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Boric acid Catalyzed efficient Synthesis of Dipyrromethanes in Water

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Abstract

A simple and efficient methodology has been demonstrated for the synthesis of dipyrromethanes. Boric acid catalyzed condensation of two equivalent of pyrrole with one equivalent of aldehyde gives dipyrromethane in good yield at room temperature in aqueous medium.

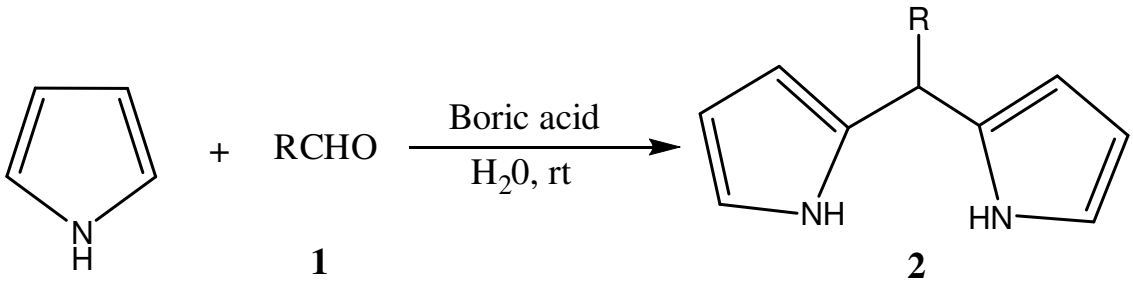
Keywords: Boric acid, dipyrromethane, condensation reaction, green chemistry, pyrrole, aldehyde.

Introduction

Dipyrromethanes have been extensively used as prime precursors in the synthesis of various functional porphyrins[1] and related macrocyclic molecules such as calixpyrroles[2] and corroles[3]. Meso substituted dipyrromethanes have also been utilized in various fields such as material science[4], optics[5], medicine[6], organometallic synthesis and catalysis[7]. Various methodologies have been developed for the synthesis of dipyrromethanes which are based on the acid-catalyzed condensation of pyrrole with carbonyl compounds. Various acid catalysts such as $BF_3.OEt_2$[8], trifluoroacetic acid[9], *p*-toluene sulfonic acid[10], ionic liquid [Hmim] BF_4[11] and hydrochloric acid[12] have been used to achieve the dipyrromethanes from the reaction of pyrrole and carbonyl compounds. However, these methods suffer from many disadvantages such as use of expensive reagents, low yield of product, exotic reaction conditions and use of pyrrole in excess. A careful time control is required to prevent the formation of other oligomeric side products. The yields are reduced on prolonging the reaction time due to the formation of oligomeric by-products. This is attributed to the sensitivity of pyrrole towards acids[13]. There is a great upsurge of interest to develop a simpler, economic viable and high yielding method for the synthesis of dipyrromethanes at lowest pyrrole/aldehyde ratio.

Recently, there has been growing interest in development of green synthetic methodologies[14]. In particular, organic synthesis in aqueous medium is receiving more attention in terms of its green aspects[15]. Boric acid is also considered as an ecofriendly reagent due to its excellent solubility in water, nontoxic nature, easy availability, inexpensiveness and easiness for work up. Boric acid has been used as an acid catalyst for a number of synthetic transformations such as transamidation,[16] aza-Michael addition[17], thia-Michael addition,[18] Biginelli reaction[19] and Ugi three-component reaction[20]. Herein, we report a simple, convenient and efficient method for the synthesis of dipyrromethanes by boric acid catalyzed condensation of pyrrole with different aldehydes in aqueous medium at room temperature (Scheme 1).

Melting point sof compounds are uncorrected and obtained on Thomas Hoover Unimelt capillary melting point apparatus. Infrared spectra are recorded on Perkin-Elmer FT-2000 spectrometer and ν_{max} in expressed in cm^{-1}. The ^1H NMR spectra are recorded on Jeol-delta-400 spectrometer using tetramethylsilane (TMS) as an internal standard. The chemical shifts (δ) are expressed in ppm and spectra are recorded in $CDCl_3$ solvent. The mass spectra areobtainedon Micromass LCT KC455. The starting materials are purchased from Spectrochem Chemicals India. The pyrrole is purified by distillation prior to use and analytical grade solvents are used.



1 **2**

Scheme-1
Synthesis of dipyrromethanes (2a-2k) by condensation of pyrrole with aldehydes (1a-1k)

Material and Methods

General experimental procedure for synthesis of dipyrromethanes (2a-2k): Pyrrole (2 equiv., 34.6ml, 0.5mol) was added to aqueous solution of boric acid (12g, 0.2mol in 500mlof water) followed by addition of aldehyde (**1a-1k**) (0.25mol) to it. For the synthesis of **2a**, formaldehyde solution (37%) was used. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by thin layer chromatographic (TLC) analysis. After the indicated time (table 3), the aqueous layer was extracted with dichloromethane. The dichloromethane extract was subjected to column chromatography. Elution of column with petroleum ether-chloroform (varying ratio) gives dipyrromethane (**2a-2k**).

Dipyrromethane (2a): White solid; mp: 72-73 °C (lit[21] 74°C); ^{1}H NMR (400 MHz) δ= 3.97 (s, 2H, CH_2), 6.03 (s, 2H, *β*-pyrrolic-C-3-H), 6.14 (m, 2H, *β*-pyrrolic-C-4-H), 6.64 (m, 2H, *α*-pyrrolic-C-5-H), 7.80 (br s, 2H, NH); ESI-MS (m/z): calculated for $C_9H_{10}N_2$ = 146.0844,observed $[M+Na]^+$ = 169.0736.

5-Phenyl dipyrromethane (2b): White solid; mp: 100-101oC (lit.[22] 100°C); IR (KBr): 3342, 3053, 1458, 1257, 1099, 1115, 1028, 738, 726 cm^{-1}; ^{1}H NMR (400 MHz) δ = 5.44 (s, 1H, CH), 5.94 (s, 2H, *β*-pyrrolic-C-3-H), 6.16 (m, 2H, *β*-pyrrolic-C-4-H), 6.67 (m, 2H, *α*-pyrrolic-C-5-H), 7.20 (m, 5H, Ar-H), 7.83 (br s 2H, NH); ESI-MS (m/z): calculated for $C_{15}H_{14}N_2$ = 222.1157,observed $[M+Na]^+$ = 214.1067.

5-(4-Chlorophenyl) dipyrromethane (2c): yellow powder; mp: 112-113°C (lit[22] 112–114°C), IR (KBr) 3378, 2960, 2862, 1643, 1485, 1406, 1251, 1087, 1019, 766 cm^{-1}; ^{1}H NMR (400 MHz) δ = 5.42 (s, 1H, CH), 5.89 (br s, 2H, *β*-pyrrolic-C-3-H), 6.15 (dd, J = 2.8, 5.6, Hz, 2H, *β*-pyrrolic-C-4-H), 6.65 (dd, J = 2.8, 4.2, Hz, 2H, *α*-pyrrolic-C-5-H), 7.15 (d, J = 8.1, Hz, 2H, Ar-H), 7.32 (d, J = 8.1, Hz, 2H, Ar-H), 7.83 (br s, 2H, NH); ESI-MS (m/z): calculated for $C_{15}H_{13}ClN_2$ = 256.0767,observed $[M+H]^+$ = 257.0742.

5-(4-Methoxyphenyl) dipyrromethane (2d): White solid; mp: 99-100 °C (lit[21] 98-99 °C.); IR (KBr): 3347, 3093, 1612, 1514, 1462, 1256, 1178, 1113, 1033, 845, 738 cm^{-1}; ^{1}H NMR (400 MHz) δ = 3.89 (s, 3H,oCH_3), 5.49 (s, 1H CH), 6.00 (s, 2H, *β*-pyrrolic-C-3-H), 6.26 (m, 2H, *β*-pyrrolic-C-4-H), 6.77 (m, 2H, α-pyrrolic-C-5-H), 6.94 (d, *J* = 8.8, Hz, 2H Ar-H), 7.23 (d, *J* = 8.04, Hz, 2H Ar-H), 8.02 (br s, 2H, NH); ESI-MS (m/z): calculated for $C_{14}H_{16}N_2O$ = 252.1263,observed $[M+Na]^+$ = 275.1098.

5-(4-Bromophenyl) dipyrromethane (2e): Yellow powder; mp: 125-126°C (lit[22] 123–124oC); IR (KBr) 3373, 3097, 2959, 2923, 2862, 1707, 1483, 1405, 1082, 1021, 767, 723 cm^{-1}; ^{1}H NMR (400 MHz) δ = 5.43 (s, 1H, CH), 5.92 (s, 2H, *β*-pyrrolic-C-3-H), 6.16 (dd, J= 2.7, 5.6, Hz, 2H, *β*-pyrrolic-C-4-H), 6.67 (dd, J = 2.6, 4.2, Hz, 2H, α-pyrrolic-C-5-H), 7.15 (d, J= 8.2, Hz, 2H, Ar-H), 7.48 (d, J = 8.2, Hz, 2H, Ar-H), 7.81 (br s, 2H, NH); ESI-MS (m/z): calculated for $C_{15}H_{13}BrN_2$ = 300.0262,observed $[M+H]^+$ = 301.0283.

5-(4-nitrophenyl) dipyrromethane (2f): Yellow powder; mp: 159–160oC (lit[22] 159-160oC), IR (KBr) 3389, 3362, 3101, 1598, 1517, 1345, 1123, 1027, 808, 739 cm^{-1}; ^{1}H NMR(400 MHz) δ = 5.56 (s, 1H, CH), 5.87 (s, 2H, *β*-pyrrolic-C-3-H), 6.18 (dd, J = 2.8, 5.7, Hz, 2H, *β*-pyrrolic-C-4-H), 6.75 (dd, J = 2.8, 4.2, Hz, 2H, α-pyrrolic-C-5-H), 7.36 (d, J = 8.6, Hz, 2H, Ar-H), 8.01 (br s, 2H, NH), 8.14 (d, J = 8.8, Hz, 2H, Ar-H); ESI-MS (m/z): calculated for $C_{15}H_{13}N_3O_2$ = 267.1008,observed $[M]^+$ = 267.1109.

5-(4-methylphenyl)dipyrromethane (2g): Colourless crystal; mp: 110-112 °C (lit[22] 110 °C); IR (KBr): 3345, 2957, 1462, 1253, 1118, 854, 734, 728 cm^{-1}; ^{1}H NMR (400 MHz) δ = 2.06 (s, 3H, -CH3), 5.98 (d, 2H, *β*-pyrrolic C-3-H), 6.14 (m, 2H, *β*-pyrrolic C-4-H), 6.69 (d, *J* =2.2, Hz, 2H, *α*-pyrrolic C-5-H), 7.14 (m, 5H. Ar-H), 7.38 (br s, 2H, NH); ESI-MS (m/z): calculated for $C_{16}H_{16}N_2$) = 236.1313, observed $[M]^+$ = 236.5767.

5-(4-Fluorophenyl) dipyrromethane (2h): Brown crystals; mp: 81–82oC (lit[22] 80-81°C); IR (KBr) 3416, 2930, 1608, 1496, 1450, 1287, 1174, 1100, 964, 764, 558 cm^{-1}; ^{1}H NMR (400 MHz) δ = 5.47 (s, 1H, CH), 5.88 (br s, 2H, *β*-pyrrolic C-3-H), 6.17 (dd, J 2.7, 5.8, 2H, *β*-pyrrolic C-4-H), 6.67 (br s, 2H, *α*-pyrrolic C-5-H), 7.02–7.07 (m, 2H, Ar-H), 7.18–7.24 (m, 2H, Ar-H), 7.80 (s, 2H, NH); ESI-MS (m/z): calculated for $C_{15}H_{13}FN_2$ = 240.1063,observed $[M]^+$ = 240.1562.

5-Pentafluorophenyldipyrromethane (2i): Gray solid; mp: 130-131 °C (lit[21] 131-132 °C); IR (KBr): 3343, 2956, 1460, 1255, 1117, 853, 731, 727 cm^{-1}; ^{1}H NMR (400 MHz) δ = 5.87 (s, 1H, CH), 6.00 (s, 2H, *β*-pyrrolic, C-3-H) 6.13-6.16 (m, 2 H, *β*-pyrrolic, C-4-H), 6.70 (d, *J* = 1.84 Hz, 2H, *α*-pyrrolic, C-5-H), 8.14 (br s, 2H, NH); ESI-MS (m/z) = calculated for $C_{15}H_9F_5N_2$) = 312.0686,observed $[M+H]^+$ = 313.1068.

5-(2,4,6-Trimethylphenyl) dipyrromethane (2j): Grey solid; mp: 166-168 °C(lit[21] 166-167 °C); IR (KBr): 3343, 2956, 1460, 1255, 1117, 853, 731, 727 cm^{-1}; ^{1}H NMR (400 MHz) δ = 2.05 (s, 6 H, CH_3), 2.27 (s, 3H, CH_3), 5.91 (s, 1H, CH), 6.00 (s, 2H, *β*-pyrrolic-C-3-H) 6.15-6.18 (m, 2 H, *β*-pyrrolic-C-4-H), 6.65 (s, 2 H, *α*-pyrrolic-C-5-H), 6.86 (s, 2H, Ar-H), 7.93 (br s, 2H, NH); ESI-MS (m/z): calculated for $C_{18}H_{20}N_2$ = 264.1626,observed $[M+H]^+$ = 265.1892.

5-(4-*tert*-butyl-phenyl) dipyrromethane (2k): Colourless crystal; mp: 162-163 °C (lit[23] 160 °C); IR (KBr): 3343, 2956, 1460, 1255, 1117, 853, 731, 727 cm^{-1}; ^{1}H NMR (400 MHz) δ = 1.28 (s, 9H, -($C(CH_3)_3$), 5.43 (s, 1H, CH), 5.90 (s, 2H, *β*-pyrrolic C-3-H), 6.13 (d, *J*= 2.92 Hz, 2H, *β*-pyrrolic C-4-H), 6.66 (s, 2H, *α*-pyrrolic C-5-H) 7.11 (d, J = 8.08 Hz, 2H. Ar-H), 7.29 (d, J = 8.08 Hz, 2H. Ar-H), 7.93 (br s, 2H, NH); ESI-MS (m/z): calculated for $C_{19}H_{22}N_2$ = 278.1783 observed $[M+Na]^+$ = 301.4315.

Results and Discussion

The condensation of formaldehyde (37%) (1a) with pyrrole in absence of boric acid did not give any product even after 120 min. However, the presence of boric acid facilitated the condensation reaction leading to formation of dipyrromethane (2a) in 90% yield in 30 min. at room temperature (table-3) in aqueous medium. The condensation of benzaldehyde (1b) with pyrrole in similar conditions gave *meso*-phenyldipyrromethane (2b) in 85% yield in 40 min (tabl-3). The amount of boric acid was optimized by performing the condensation reaction with different mol% of boric acid (table-1). The use of 10mol% boric acid can effectively catalyze the condensation reaction to give 2b. The reaction was also performed in different solvents (table-2). It took longer time for completion of reaction and yield of the product (2b) was also low due to the formation of side products like tripyrromethane and polypyrrole. In chloroform solvent, a black tarry side product polypyrrole was also detected. It was observed that polar protic solvents such as methanol, ethanol and water are better solvents than aprotic solvents and aqueous medium providesoptimum conditions for the synthesis of dipyrromethanes.

To study the scope of the reaction, various aromatic and aliphatic aldehydes were used in condensation reaction with pyrrole using boric acid as catalyst in water at room temperature (table-3). Different meso substituted dipyrromethanes were obtained in good yields and their structures were identified by their melting points (mp) and different spectroscopic analysis (IR, ^{1}H-NMR and MS) that concur with the published data[21-22].

Table-1
Effectof concentartionof boric acidon the condensationof pyrrole with formaldehyde (1a)[a]

Entry	Boric acid (mol%)	Time (min)	Yield of 2a (%)[b]
1	0	120	0
2	5	60	75
3	10	30	90
4	15	30	91

[a] reactions condition: formaldehyde (37%, 0.25 mol), pyrrole (0.5 mol) and aqueous solution of boric acid at room temperature.
[b] solated yields

Table-2
Effect of solventon the yield of dipyrromethane (2b)[a]

Entry	Solvent	Time (min)	Yield of 2a (%)[b]
1	$CHCl_3$	50	52
2	MeOH	40	77
3	EtOH	40	75
4	CH_3CN	40	68
5	THF	60	60
6	EtOAc	70	54
7	H_2O	40	85

[a]reactions condition: formaldehyde (37%, 0.25 mol), pyrrole (0.5 mol) and boric acid (0.2mol) at room temperature in different solvents. [b]isolated yields

Table-3
Synthesis of different dipyrromethanes (2a-2k) by condensation of pyrrole and aldehyde (1a-1k) [a]

Entry	-R	Product (2)	Time (min)	Yield (%)[b]	mp (^{o}C)
1	H	2a	30	90	72-73
2	C_6H_5	2b	40	85	100-101
3	4-ClC_6H_4	2c	35	78	112-113
4	4-$OCH_3C_6H_4$	2d	35	88	99-100
5	4-BrC_6H_4	2e	35	82	125-126
6	4-$NO_2C_6H_4$	2f	45	79	159-160
7	4-$CH_3C_6H_4$	2g	35	89	110-112
8	4-FC_6H_4	2h	40	77	81-82
9	C_6F_5	2i	30	94	130-131
10	2,4,6-$(CH_3)_3C_6H_2$	2j	35	72	166-168
11	4-$C(CH_3)_3C_6H_4$	2k	40	78	162-163

[a] reactions condition: formaldehyde (37%, 0.25 mol), pyrrole (0.5 mol) and aqueous solution of boric acid (0.2mol in 0.5Lof H_2O) at room temperature. [b]isolated yields

The condensation of pyrrole with aldehyde proceeds with nucleophilic attack of α-position of pyrrole to carbonyl carbon of aldehyde followed by protonation and subsequent reaction with second mole of pyrrole to form dipyrromethane products (**2a-2k**). The condensation takes place at the inter phase for ganic and aqueous layers. Dipyrromethane so formed at the inter phase moves to organic layer and hence further reaction of dipyrromethane with pyrrole to form higher homologues is prevented. However, the formation of some undesirable products such as tripyrromethane and other higher oligomers were observed on prolonging the reaction time. A cautious time control is needed to obtain dipyrromethane product selectively. The formations of these compounds were detected in synthesis of dipyrromethanes or porphyrins as by-products[24].

Conclusion

The present work demonstrates a green, convenient and efficient methodology for the synthesis of dipyrromethanes by condensation of two equivalents of pyrrole with one equivalent of aldehyde in aqueous medium. Boric acid which is a very mild, easily available and non-toxic acid was used to catalyze the condensation reactions. Boric acid being water soluble makes the separation procedure for dipyrromethanes very convenient, easy and simple. This method provides an important synthetic tool for the synthesis of dipyrromethanes at minimum pyrrole/aldehyde ratio.

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