considerable experience with the preparation. For each solid product the melting point **range** should be reported, and for each liquid product the **range** of boiling point and refractive index should be included. In some instances, it is desirable to include additional physical properties of the product, such as ultraviolet, infrared, or nuclear magnetic resonance spectra. The methods of preparation or sources of the reactants should be described in notes, and the physical properties (such as boiling point, index of refraction, melting point) of the reactants should be included except where rather standard commercial grades are specified.

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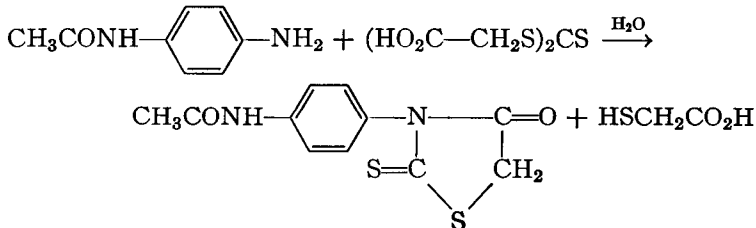
Additions, corrections, and improvements to the preparations previously published are welcomed and should be directed to the Secretary.

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## N-(*p*-ACETYLAMINOPHENYL)RHODANINE

[Rhodanine, 3-(*p*-acetamidophenyl)-]



Submitted by R. E. STRUBE.<sup>1</sup>

Checked by JOHN D. ROBERTS and STANLEY L. MANATT.

### 1. Procedure

In a 2-l. round-bottomed flask fitted with a mechanical stirrer and a reflux condenser are placed 30.0 g. (0.20 mole) of *p*-aminoacetanilide (Note 1) and 400 ml. of water. The mixture is heated on a steam bath with stirring, and to the clear solution is added at once a hot solution of 45.2 g. (0.20 mole) of trithiocarbodiglycolic acid (Note 2) in 500 ml. of water. Heating and stirring are continued for 5 hours (Note 3). The steam bath is then replaced by an ice bath, and the reaction mixture is cooled to 20–25°. The precipitate is removed by suction filtration. The solid is transferred to a 500-ml. Erlenmeyer flask containing 200 ml. of water. The mixture is heated on the steam bath to 70–75° while the lumps are crushed by a glass rod to obtain a homogeneous mixture. The mixture is filtered with suction while hot, and the flask is cleaned by rinsing it with small amounts of hot water. The solid on the filter is sucked as dry as possible and then transferred to a 2-l. round-bottomed flask fitted with a reflux condenser. Glacial acetic acid (1.5 l.) is added and the mixture is heated in an oil bath to vigorous reflux for 5 minutes (Note 4). A small amount of solid does not dissolve, and this is removed by filtra-

tion while hot (Note 5). The filtrate is stirred mechanically and cooled to 15–20° by an ice bath and kept at this temperature for 1 hour. The slightly yellow crystals are collected by suction filtration, washed successively with 25 ml. of glacial acetic acid, 100 ml. of ethanol, and 100 ml. of ether. The yield of air-dried material is 26–28 g. (49–53% yield). The compound decomposes on heating above 240° (Note 6).

## 2. Notes

1. *p*-Aminoacetanilide (white label) supplied by Eastman Kodak Company was used.

2. Strube, *Org. Syntheses*, **39**, 77 (1959).

3. Within 10 minutes a precipitate is formed; the greater part of the reaction product is present after 2 hours' heating.

4. The purification should be carried out in a hood, since gas escapes during the heating and hot acetic acid is irritating to the eyes. The checkers used a 2-l. heating mantle instead of an oil bath.

5. The filtration of the hot acetic acid solution should be done with care. The flask was surrounded by a towel and rubber gloves were worn. The filtration can best be done in two steps. Approximately half of the hot acetic acid solution is filtered through a large, fluted filter paper; the other half is heated again to reflux and then filtered through another fluted filter paper. Filtration through a steam-heated Büchner funnel may sometimes be troublesome, since the suction accelerates crystallization causing plugging of the funnel stem.

6. Analytical values: Calcd. for  $C_{11}H_{10}N_2O_2S_2$ : C, 49.62; H, 3.78; N, 10.52; S, 24.08. Found: C, 49.76; H, 3.76; N, 10.36; S, 24.07.

## 3. Methods of Preparation

This procedure is based on the method of Holmberg<sup>2</sup> for preparing N-substituted rhodanines. The synthesis of N-(*p*-acetylaminophenyl)rhodanine has not yet been reported in the literature.

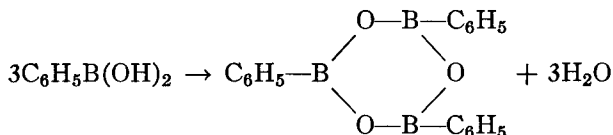
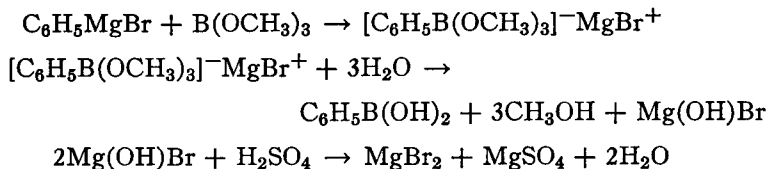
<sup>1</sup> The Chemistry Department, The Upjohn Company, Kalamazoo, Michigan.

<sup>2</sup> Holmberg, *J. prakt. Chem.*, **81**, 451 (1910).



## BENZENEBORONIC ANHYDRIDE

(Boroxine, triphenyl-)



Submitted by ROBERT M. WASHBURN, ERNEST LEVENS,  
CHARLES F. ALBRIGHT, and FRANKLIN A. BILLIG.<sup>1</sup>

Checked by B. C. MCKUSICK and H. C. MILLER.

## 1. Procedure

*Caution! Benzeneboronic acid and its anhydride are toxic substances and may irritate mucous tissues such as those of the eyes. In case of contact, carefully wash exposed parts of the body with soap and water (Note 1).*

The apparatus consists of a four-necked 5-l. round-bottomed Morton flask<sup>2</sup> fitted with a 500-ml. graduated dropping funnel with a pressure-equalizing side arm, a 1-l. graduated dropping funnel of the same type, a thermometer, an efficient mechanical stirrer (Note 2), and an inlet for dry nitrogen. The apparatus is thoroughly swept with dry nitrogen, and the reaction flask is charged with 1.5 l. of anhydrous ether, dry nitrogen (Note 3) being used for pressure transfer.

Three hundred thirty-six milliliters (312 g., 3.00 moles) of methyl borate is distilled directly into the 500-ml. dropping funnel shortly before starting the reaction (Note 4). One liter (544 g., 3.0 moles) of a 3*M* ethereal solution of phenylmagnesium bromide is pressure-transferred with dry nitrogen into the 1-l.

dropping funnel (Note 5). During subsequent operations until the hydrolysis step, a positive pressure of 10–20 mm. of nitrogen is maintained in the closed system by means of a mercury bubbler to prevent access of atmospheric moisture. The ether is cooled to below  $-60^{\circ}$  by a bath of Dry Ice and acetone and is kept below  $-60^{\circ}$  all during the reaction (Note 6). The reactants are added to the well-stirred reaction mixture alternately in small portions, first 10 ml. of methyl borate and then 30 ml. of phenylmagnesium bromide, the rate of addition being as rapid as is possible without the temperature of the mixture rising above  $-60^{\circ}$  (Note 7). Stirring is continued for an additional 20 minutes below  $-60^{\circ}$  after the addition of the reagents is completed.

The stirred mixture, maintained at or below  $0^{\circ}$ , is hydrolyzed by the addition of 200 ml. of distilled water during 5 minutes. It is then neutralized by addition of a solution of 84 ml. of concentrated sulfuric acid in 1.7 l. of distilled water during 15 minutes. The mixture is transferred to a 5-l. separatory funnel, the ether layer is separated, and the aqueous layer is extracted with three 250-ml. portions of ether.

The combined ether layer and extracts are transferred to a 5-l. round-bottomed flask equipped with a Hershberg stirrer,<sup>3</sup> a dropping funnel, a Claisen head with a water-cooled condenser, an electric heating mantle, and an ice-cooled receiver (Note 8). After approximately one-half of the ether has been removed by distillation from the stirred mixture, 1.5 l. of distilled water is added slowly while the distillation is continued until a head temperature of  $100^{\circ}$  is reached (Note 9).

While stirring is continued, the aqueous distilland is cooled in an ice bath (Note 10). The benzeneboronic acid, which separates as small white crystals, is collected on a Büchner funnel and washed with petroleum ether. The petroleum ether removes traces of dibenzeneboronic acid, which are seen in the hot mother liquor as globules of brown oil and which may color the product. The acid is dehydrated to benzeneboronic anhydride by heating it in an oven at  $110^{\circ}$  and atmospheric pressure for 6 hours (Note 11). Benzeneboronic anhydride is obtained as a colorless solid, weight 240–247 g. (77–79%) (Note 12), m.p.  $214-216^{\circ}$ .

## 2. Notes

1. A summary of the physiological activity of benzeneboronic acid may be found in reference 4a.

2. The submitters found that for a preparation of this size a 1-inch Duplex Dispersator (Premier Mill Corp., Geneva, New York) operating at 7500 r.p.m. provided excellent agitation of the heterogeneous reaction mixture. For smaller preparations (1-l. flask) they found that a Stir-O-Vac (Labline, Inc., 217 N. Desplainer St., Chicago 6, Illinois) operating at 5000 r.p.m. was satisfactory. The type of agitation is very important for, whereas the submitters obtained yields of around 91%, the checkers obtained yields of only 77–80% with either a Morton stirrer<sup>2</sup> (excessive splashing deposited some of the reaction mixture on the warm upper walls of the flask) or a Polytron dispersion mill type of stirrer (there was too much hold-up in the stirrer housing).

3. Tank nitrogen was dried with phosphorus pentoxide.

4. Methyl borate (b.p. 68°) forms a 1:1 azeotrope (b.p. 54.6°) with methanol (b.p. 64°).<sup>5</sup> Since the presence of even a small amount of methanol reduces the yield considerably more than would be expected from the stoichiometry,<sup>4,6</sup> methyl borate stocks should be freshly distilled through a good column to remove as fore-run any methyl borate-methanol azeotrope which may have been formed by hydrolysis during storage.

5. Mallinckrodt analytical reagent grade ether, dried over sodium, was used. The methyl borate was the commercial product of American Potash and Chemical Corporation containing 99% ester as received. The phenylmagnesium bromide was purchased as a 3.0M solution in ether from Arapahoe Special Products, Inc., Boulder, Colorado.

6. The yield of benzeneboronic anhydride is highly dependent upon the reaction temperature, as the following data of the submitters show. At a reaction temperature of 15° the yield was 49%; at 0°, 76%; –15°, 86%; –30°, 92%; –45°, 92%; –60°, 99%. The yields are based on the combined first and second crops of benzeneboronic acid.

7. At a given temperature, the maximum yield of benzeneboronic acid and the minimum amount of by-product dibenzene-

borinic acid are obtained when neither reagent is present in excess. The addition of small increments of reactants is a convenient approximation imposed by the difficulty of adjusting stopcocks to small rates of flow. Alternatively, the Hershberg dropping funnel<sup>7</sup> or other metering device may be used to maintain the stoichiometry. Addition times, which depend upon the efficiency of stirring and heat transfer, vary from about 1 hour at  $-60^{\circ}$  to 15 minutes at  $0^{\circ}$ .

8. Stirring is helpful during the ether distillation to prevent superheating.

9. Small amounts of benzene, phenol, and biphenyl, which may be formed in the reaction, are removed by the steam distillation. Enough water has been added to ensure solution of all of the product.

10. The product crystallizes at  $43^{\circ}$  with a temperature rise to  $45^{\circ}$ . The solubility of benzeneboronic acid in water (g./100 g. of water) is approximately 1.1 at  $0^{\circ}$  and 2.5 at  $25^{\circ}$ ; the solubility-temperature relationship is linear to at least  $45^{\circ}$ .

11. If benzeneboronic acid rather than its anhydride is desired, it can be obtained by air-drying the moist acid in a slow stream of air nearly saturated with water. The yield of acid is 282–332 g. One can readily convert the anhydride to the acid by recrystallizing it from water. Benzeneboronic acid gradually dehydrates to the anhydride if left open to the atmosphere at room temperature and 30–40% relative humidity. The melting point observed is that of the anhydride because the acid dehydrates before it melts.

12. The submitters report a yield of 91% and state that an additional 27 g. (9%) of acid can be obtained from the aqueous mother liquor.

### 3. Methods of Preparation

The procedure described<sup>4</sup> is a modification of the method of Khotinsky and Melamed,<sup>8</sup> who first reported the preparation of boronic acids from Grignard reagents and borate esters. Benzeneboronic acid and the corresponding anhydride also have been prepared by reaction of phenylmagnesium bromide with boron

trifluoride,<sup>9</sup> by reaction of phenyllithium with butyl borate,<sup>10</sup> and by reaction of diphenylmercury with boron trichloride.<sup>11</sup>

The present procedure is also applicable to the synthesis of substituted benzeneboronic acids.<sup>4a</sup> Benzeneboronic acid and its anhydride are of use as starting materials for the synthesis of phenylboron dichloride<sup>12</sup> and of various substituted boronic and borinic acids and esters.<sup>6, 13</sup>

<sup>1</sup> American Potash and Chemical Corporation, Whittier, California.

<sup>2</sup> Morton, *Ind. Eng. Chem., Anal. Ed.*, **11**, 170 (1939); Morton and Redman, *Ind. Eng. Chem.*, **40**, 1190 (1948).

<sup>3</sup> Pinkney, *Org. Syntheses*, Coll. Vol. **2**, 117 (1943).

<sup>4</sup> (a) Washburn, Levens, Albright, Billig, and Cernak, presented before the Division of Industrial and Engineering Chemistry, *131st National Meeting, American Chemical Society*, Miami, April 8, 1957, *Abstracts of Papers*, p. 12L; (b) Washburn, Billig, Bloom, Albright, and Levens, presented before the Division of Inorganic Chemistry, *133rd National Meeting, American Chemical Society*, San Francisco, April 18, 1958, *Abstracts of Papers*, pp. 45L-46L.

<sup>5</sup> Schlesinger, Brown, Mayfield, and Gilbreath, *J. Am. Chem. Soc.*, **75**, 213 (1953).

<sup>6</sup> Seaman and Johnson, *J. Am. Chem. Soc.*, **53**, 711 (1931).

<sup>7</sup> Hershberg, *Org. Syntheses*, Coll. Vol. **2**, 129 (1943).

<sup>8</sup> Khotinsky and Melamed, *Ber.*, **42**, 3090 (1909).

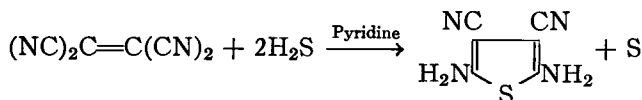
<sup>9</sup> Krause and Nitsche, *Ber.*, **55B**, 1261 (1922); Krause, German Patent 371,467 (1923) [*C.A.*, **18**, 992 (1924)].

<sup>10</sup> Brindley, Gerrard, and Lappert, *J. Chem. Soc.*, **1955**, 2956.

<sup>11</sup> Michaelis and Becker, *Ber.*, **15**, 180 (1882).

<sup>12</sup> Dandegaonker, Gerrard, and Lappert, *J. Chem. Soc.*, **1957**, 2893.

<sup>13</sup> Lappert, *Chem. Revs.*, **56**, 987, 1013 (1956).

**2,5-DIAMINO-3,4-DICYANOTHIOPHENE****(3,4-Thiophenedicarbonitrile, 2,5-diamino-)**Submitted by W. J. MIDDLETON.<sup>1</sup>

Checked by JAMES CASON and RALPH J. FESSENDEN.

**1. Procedure**

*Caution! Since carbon disulfide is highly flammable and hydrogen sulfide highly toxic, this reaction should be carried out in a hood, with due precaution against fire. It is also recommended that tetracyanoethylene not be allowed to come into contact with the skin.*

A 1-l. three-necked flask is fitted with a sealed mechanical stirrer, a condenser protected by a drying tube, a thermometer, and an inlet tube extending to the bottom of the flask. A solution of 25.6 g. (0.2 mole) of recrystallized tetracyanoethylene<sup>2</sup> in 300 ml. of acetone is placed in the flask, and 300 ml. of carbon disulfide is added. The flask and its contents are cooled to 0° by means of a salt-ice bath. With good stirring, hydrogen sulfide is passed into the reaction mixture at a moderate rate while the temperature is maintained at 0–5°. The solution becomes milky after a few minutes owing to the formation of colloidal sulfur. The hydrogen sulfide addition is continued for about 30 minutes, or until the solution is thoroughly saturated.

The hydrogen sulfide addition is temporarily suspended, and 100 ml. of pyridine is added rapidly in one portion through the condenser as the solution is stirred vigorously (Note 1). The solution becomes clear, and then 2,5-diamino-3,4-dicyanothiophene begins to precipitate immediately. The hydrogen sulfide addition is resumed and is continued for about 30 minutes while the temperature of the reaction mixture is maintained at 0–5°. Finally, the reaction mixture is stirred for an additional 30 minutes at 0–5°, then the yellow precipitate of the thiophene is

collected on a Büchner funnel, thoroughly washed with about 500 ml. of acetone, and dried in the air or in a vacuum desiccator. The yield of crude product of yellow or buff color amounts to 30–31 g. (92–95%).

This material is sufficiently pure for most purposes. If a purer product is desired, the crude material is dissolved in 300 ml. of dimethylformamide, 10 g. of activated alumina (48–100 mesh) is added, and the mixture is filtered. The filtrate is heated to 80–90° on a steam bath, then 1 l. of boiling water is added immediately (Note 2). The resultant mixture is cooled in an ice bath, and the light buff crystals of 2,5-diamino-3,4-dicyanothiophene that separate are collected on a Büchner funnel and thoroughly washed with 500 ml. of acetone; weight 26–28 g. (79–85%). The product has no definite melting point but sublimes with some decomposition when heated above 250°.

## 2. Notes

1. Unless the pyridine is added quite rapidly, some of the product will begin to precipitate before all of the sulfur has dissolved, and the final product will be contaminated with sulfur.

2. This operation should be carried out as rapidly as possible, since prolonged heating in dimethylformamide results in loss of product.

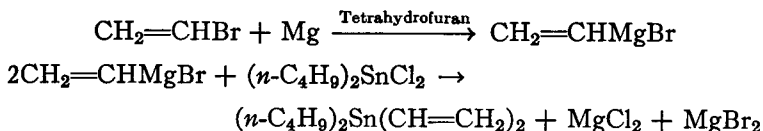
## 3. Methods of Preparation

2,5-Diamino-3,4-dicyanothiophene has been prepared only by the action of hydrogen sulfide or sodium sulfide on tetracyanoethylene or tetracyanoethane.<sup>3</sup> Unlike most aminothiophenes, 2,5-diamino-3,4-dicyanothiophene is very stable and can be stored indefinitely. Its amino groups show the normal reactivity of aromatic amines. For example, they readily condense with aromatic aldehydes to form highly colored bis-anils.<sup>3</sup> Hot 10% sodium hydroxide rearranges 2,5-diamino-3,4-dicyanothiophene to 2-amino-3,4-dicyano-5-mercaptopyrrole.<sup>3</sup>

<sup>1</sup> Contribution No. 483 from Central Research Department, Experimental Station, E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Delaware.

<sup>2</sup> Carboni, *Org. Syntheses*, **39**, 64 (1959).

<sup>3</sup> Middleton, Englehardt, and Fisher, *J. Am. Chem. Soc.*, **80**, 2822 (1958).

**DI-*n*-BUTYLDIVINYLTIN****(Tin, dibutyldivinyl-)**Submitted by DIETMAR SEYFERTH.<sup>1</sup>

Checked by MELVIN S. NEWMAN and S. RAMACHANDRAN.

**1. Procedure**

In a 2-l. three-necked flask, equipped with a Dry Ice-acetone reflux condenser, a mechanical stirrer, and a 250-ml. dropping funnel, is placed 29.2 g. (1.2 g.-atoms) of magnesium turnings. Enough tetrahydrofuran (THF) (Note 1) to cover the magnesium is added, stirring is begun, and about 5 ml. of vinyl bromide (Note 2) is added. After the reaction has started (Note 3), an additional 350 ml. of the THF is added. The rest of the vinyl bromide (140 g., 1.3 moles, total), dissolved in 120 ml. of THF, is added at such a rate that a moderate reflux is maintained. After the addition has been completed, the solution is refluxed for 30 minutes (Note 4). The Grignard solution is then cooled to room temperature, and the Dry Ice-acetone condenser is replaced with a water condenser which is fitted with a Drierite-filled drying tube. A solution of 135 g. (0.44 mole) of di-*n*-butyltin dichloride (Note 5) in 250 ml. of THF (Note 6) is then added, with stirring, at such a rate that a moderate reflux is maintained. After the addition has been completed, the reaction mixture is refluxed for 20 hours. The mixture is then cooled to room temperature and is hydrolyzed by the slow addition of 150 ml. of a saturated ammonium chloride solution (Note 7). The organic layer is then decanted and the residual salts are washed thoroughly with 3 portions of ether, the washings being added to the organic layer. The ether and the THF are stripped off at atmospheric pressure;



a Claisen distillation head is used. The residue is then distilled at reduced pressure using a vacuum-jacketed Vigreux column equipped with a total-reflux partial take-off head to give 95–116 g. (74–91%) of di-*n*-butyldivinyln, b.p. 60° at 0.4 mm.,  $n_D^{25}$  1.4797 (Notes 8 and 9).

## 2. Notes

1. Tetrahydrofuran, obtained from the Electrochemicals Department of E. I. du Pont de Nemours & Co. (Inc.), was distilled from lithium aluminum hydride prior to use. It is not advisable to leave THF purified in this manner standing around for longer periods, since, in the absence of the inhibitor present in the commercial material, peroxides form fairly rapidly. (See also p. 57; Note 2).

2. Vinyl bromide, obtained from the Matheson Company, was redistilled prior to use. The distillate was collected in a receiver cooled with a Dry Ice-acetone mixture and protected from daylight.

3. In most cases the formation of the Grignard reagent began in the absence of any initiator. In cases where the reaction did not begin within a few minutes, 0.5 ml. of methyl iodide served to initiate attack on the magnesium.

4. In small-scale preparations of vinylmagnesium bromide it is advisable to carry out the reaction in an atmosphere of dry nitrogen in order to prevent hydrolysis and oxidation of the Grignard reagent. In larger-scale preparations such as the one described here, where a considerable excess of Grignard reagent is used, such precautions are not necessary.

5. Di-*n*-butyltin dichloride is a commercial product of Metal and Thermit Corporation, Rahway, New Jersey.

6. The checkers found that 250 ml. of dry ether was equally effective.

7. Enough saturated ammonium chloride solution is added to cause coagulation of the inorganic salts to a particle size of about 2–5 mm. in diameter; the volume of solution required varies but averages about 100–120 ml. per mole of Grignard reagent. If the hydrolysis is stopped at this point, a clear, essentially dry organic