Title	Bis(pinacolato)diboron
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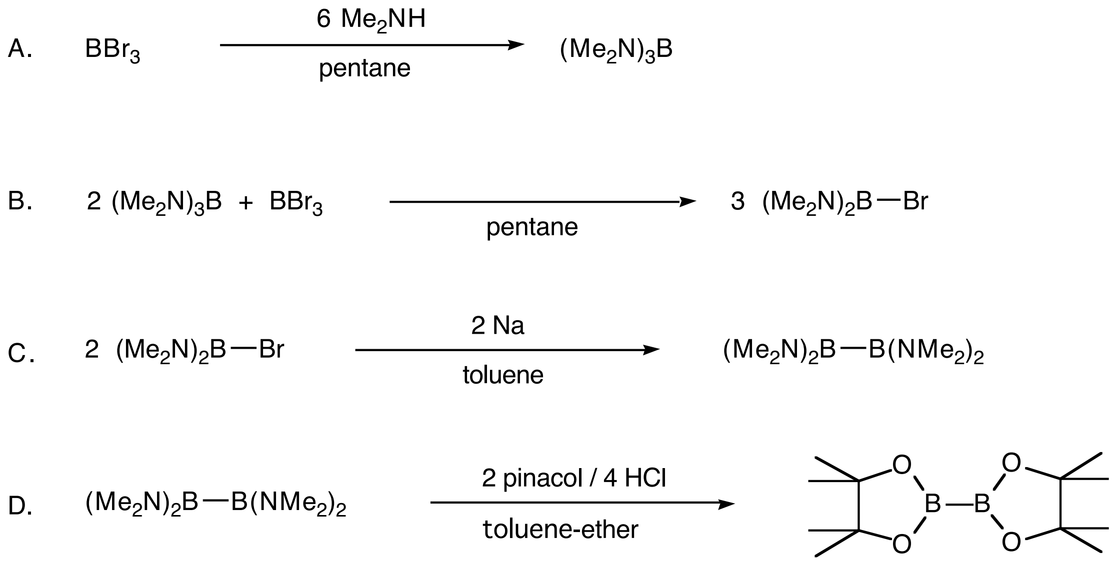
Citation	Organic Syntheses, 77, 176-185 https://doi.org/10.15227/orgsyn.077.0176
Issue Date	2000
Doc URL	https://hdl.handle.net/2115/56239
Type	journal article
File Information	(21) B-B (OS).pdf

BIS(PINACOLATO)DIBORON



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Submitted by Tatsuo Ishiyama, Miki Murata, Taka-aki Ahiko, and Norio Miyaura.[1]

1. Procedure

Caution! All the operations should be carried out in a well-ventilated hood, since bromoborane derivatives fume in air and are rapidly hydrolyzed with the evolution of considerable heat.

A. Tris(dimethylamino)borane (Note 1). A 2-L, three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a dry ice-cooled reflux condenser connected to nitrogen source and a bubbler is flushed with nitrogen (Note 2). The flask is charged with 800 mL of pentane (Note 3) and 218 g (4.84 mol) of dimethylamine (Note 4), and cooled to ca. -30°C with a dry ice-methanol bath. A solution of 201 g (0.801 mol) of boron tribromide

(Note 5) in 400 mL of pentane is dropwise added over 3 hr to the vigorously-stirred solution while maintaining the bath-temperature at -20 to -10°C (Note 6). As soon as the addition is begun, a white precipitate of dimethylamine hydrobromide appears. Allow the temperature to rise to ambient temperature without removing the cooling bath, and then the slurry is stirred for 16 h at room temperature. The precipitate is removed by filtration through a Celite pad on a glass-fritted filter funnel (Note 7). The flask and filter cake are rinsed three times with 60 mL of pentane. The pentane solution is distilled to give 92.7 g (81%) of tris(dimethylamino)borane as a colorless liquid, bp 44-45°C (12 mm), lit.[2] bp 39°C (10 mm) (Note 8).

B. Bromobis(dimethylamino)borane. A 500-mL, two-necked flask equipped with a magnetic stirring bar, a dropping funnel, and a distillation apparatus connected to nitrogen source and a bubbler is flushed with nitrogen (Note 2). The flask is charged with 100 mL of pentane (Note 3) and 92.7 g (0.648 mol) of tris(dimethylamino)borane, and cooled to -40°C with a dry ice-methanol bath. A solution of 81.3 g (0.324 mol) of boron tribromide (Note 5) in 80 mL of pentane is dropwise added to the stirred solution over a period of 1.5 hr maintaining the temperature at -40°C. The cooling bath is removed and the solution is stirred at room temperature for 30 min. Distillation affords 172.8 g (99%) of bromobis(dimethylamino)borane as a colorless liquid, bp 56-58°C (12 mm), lit.[3] bp 20-28°C (0.5 mm) (Note 9).

C. Tetrakis(dimethylamino)diboron. A 500-mL, three-necked flask equipped with an airtight mechanical stirrer, a dropping funnel, and a reflux condenser connected to nitrogen source and a bubbler is flushed with nitrogen (Note 2). The flask is charged with 100 mL of toluene (Note 10) and 27.2 g (1.18 g-atom) of sodium. The mixture is brought to reflux with an oil bath and the sodium is finely pulverized by vigorous stirring. A solution of 172.8 g (0.965 mol) of bromobis(dimethylamino)borane in 70 mL of toluene is dropwise added at a rate sufficient to maintain a gentle reflux over 45 min. As soon as the addition is begun, a deep-blue precipitate appears. The suspension is heated at reflux for additional 2.5 hr. The slurry is cooled to room temperature, and filtered through a Celite pad on a sintered-glass funnel (Note 7). The flask and filter cake are rinsed three times with 50 mL of toluene (Note 11). The yellow filtrate is concentrated in vacuo, and the residual oil is then distilled under reduced pressure to give 64.4 g (67%) of tetrakis(dimethylamino)diboron as a colorless liquid, bp 92°C (12 mm), lit.[3] bp 55-57°C (2.5 mm) (Note 12).

D. Bis(pinacolato)diboron (**1**). A 2-L, three-necked flask fitted with a mechanical stirrer, a dropping funnel, and a reflux condenser connected to nitrogen source and a bubbler is flushed with nitrogen (Note 2). To the flask are added 64.4 g (0.325 mol) of tetrakis(dimethylamino)diboron and 600 mL of toluene (Note 10), and then a solution of 76.9 g (0.652 mol) of pinacol (Note 13) in 400 mL of toluene. The flask is immersed in a ice-water bath and a 6.6 M ethereal solution of hydrogen chloride (Note 14) (200 mL, 1.32 mol) is dropwise added during 2 hr. As soon as the addition is started, a white precipitate of dimethylamine hydrochloride appears. The slurry is stirred at room temperature for additional 4 hr. The precipitate is removed by filtration in a Buchner funnel with suction, and the filtrate is concentrated on a rotary evaporator to give a white solid. The solid is dissolved in ca. 700 mL of pentane and the remaining solid is again removed by filtration. The filtrate is washed three times with 500 mL of water and dried over anhydrous magnesium sulfate. The drying agent is removed by filtration and the filtrate is then concentrated to ca. 150 mL. The flask is heated to dissolve the resulting precipitate, allowed to cool to room temperature, and then thoroughly chilled in a freezer (-30°C). The first crop is collected by filtration and is washed twice with 30 mL of cold pentane. The mother liquor is again concentrated to give another crop of crystal. The procedure is repeated twice. Combined crystals are dried under reduced pressure (0.1 mm) for 16 hr at room temperature to give 75.4 g (91%) of **1** as colorless plates, mp 138°C, lit.[4] mp 138°C (Note 15).

2. Notes

1. Tris(dimethylamino)borane is available from Aldrich Chemical Company, Inc. It is also synthesized from boron trichloride.[2]

2. All glassware is pre-dried in an oven at 120°C for 1 hr, assembled while hot, and allowed to cool under a stream of nitrogen.

3. Pentane is distilled from lithium aluminum hydride before use.

4. Dimethylamine (bp 6°C) is condensed at -78 °C into a 500-mL flask fitted with an inlet tube and a nitrogen bubbler. It is either taken from a cylinder (Aldrich Chemical Company, Inc.) or from a mixture of 50% aqueous solution of dimethylamine and potassium hydroxide.[5]

5. Boron tribromide purchased from Wako Pure Chemical Industries, Ltd. is used without further purification.

6. *Caution! The addition at lower than -20 °C leads to a violent reaction during warming up the temperature to -10-0 °C.*

7. A large filter area is recommended. A 1-cm layer of Celite is pressed on a sintered-glass funnel (6 cm X 17 cm). The Celite is dried in an oven at 120 °C for 12 hr. A 6-mm Teflon tube is used to connect the flask and the filter funnel through the septums, and the stirred slurry is then transferred to the funnel in an aid of nitrogen pressure. Inner pressure of the receiver flask and the funnel is leaked through oil bubblers.

8. Moisture sensitive. ^{1}H NMR ($CDCl_3$) δ: 2.52 (s, 18 H).

9. Moisture sensitive and fumes in air. ^{1}H NMR ($CDCl_3$) δ: 2.75 (s, 12 H).

10. Toluene is distilled from molten sodium before use.

11. The residual solid containing unreacted sodium is carefully treated with ethanol.

12. Moisture sensitive. ^{1}H NMR ($CDCl_3$) δ: 2.67 (s, 24 H).

13. Pinacol purchased from Tokyo Kasei Kogyo Co., Ltd. is used without further purification.

14. An ethereal solution of hydrogen chloride is titrated with a 0.1 M sodium hydroxide before use.

15. The crystal can be handled in air and stored in a capped bottle. ^{1}H NMR ($CDCl_3$) δ: 1.26 (s, 24 H); ^{11}B NMR (toluene) δ: 29.94. The compound is now commercially available from Lancaster Synthesis Ltd., Callery Chemical Co., and Frontier Scientific Inc.

Waste Disposal Information

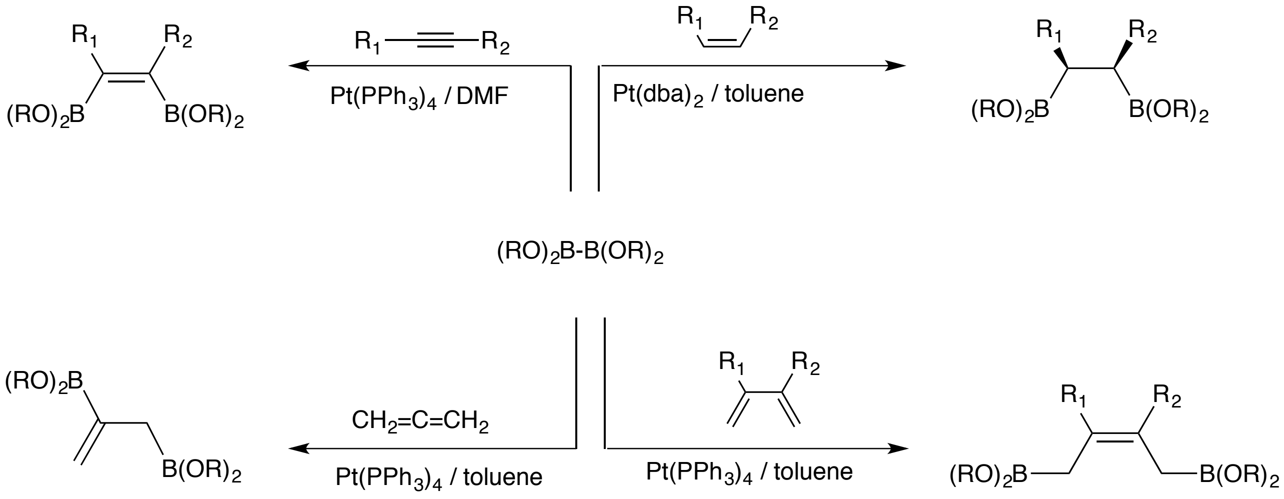
All toxic materials were disposed of in accordance with “Prudent Practices for Disposal of Chemicals from Laboratories”; National Academic Press; Washington, DC, 1983.

3. Discussion

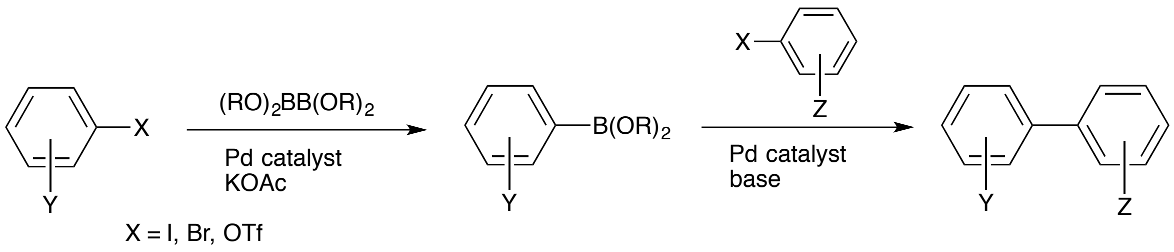
This method is an adaption of the U. S. Borax Research group's procedure[3] which illustrates a practical and efficient method for the synthesis of tetra(alkoxo)diborons. Several (alkoxo)diborons, such as tetra(methoxo)-,[3] bis(catecholato)-,[6] and bis(pinacolato)diboron[4] (**1**), are synthesized from tetrakis(dimethylamino)diboron. The diborons are an excellent reagent for the synthesis of various organoboronic esters via the transition metal-catalyzed addition and cross-coupling reactions.[7-15]

The platinum(0) complexes catalyze the addition of **1** to unsaturated hydrocarbons (Scheme 1). The addition to alkynes,[7] alkenes,[8] 1,3-dienes,[9] or allenes[10] stereoselectively provides *cis*-addition products.

Scheme 1



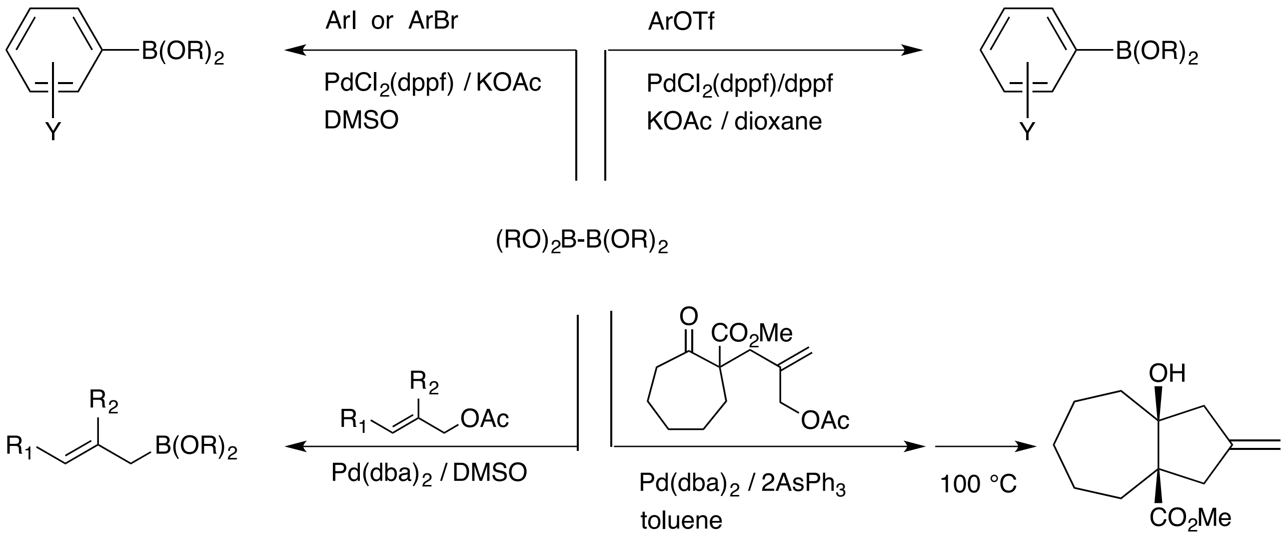
The cross-coupling reaction of **1** with palladium catalyst provides a convenient method for the synthesis of organoboronic esters from organic electrophiles (Scheme 2). Aromatic halides[11] and triflates[12] couple with **1** in the presence of $PdCl_2(dppf)$ and KOAc to give arylboronates in high yields. The procedure have a broad generality over the conventional synthesis based on the addition of aryllithium or Grignard reagents to trialkyl borates because the reaction tolerates various functional groups, e.g., CO_2Me, COMe, CN, and NO_2. Arylboronic acids and esters have been used for the synthesis of biaryls via the palladium-catalyzed cross-coupling reaction with aryl electrophiles. The use of diboron allows the sequential double cross-couplings in a same flask to provide biaryls (eq. 1).[12, 13]



(1)

The coupling with allyl acetates gives allylboronates[14] which exhibit a high diastereoselectivity in the intramolecular allylboration of carbonyl compounds[15] (Scheme 2).

Scheme 2



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