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Iodine catalyzed and tertiary butyl ammonium bromide promoted preparation of benzoxazaphosphininyl phenylboronates

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Abstract: Benzoxazaphosphininyl Phenylboronates were prepared by *O*-Phosphorylation of potassium salt of phenylboronic acid with cyclic phosphoromonochloridates in the presence of stoichiometric amount of Iodine and catalytic amount of tertiary butyl ammonium bromide at 50-60 °C in dry toluene.

Keywords: Phosphaphenylboronates; *O*-Phosphorylation; iodine; tertiary butyl ammonium bromide.

1. Introduction

Organoboron compounds were found to possess tremendous utility in organic synthesis. Boronic acids have a leading role in the synthesis[1,2] of organic molecules, analytical chemistry[3,4] and in biological systems as catalysts.[5,6] The discovery of new chemistry involved in Suzuki-Miyaura cross-coupling reaction combined with readily accessibility and ease of handling of products and reagents have established boronic acids and boronates as very useful intermediates in general organic synthesis.[2] Moreover, because of low toxicity and degradation in the environment to friendly boric acid, the organoboronates are regarded as "green compounds".[2]

Organophosphorus compounds such as Phosphoramides are important class of alkylating antitumor agents with activity against a broad spectrum of human cancers including slow-growing solid tumors.[7,8] The field so potential that facture research in it may lead to the discovery of potential drug activity against different bacterial and viral dieses manifestations. Organophosphorus compounds also constitute a family of promising flame retardants due to their unique combustion inhibition properties[9,10] They have been known to act in both gas phase and condensed phase and possibly

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concurrently in both phases[11,12] Synthesis of flame retardants with low flammability and melt dripping limits is in urgent need now-a-days and is gaining much attention.[13]

The idea that compounds embedded with organoboron/phosphorus structural features may have interesting properties led to the synthesis of several new organo phosphaboron esters by simple route through the reaction of phosphorochloridates with $PhB(OK)_2$ in presence of tertiary butyl ammonium bromide (TBAB).[14] These heterocycles containing exocyclic X=P-O-B and endocyclic O-P-N bond systems are of novel type which are likely to possess remarkable thermal stability and good flame retardant properties. Further, this work gains significance since so far only phosphorus heterocycles with P-B bond were reported and no mention was made on their fire/flame resistant/retarding properties.

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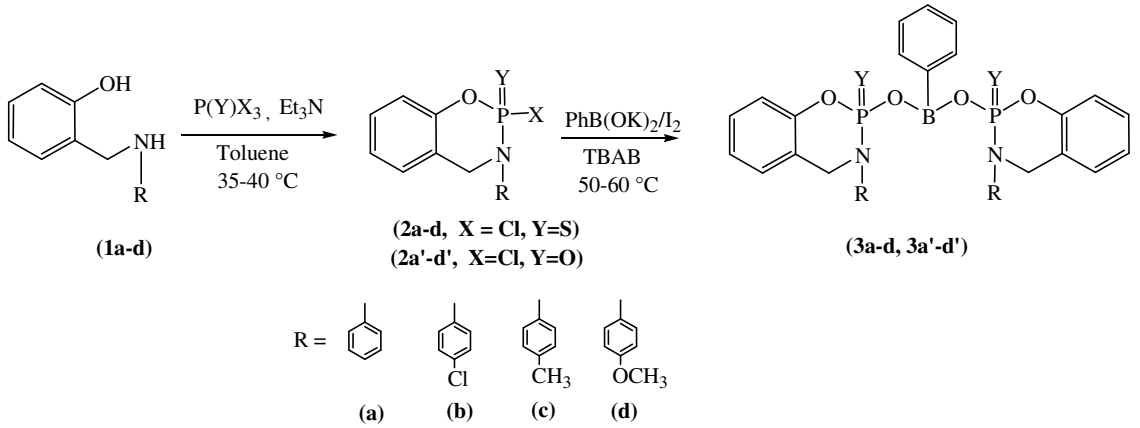
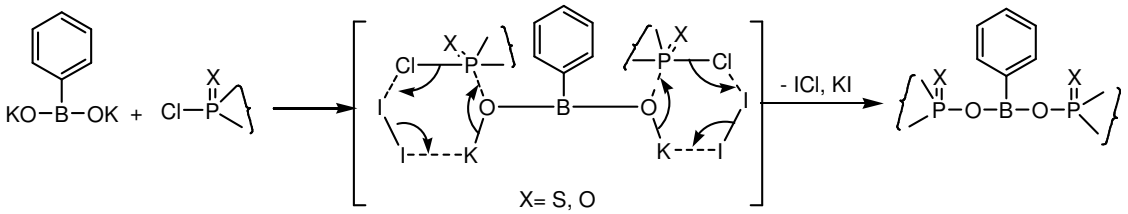
2. Results and Discussion

The synthesis of Benzoxazaphosphininyl Phenylboronates (**3a-d** and **3a'-d'**) involves, cyclisation of (2-[(4-substitutedanilino)methyl]phenol **(1a-d)** with phosphoryl and thio-phosphoryl chlorides in the presence of triethylamine in dry toluene at 35-40 °C to afford 2-chloro-3-(4-substititutedphenyl)-3,4-dihydro-2*H*-1,3,2λ^5-benzoxazaphosphinine-2-thione/one (**2a-e, 2a'-e'**) (Scheme 1). Reaction of **2a-e, 2a'-e'** with dipotassium salt of phenylboronic acid gave di[3-(4-substitutedphenyl)-2-thio/oxo-3,4-dihydro-2*H*-1,2λ^5-benzoxaphosphinin-2-yl]phenyl boronate **(3a-e** and **3a'-e')** (Scheme 1). All reactions are carried out in dry toluene at 40-60 °C in presence of stoichiometrically required quantity of Iodine and catalytic amount of TBAB.



Scheme 1. Synthesis of Benzoxazaphosphininyl Phenylboronates

O-Phosphorylation of potassium salt of phenylboronic acid with cyclic phosphoromonochloridates **2a-d, 2a'-d'** was found to occur selectively at the two '-OK' groups of $PhB(OK)_2$, *O*-Phosphorylation occurs selectively at one -OK' group of $PhB(OK)_2$, when the reaction was carried out initially at 0 °C and later at 50-60 °C in a mixture of toluene in the presence of stoichiometric amount of Iodine. Iodine was found to be essential for the completion of the reaction at a faster rate and to form the products **3a-d** and **3a'-d'** in relatively pure state and in high yield. Iodine appears weaken to the P-Cl bond and helps formation of P-O bond (Scheme 2). The infrared, multi nuclear NMR and Mass spectral studies have been done to confirm their structures (**3a-d** and **3a'-d'**).



Scheme 2. Mechanisum for P-O-B bond formation

All the compounds **3a-d** and **3a'-d'** exhibited characteristic absorption bands[14] for P=S and P=O functional groups in the normal region 788-754 and 1261-1215 cm^{-1} showing that they are not involved in hydrogen bonding. Characteristic absorption bands for P-O-(C_{ar}) and (P)-O-$C_{(ar)}$ stretching vibrations were observed in the region 999-912 and 1185-1174 cm^{-1} respectively[14] for **3a-d** and **3a'-d'**.

In the ^{1}H NMR spectra, the aromatic protons of **3a-d** and **3a'-d'**, resonated as multiples in the region δ 7.81-6.46. The chemical shift of C-4 methylene protons resonated as multiplets or doublet of doublets at δ 5.17-4.84, 4.87-4.44, indicating their non-equivalence and coupling with each other[14] in the six-membered chair conformation of the benzoxazaphosphinin-2-sulfide system (Fig.1).[14] The methyl, methoxy protons resonated as singlet the region δ 2.50-2.33, 4.20-4.13 respectively.

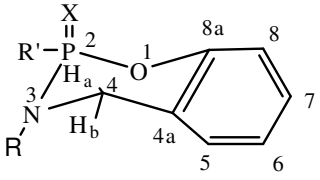


Figure 1 Numbering and Conformation of Benzoxazaphosphininyl Phenylboronates

The ^{13}C NMR chemical shifts were interpreted based on comparison with carbon chemical shifts of **1a-d**, additivity rules and intensity of the signals and coupling with phosphorus.[14] C-8a bonded to endocyclic oxygen gave signals at δ 151.7-149.1. The methylene C-4 chemical shift appears in region δ 59.3-45.5. The methyl and methoxy carbons substituted to the phenyl ring resonated at δ 41.0-53.6 and 20.0-22.1 respectively. The remaining carbon shifts were observed in the expected regions.[15]

Phosphorous resonance signals in **3a-d**, **3a'-d'** for P=S, P=O were observed at δ 45.89-60.80, 4.17-8.24 respectively.[14] Boron chemical shift for **3a-d**, **3a'-d'**, occurred at δ 16.80-22.40.[16] LCMS of **3a-d**, **3a'-d'** exhibited $M^{+\bullet}$ and characteristic daughter ion peaks at their respective expected m/z values.[17]

3. Conclusion

Iodine catalyzed and tertiary butyl ammonium bromide promoted Preparation method for Benzoxazaphosphininyl Phenylboronates has been reported. These novel heterocycles contain exocyclic X=P-O-B and endocyclic O-P-N bond systems are not reported so far and are likely to posses remarkable thermal stability and good flame retardant properties.

4. Experimental

Preparation of 2-chloro-3-(4-substititutedphenyl)-3,4-dihydro-2H-1,3,2λ^5- benzoxazaphosphinine -2-thione/one[14] (2a-d, 2a'-d'):

A solution of thiophosphoryl chloride/phosphoryl chloride (0.004 moles) in 10 mL of dry toluene was added drop wise to a stirred solution of respective phenol (**1a-d**) aminophenols 2-(anilinomethyl)-phenol (a), 2-[(4-chloroanilino)methyl]phenol (b), 2-(4-toluidinomethyl)phenol (c) and 2-[(4-methoxyanilino)methyl]phenol (d) (0.004 moles) in 40 mL of dry toluene and triethylamine (0.008 moles) at 0°C for a period of 20 min. Later temperature was increased to 55-60°C and stirring was continued for 3-4 h. Formation of corresponding cyclic-phosphorothio/oxychloridates (2-chloro-3-(4-substititutedphenyl)-3,4-dihydro- 2*H*-1,3,2λ^5-benzoxazaphosphinine-2-thione, **2a-d**/2-chloro-3-(4-substituted phenyl)-3,4-dihydro-2*H*-1,3,2λ^5-benzoxazaphos-phinin-2-one, **2a'-d'** was ascertained by TLC analysis. Triethylamine hydrochloride was separated from the reaction mixture by filtration. The filtrate containing **2a-d, 2a'-d'** was used for further reactions (after evaporation of the sample).

Preparation of di[3-(4-substtutedphenyl)-2-thio/oxo-3,4-dihydro-2H-1,2λ^5-benzoxaphos-phinin-2-yl] phenylboronate (3a-d, 3a′-d′):

The cyclic phosphorochloridate ***(2a-d, 2a'-d')*** of (2-[(4-substitutedanilino)methyl]-phenol (**1a-d**) (0.004 moles) in 20 mL of dry toluene was transferred into a 100 mL two necked round-bottomed flask equipped with a 50 mL pressure equalizing dropping funnel. The solution was cooled to 0 °C before addition of $PhB(OK)_2$ (0.002 moles), dry toluene (40 mL) and a catalytic amount of TBAB[14]and sufficient amount I_2.[18,19] The reaction mixture was allowed to warm up to room temperature and stirred for 20 min. It was then stirred for 20-22 h at 55-60 °C. When TLC analysis indicated the consumption of the starting material, the solid formed was filtered off and the filtrate was concentrated under reduced pressure. The residue obtained was washed with water and recrystallized from acetone to yield the required pure di[3-(4-substitutedphenyl)-2-thioxo/oxo-3,4-dihydro-2*H*-1,2λ^5-benzoxaphosphinin-2-yl]phenylboronate **(3a-d, 3a′-d′)**.

Di(3-phenyl-2-thioxo-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl)phenylboronate (3a): Yield: 54%; m.p. 163-165 ^{0}C. Anal: calcd. for $C_{32}H_{27}BN_2O_4P_2S_2$; C, 60.01; H, 4.25. Found: C, 59.85, H, 4.33; IR (KBr): 760 (P=S), 959, 1181 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (400MHz, $CDCl_3$): δ 7.47-7.05 (23H, m, Ar-H), 4.95 (2H, m, -2x^{4}Hb), 4.80 (2H, m, -2x^{4}Ha); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.8 (C-1"), 151.7 (C-8a), 144.3 (C-1'), 132.1 (C-2", C-6"), 131.9 (C-3", C-5") ,131.7 (C-2', C-6'), 130.4 (C-7), 129.9 (C-3', C-5'), 129.8 (C-6), 129.4 (C-4"), 127.4 (C-5), 127.0 (C-4'), 121.6 (C-8), 115.9 (C-4a), 55.8 (C-4); ^{31}P NMR (121 MHz, $CDCl_3$): δ 57.9; ^{11}B NMR (86 MHz, $CDCl_3$): δ 17.88; LCMS(EI): m/z (%): 640 (14)[MH^+], 623 (10), 487 (68), 460 (89).443 (51), 395 (13), 380 (20), 366 (21), 351 (21), 337 (24), 323 (17), 306 (27), 292 (25), 242 (100).

Di(2-oxo-3-phenyl-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl)phenylboronate (3a'): Yield: 46%; m.p. 138-140 °C; Anal: calcd. For $C_{32}H_{27}BN_2O_6P_2$; C, 63.18; H, 4.47. Found: C, 63.09; H, 4.53; IR (KBr): 1215 (P=O), 934, 1179 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (400MHz, $CDCl_3$): δ 7.43-6.77 (23H, m, Ar-H), 4.96 (2H, br, -2x^{4}Hb), 4.64 (2H, br, *J*=15.6 Hz, -2x^{4}Ha); ^{31}P NMR (121 MHz, $CDCl_3$): δ -4.17; ^{11}B NMR (86 MHz, $CDCl_3$): δ 16.23; LCMS(EI): m/z (%): 631 (100) [M^++Na], 553 (68), 473 (53), 390 (50), 276 (59).

Di[3-(4-chlorophenyl)-2-thioxo-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl]phenyl-boronate (3b): Yield: 51%; m.p. 121-123 °C; Anal: calcd. for $C_{32}H_{25}BCl_2N_2O_4P_2S_2$; C, 54.18; H, 3.55. Found C, 54.10; H, 3.41; IR (KBr): 756 (P=S), 936, 1182 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (400MHz, DMSO-d_6): δ 7.45-7.03 (17H, m, Ar-H), 6.46 (4H, d, *J*= 8.8 Hz, Ar-H), 4.92-4.75 (4H, m, -4x^{4}H); ^{31}P

NMR (121 MHz, DMSO-d_6): δ 51.50; ^{11}B NMR (86 MHz, DMSO-d_6): δ 19.17; LCMS(EI): m/z (%): 732 (20), [M^+ +Na], 699 (38), 641(32), 621(73), 543 (88), 506 (87), 461 (41), 432 (15), 324 (20), 310 (50), 268 (100);

Di[3-(4-chlorophenyl)-2-oxo-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl]-phenyl-boronate (3b'): Yield: 57%; m.p. 96-98 °C; Anal: calcd. for $C_{32}H_{25}BCl_2N_2O_6P_2$; C, 56.75; H, 3.72. Found C, 56.68; H, 3.81; IR (KBr): 1221 (P=O), 928, 1185 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (500MHz, $CDCl_3$): δ 7.38-7.11 (17H, m, Ar-H), 6.54 (4H, s, Ar-H), 4.94 (2H, dd, $J_{Ha,Hb}$= 13.2 Hz, $J_{P,Hb}$= 28.1Hz, -2x^{4}Hb), 4.59 (2H, dd, $J_{Ha,Hb}$= 14.9, $J_{P,Hb}$= 24.68 Hz, -2x^{4}Ha); ^{13}C NMR (400 MHz, $CDCl_3$): δ 150.1 (C-1''), 145.2 (C-1'), 134.9 (C-2'', C-6'') 132.2 (C-3'', C-5''), 130.3 (C-4''), 129.4 (C-5), 128.5 (C-7), 127.4 (C-3', C-5'), 124.1 (C-4'), 122.5 (C-6), 122.0 (C-8), 121.9 (C-4a), 114.2 (C-2', C-6'), 51.9 (C-4); ^{31}P NMR (121 MHz, $CDCl_3$): δ 19.76; ^{11}B NMR (86 MHz, $CDCl_3$): δ 21.97; LCMS(EI): m/z (%): 679 (42) [MH^++2], 677 (100) [MH^+].

Di[3-(4-methylphenyl)-2-thioxo-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl]phenyl-boronate (3c): Yield: 43%; m.p. 103-105 °C. Anal: calcd. For $C_{34}H_{31}BN_2O_4P_2S_2$; C, 61.09; H, 4.67. Found: C, 60.98; H, 4.76; IR (KBr): 754 (P=S), 955, 1182 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (400MHz, DMSO-d_6): δ 7.55-6.71 (21H, m, Ar-H), 4.92-4.87 (2H, m, -4x^{4}H), 4.79-4.55 (2H, m, -2x^{4}Ha), 2.50 (6H, s, 2xAr-CH_3); ^{31}P NMR (121 MHz, DMSO-d_6): δ 60.08; ^{11}B NMR (86 MHz, DMSO-d_6): δ 22.40; LCMS(EI): m/z (%): 691 (18) [M^++Na], 641 (41), 621 (32), 561 (100), 516 (24), 421 (35), 305 (21), 266 (12), 232 (44).

Di[3-(4-methylphenyl)-2-oxo-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl]phenyl-boronate (3c'): Yield: 37%; m.p. 114-116 °C; Anal: calcd. For $C_{34}H_{31}BN_2O_6P_2$; C, 64.17; H, 4.91. Found: C, 63.08; H, 4.99; IR (KBr): 1215 (P=O), 956, 1179 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (400MHz, DMSO-d_6): δ 7.29 (21H, br, Ar-H), 4.91 (2H, br, -2x^{4}Hb), 4.80 (2H, br, -2x^{4}Ha), 2.33 (6H, s, Ar-CH_3); ^{13}C NMR (75 MHz, DMSO-d_6): δ 154.0 (C-1''), 150.0 (C-8a), 137.7 (C-1'), 134.2 (C-2'', C-6''), 134.0 (C-3'', C-5''), 130.7 (C-2', C-6'), 132.4 (C-7), 130.1 (C-3', C-5'), 128.8 (C-6), 127.3 (C-4''), 124.6 (C-5), 124.2 (C-4'), 123.0 (C-8), 122.1 (C-4a), 45.5 (C-4), 20.4 (Ar-C); ^{31}P NMR (121 MHz, DMSO-d_6): δ 3.40; ^{11}B NMR (86 MHz, DMSO-d_6): δ 16.80; LCMS(EI): m/z (%): 635 (70) [M-H], 568 (59), 500 (30), 445 (38), 422 (50), 367 (61), 360 (74), 307 (85), 238 (100).

Di[3-(4-methoxyphenyl)-2-thioxo-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl]phenyl-boronate (3d): Yield: 47%; m.p. 110-112 °C; Anal: calcd. for $C_{34}H_{31}BN_2O_6P_2S_2$; C, 58.30; H, 4.46. Found: C, 58.26; H, 4.51; IR (KBr): 754 (P=S), 958, 1180 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (400MHz, DMSO-d_6): δ 7.75-7.07 (21H, m, Ar-H), 4.86 (2H, br, -2x^{4}Hb), 4.53 (2H, br, -2x^{4}Ha), 4.13 (6H, s, 2xAr-OCH_3); ^{13}C NMR (75 MHz, DMSO-d_6): δ 149.86 (C-1''), 149.1 (C-8a), 134.0 (C-1'), 132.6 (C-2'', C-6''),129.6 (C-3'', C-5''), 129.3 (C-2', C-6'), 127.5 (C-7), 128.5 (C-3', C-5'), 126.7 (C-6), 125.6 (C-4''), 125.3 (C-5), 124.9 (C-4'), 124.5 (C-8), 121.0 (C-4a), 54.8 (C-4), 53.6 (Ar-O-C); ^{31}P NMR (121 MHz, DMSO-d_6): δ 45.89; ^{11}B NMR (86 MHz, DMSO-d_6): δ 21.77; LCMS(EI): m/z (%): 701 (91)[MH^+], 699 (100)[M-H]$^+$, 641 (22), 621 (26), 545 (53), 312 (69), 268 (95), 232 (70).

Di[3-(4-methoxyphenyl)-2-oxo-3,4-dihydro-2H-1,3,2λ^5-benzoxazaphosphinin-2-yl]phenyl-boronate (3d'): Yield: 42%; m.p. 71-73 °C; Anal: calcd. for $C_{34}H_{31}BN_2O_8P_2$; C, 61.10; H, 4.67. Found: C, 59.98; H, 4.73. IR (KBr): 1215 (P=O), 954, 1182 cm^{-1} (P-O-$C_{aromatic}$); ^{1}H NMR (400MHz, $CDCl_3$): 7.55-7.06 (21H, m, Ar-H), 5.10-4.79 (4H, m, 4x^{4}H), 4.20 (6H, s, 2xAr-OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.20 (C-1''), 141.6 (C-1'), 129.4 (C-2'', C-6'') 129.2, (C-3'', C-5''), 129.1 (C-2', C-6'), 127.8 (C-7), 127.2, (C-3', C-5'), 127.1 (C-6), 126.7(C-4''), 124.8 (C-5), 121.3 (C-4'), 119.1 (C-8), 119.0 (C-4a), 53.8 (C-4), 53.2 (Ar-O-C); ^{31}P NMR (121 MHz, $CDCl_3$): δ 0.92; ^{11}B NMR (86 MHz, $CDCl_3$): δ 19.18; LCMS(EI): m/z (%): 691 (61) (M+Na), 689 (100).

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