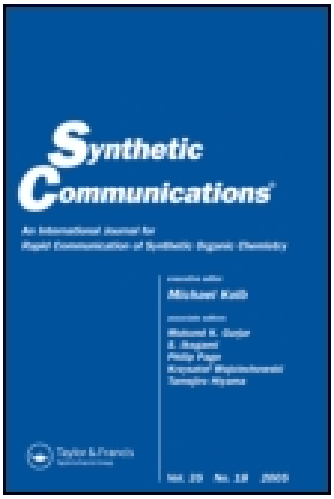

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Preparation of Tetraoxadiphosphadiborocane-2,6-diones

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PREPARATION OF TETRAOXADIPHOSPHADIBOROCANE-2,6-DIONES

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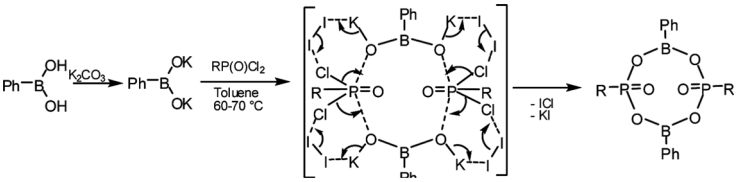
GRAPHICAL ABSTRACT



Abstract *Cyclization of aryl/alkyl phosphonic dichlorides (**2a–f**) with phenylboronic acid/K_2CO_3/I_2 in dry toluene at 60–70 °C afforded 2,6-diaryl/alkyl-4,8-diphenyl-1,3,5,7, 2λ^5,6λ^5,4,8-tetraoxadiphosphadiborocane-2,6-diones (**3a–f**).*

Keywords Akyl/aryl phosphorous dichlorides; phenylboronic acid; 1-phenylboryl (1-phenylboryl)phenylphosphinate; tetraoxadiphosphadiborocane-2,6-diones

INTRODUCTION

Phosphorus-containing macrocycles are interesting molecules with potential application in supramolecular and synthetic organic chemistry.[1–3] Past and present research has led to the construction of phosphorane macrocycles with large preorganized macrocyclic cavities bearing concave functionalities.[4–6] Being phosphorus analogs of crown ethers with potential catalytic activity and ion-carrying ability,[7–11] they have become important molecules in the field of host–guest complexation.[12,13]

Similarly, interest in the synthesis and characterization of organoboron macrocycles is evident from applications as anticancer agents and in boron neutron capture therapy (BNCT).[14] They also have a wide range of other uses as fluorescent,[15] electro- and nonlinear optical materials,[16,17] and as reagents in organic synthesis.[18,19] Recently, several dimeric boron complexes found application in host–guest chemistry.[20,21]

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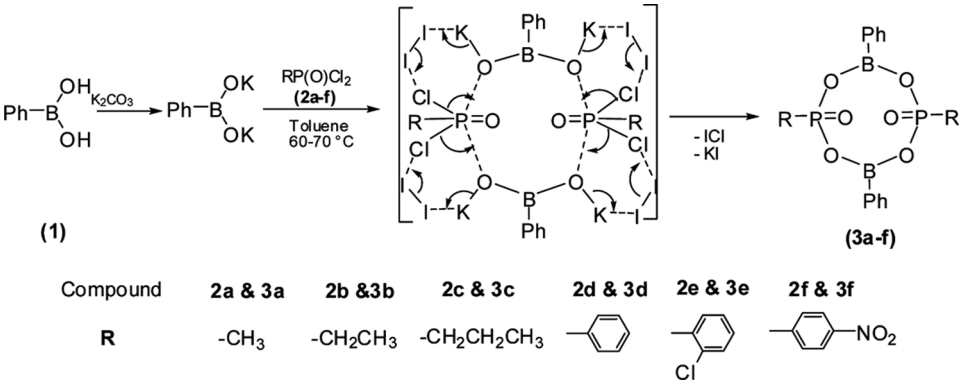


Scheme 1. Synthesis of tetraoxadiphosphadiborocane-2,6-diones (**3a–j**).

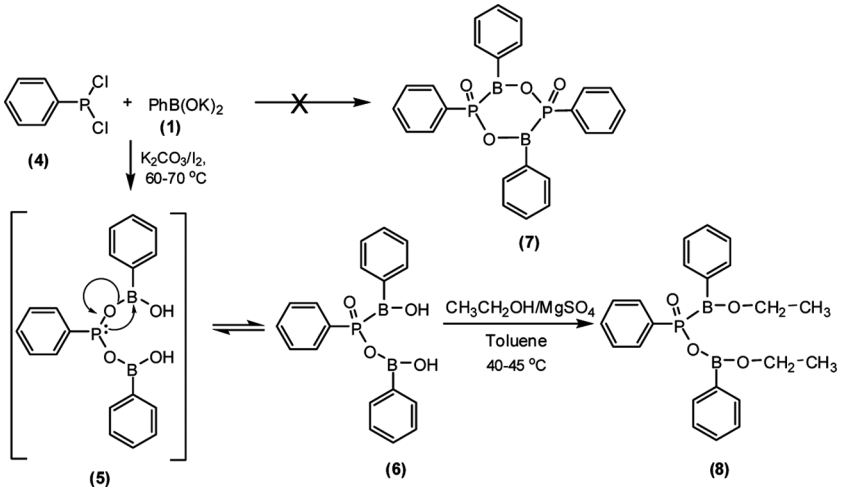
Macrocycles were prepared by reacting dithiols with 1,4-dibromobutane in the presence of K_2CO_3 at room temperature.[22] Direct addition of dichlorophenylphosphine to tetraethylene glycol bis(2-lithiophenyl) ether or its reaction with the disodium salt of ethylene glycol ditosylates[3] led to the monophospha-crown ethers.

New spiro and ansa phosphazene derivatives were formed by the reaction of sodium [2,2-methylenebis (4-chlorophenoxide)] and hexachlorocyclotriphosphazene.[23] No report exists on phosphorus–boron macrocycles with a C–B–O–P–C bond system, which may have several interesting applications. The eight-membered tetraoxadiphosphoadiborocane ring system in **3a–f** with two phosphoryl oxygens, being rich in electron density, can serve as a trap for heavy-metal cations, catalyst for electrophilic substituents, and molecular capsule for drugs. In this context, several of them (**3a–f**) have been synthesized by simple cyclization of aryl/alkyl phosphonic dichlorides (**2a–f**) with phenylboronic acid/K_2CO_3/I_2 in dry toluene at 60–70 °C (Scheme 1).

RESULTS AND DISCUSSION

Phenylboronic acid (**1**) reaction with K_2CO_3 converts it into its potassium salt. *O*-Phosphorylation of potassium salt of phenylboronate with phosphonic dichlorides **2a–f** at 60–70 °C in toluene in the presence of stoichiometric amount of I_2 led to formation of macrocycles **3a–f** with P–O–B–O bond system. The Lewis acidic nature of boronic acid helps to close the molecules by formation of a coordinate bond from the P=O lone pair electron to boron. Iodine was found to be essential for phosphorylation of $PhB(OK)_2$ at a faster rate and for completion of the reaction to form the products **3a–f** in relatively pure state in moderate yield. Iodine, by virtue of its affinity to potassium and chlorine atoms, weakens O–K and P–Cl bonds and facilitates nucleophlic attack of oxygen atoms on phosphorus with the formation of the macrocyclic ring (Scheme 1).

During the reaction of dichlorophenyl phosphine (**4**) with trivalent phosphorus with dipotassium salt of phenylboronic acid, we observed formation of acylic 1-phenylboryl (1-phenylboryl) phenylphosphinate (**6**), through the intermediate phenylphosphaboronic acid (**5**) rather then the expected cyclic product (**7**). Formation of



Scheme 2. Conformation test for the formation of acylic 1-phenylboryl (1-phenylboryl) phenylphosphinate.

6 was further confirmed by its esterfication with ethanol and $MgSO_4$ in dry toluene at 40–45 °C and isolation of the corresponding 1-ethoxy-1-phenylboryl (1-ethoxy-1-phenylboryl)phenylphosphinate (**8**) (Scheme 2).

In the conversion of **4** to **6** through the intermediate **5**, the trivalent phosphorus of the P–O–B bonds is rearranged to pentavalent phosphorus as O=P–B bond system.

Phenyl boronic acids, when reacted with same dichloride in the presence of NaH and I_2 in toluene at reflux temperature, gave poor product yields with long reaction time. When carried out without catalyst in dry toluene, the expected products were not formed.

The obtained crude products (**3a–f**) were purified by dissolving the crude product mixture of sodium salt of phenylboronic acid and liquid phosphoric dichloride in water and keeping it for 30 min, followed by extraction with diethyl ether. Evaporation of ether afforded pure products. They were fully characterized by elemental analysis; infrared (IR), ^{1}H, ^{11}B, ^{13}C, and ^{31}P–NMR, and mass spectral data.

A multiplet in the region δ 8.30–6.84 for aromatic protons and a broad singlet at δ 3.16–2.29 for phosphorus-linked aliphatic group protons is observed in the ^{1}H NMR. The presence of ^{31}P and ^{11}B NMR chemical shifts at δ 4.13–9.52[24] and δ 18.12–24.35[25] respectively is in good agreement with the proposed structures for **3a–f**.

EXPERIMENTAL

2,6-Diaryl/alkyl-4,8-diphenyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxa-diphosphadi-borocane-2,6-dione[24](3a–f)

A solution of aryl/alkyl phosphonic dichloride (4 mmol) in 10 mL of dry toluene was added dropwise to a stirred solution of dipotassium salt of phenylboronic acid (4 mmol) in 40 mL of dry toluene at 0 °C for 20 min. A stoichiometric amount of iodine[26,27] was added to the mixture, and its temperature was increased to

60–70 °C with stirring for 40–50 h. When thin-layer chromatographic (TLC) analysis indicated completion of the reaction, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure, washed with water, and extracted with diethyl ether (3 × 20 mL). The combined organic layer was concentrated in vacuum, and the residue was washed with hexane repeatedly to remove any residual impurities and recrystallized from diethyl ether to yield pure 2,6-diaryl/alkyl-4,8-diphenyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxadiphosphadiborocane-2,6-diones **(3a–f)**.

2,6-Dimethyl-4,8-diphenyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxadiphosphadiborocane-2,6-dione (3a). Molecular formula (MF): $C_{14}H_{16}B_2O_6P_2$; yield: 49%; mp: 159–161 °C. Anal. calcd. (%): C, 46.22; H, 4.43. Found: C, 46.15; H, 4.35, IR (KBr) (ν_{max} cm^{-1}): 1217 (P=O), 1094 (P-O); ^{31}P NMR (121 MHz, $CDCl_3$): δ 4.13; ^{11}B-NMR (64 MHz, $CDCl_3$): δ 22.82; ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62–7.16 (10H, m, Ar-H), 2.29–2.20 (6H, br, P-C<u>H</u>); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.63, 132.68, 127.98, 23.08; LCMS: m/z (%): 362 (29), [M – H$^+$], 360 (47), 314 (32), 270 (44), 226 (100), 156 (17), 112 (88).

2,6-Diethyl-4,8-diphenyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxadiphosphadiborocane-2,6-dione (3b). MF: $C_{16}H_{20}B_2O_6P_2$; yield: 63%; mp: 228–230 °C. Anal. calcd. (%): C, 49.04; H, 5.14. Found: C, 48.99; H, 5.12, IR (KBr) (ν_{max} cm^{-1}): 1222 (P=O), 1027 (P-O); ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.87; ^{11}B NMR (64 MHz, $CDCl_3$): δ 22.78; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75–7.17 (10H, m, Ar-H), 2.97 (4H, br, P-C<u>H</u>), 1.07 (6H, br, P-CH-C<u>H</u>); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.52, 128.02, 127.95, 40.02, 22.16; LCMS: *m/z* (%): 391 (23) [M$^+$], 390 [M – H$^+$] (47), 344 (53), 298 (50), 265 (59), 229 (100), 183 (61), 160 (51).

4,8-Diphenyl-2,6-dipropyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxadiphosphadiborocane-2,6-dione (3c). MF: $C_{18}H_{24}B_2O_6P_2$; yield: 71%; mp: 241–243 °C. Anal. calcd. (%): C, 51.48; H, 5.76. Found: C, 51.43; H, 5.81, IR (KBr) (ν_{max} cm^{-1}): 1218 (P=O), 1098 (P-O); ^{31}P NMR (121 MHz, DMSO-d_6): δ 9.52; ^{11}B NMR (64 MHz, DMSO-d_6): δ 22.89; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.65, 7.36 (10H, brs, Ar-H), 3.16 (4H, br, P-C<u>H</u>), 1.35 (4H, br, P-C-C<u>H</u>), 0.93 (6H, br, P-C-C-C<u>H</u>); ^{13}C NMR (75 MHz, DMSO-d_6): 129.88 (C-2, C-6), 129.18 (C-3, C-5), 128.18 (C-4), 49.30 (C-1′), 20.55 (C-2′), 14.18 (C-3′); LCMS: *m/z* (%): 419 (47) [M$^+$], 396 (25), 354 (15), 295 (57), 242 (100), 219 (15).

2,4,6,8-Tetraphenyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxadiphosphadiboro-cane-2,6-dione (3d). MF: $C_{24}H_{20}B_2O_6P_2$; yield: 59%; mp: 190–192 °C. Anal. calcd. (%): C, 59.07; H, 4.13. Found: C, 59.12; H, 4.21, IR (KBr) (ν_{max} cm^{-1}): 1216 (P=O), 1092 (P-O); ^{31}P NMR (121 MHz, DMSO-d_6): δ 4.91; ^{11}B NMR (64 MHz, DMSO-d_6): δ 24.95; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.65–6.84 (20H, br, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.73, 134.88, 130.48, 130.26, 124.82, 122.75; LCMS: *m/z* (%): 487 (89) [M$^+$], 473 (76), 441 (64), 419 (68), 396 (62), 373 (100).

2,6-Di(2-chlorophenyl)-4,8-diphenyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxadiphosphadi-borocane-2,6-dione (3e). MF: $C_{24}H_{18}B_2Cl_2O_6P_2$; yield: 64%; mp: 218–220 °C. Anal. calcd. (%): C, 51.76; H, 3.26. Found: C, 51.72; H, 3.31, IR (KBr) (ν_{max} cm^{-1}): 1216 (P=O), 1097 (P-O); ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.63; ^{11}B NMR (64 MHz, $CDCl_3$): δ 23.01; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–7.30

(18H, m, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): 127.9 (C-3 and C-5), 131.0 (C-4′), 132.5 (C-2 and C-6), 133.5 (C-2′ and C-6′), 134.7(C-4), 135.5 (C-3′ and C-5′); LCMS: m/z (%): 557 (87) [M + H$^+$], 488 (74), 443 (69), 420 (81), 374 (45), 338 (84), 296 (56), 273 (62), 181 (59), 135 (58), 112 (100).

2,6-Di(4-nitrophenyl)-4,8-diphenyl-1,3,5,7,2λ^5,6λ^5,4,8-tetraoxadiphosphadi-borocane-2,6-dione (3f). MF: $C_{24}H_{18}B_2N_2O_{10}P_2$; yield: 53%; mp: 255–256 °C. Anal. calcd. (%): C, 49.87; H, 3.14. Found: C, 49.84; H, 3.21, IR (KBr) (ν_{max} cm^{-1}): 1225 (P=O), 1091 (P-O); ^{31}P NMR (121 MHz, $CDCl_3$): δ 6.85; ^{11}B NMR (64 MHz, $CDCl_3$): δ 28.24; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30–7.22 (18H, m, Ar-H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.92, 143.39, 142.40, 140.54, 139.88, 136.39, 125.78, 123.84; LCMS: m/z (%): 599 (38) [MH$^+$ + 23], 569 (42), 558 (63), 476 (77), 429 (64), 384 (51), 307 (100).

1-Ethoxy-1-phenylboryl(1-ethoxy-1-phenylboryl)phenylphosphinate[24] (3)

A solution of dichlorophenyl phosphine (**4**, 4 mmol) in 10 mL of dry toluene was added dropwise to a stirred solution of phenylboronic acid (**1**, 4 mmol) in 40 mL of dry toluene, and K_2CO_3 (8 mmol) and stoichiometric amount amount of I_2[26,27] at 0 °C for a period of 20 min. Later the temperature was increased to 60 °C, and stirring was continued for 3–4 h to complete the formation of corresponding 1-phenylboryl (1-phenylboryl)phenylphosphinate **6** as indicated by TLC analysis. Triethylamine hydrochloride was separated from the reaction mixture by filtration. The filtrate containing **6** was used for further reactions.

The filtrate containing **6** was cooled before addition of ethanol (4 mmol), dry toluene (40 mL), and a catalytic amount of $MgSO_4$. It was stirred and allowed to warm up to room temperature. Stirring was continued for an additional 3–4 h at 40–45 °C. When TLC analysis indicated the consumption of the starting material, the solid formed was separated by filtration, and the filtrate was concentrated under reduced pressure. The residue was washed with water and recrystallized from diethyl ether to yield the required pure 1-ethoxy-1-phenylboryl (1-ethoxy-1-phenylboryl)-phenylphosphinate (**8**).

1-Phenylboryl,1-phenylboryl phenylphosphinate (6). MF: $C_{18}H_{17}B_2O_4P$; yield: 78%; mp: 181–183 °C, Anal. calcd. (%): C, 61.78; H, 4.90. Found: C, 61.81; H, 4.99, IR (KBr) (ν_{max} cm^{-1}): 3336 (O-H), 1299 (P=O), 703 (P-B); ^{31}P NMR (121 MHz, $CDCl_3$): δ 19.06; ^{11}B NMR (64 MHz, $CDCl_3$): δ 24.52, 30.14; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.39 (11H, t, Ar-H), 7.25 (4H, m, Ar-H); LCMS: m/z (%): 350 (34) [M$^+$], 309 (40), 257 (37), 238 (78), 197 (21), 141 (43), 120 (50), 83 (100).

1-Ethoxy-1-phenylboryl(1-ethoxy-1-phenylboryl phenylphosphinate (8). MF: $C_{22}H_{25}B_2O_4P$; yield: 72%; mp: 168–170 °C. Anal. calcd. (%): C, 65.08; H, 6.21. Found: C, 65.19; H, 6.34, IR (KBr) (ν_{max} cm^{-1}): 1308 (P=O), 701 (P-B); ^{31}P NMR (121 MHz, $CDCl_3$): δ 19.76; ^{11}B NMR (64 MHz, $CDCl_3$): δ 24.68, 30.45; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85–7.80 (4H, t, Ar-H), 7.45–7.34 (6H, m, Ar-H), 6.66 (4H, s, Ar-H), 4.29 (2H, d, J = 10.4, P-O-B-OC$\underline{H}_2$) and δ 3.97 (2H, dd, J = 10.8, J = 28.4 Hz, P-B-OC$\underline{H}_2$), 1.33 (3H, d, J = 4.8 Hz, CH_3) and 0.91 (3H, d, J = 4.4, CH_3); ^{13}C NMR

(75 MHz, $CDCl_3$): δ 135.5 (C-1, C-6), 134.8 (C-4), 133.5 (C-2′, C-6′), 132.5 (C-2″, C-6″), 131.0 (C-4′), 127.9 (C-3′, C-3″, C-5′ and C-5″), 78.8 (P-O-B-O-C), 78.6 (P-B-O-C), 22.1 (P-O-B-O-C-C), 20.5 (P-B-O-C-C); LCMS: m/z (%): 407 (25) [MH^+], 399 (35), 388 (18), 373 (25), 350 (17), 288 (61), 115 (29), 102 (100).

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