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Der Pharma Chemica, 2015, 7(8):175-180
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Phenylboronic acid-catalyzed a four component synthesis of pyrano[2,3-c] pyrazole derivatives in aqueous media: an eco-friendly method

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ABSTRACT

An efficient and eco-friendly one-pot synthesis of 6-amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile derivatives by four-component phenylboronic acid-catalysed reactions of aryl aldehydes, malononitrile, ethyl acetoacetate and hydrazine hydrate in aqueous media is described. This method provides several advantages such as shorter reaction times, excellent yields, and a simple workup procedure.

Keywords: pyrano[2,3-c]pyrazole; aqueous media; multicomponent reaction and phenylboronic acid.

INTRODUCTION

Multicomponent reactions (MCRs) are those reactions whereby three or more different reactants combine in a sequential manner and in the one-pot procedure to give highly selective products that contain the majority of the atoms of the starting materials [1]. Undoubtedly, MCRs are the most suitable and efficient strategies for the synthesis of highly complex molecules, in which several bonds are formed in a chain of events and without the necessity of isolating the intermediates. Thus avoiding the complicated purification operations and allowing savings of energy, time and matter (principle pillars of green chemistry), making them an interesting tool in combinatorial chemistry.

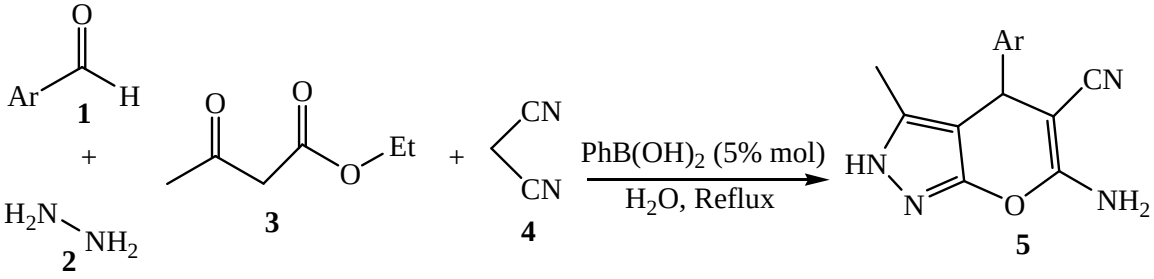
In recent years, for their anticancer [2], anti-inflammatory [3], antimicrobial [4], analgesic [5], molluciadal [6], inhibitory human Chk1 kynase [7] and antifungal [8] properties, the dihydropyrano[2,3-c]pyrazole derivatives synthesis has experienced a resurgence of interest by the organic chemists and multicomponent reactions are most commonly used for this purpose.

Since the first syntheses, reported by Junek and Aigner in 1973 [9] and then by H. Otto in 1974 [10], numerous approaches have been reported in the literature for the synthesis of these heterocyclic system including the two [11], three [12-13] and four [14-15] components polycondensations. Moreover, many catalysts and operating conditions were used for implementation of the various reactions. Among these catalysts used include trietylamine in ethanol [16], piperidine in water and ethanol [14b, 17], N-methylmorpholine [18], imidazole in water [19], glycine [20], □-cyclodextrin [21], L-proline [22], scandium triflate in water [23], ammonium acetate in ethanol [24], sodium benzoate in aqueous medium [25], $H_4[SiW_{12}O_{40}]$ [26], $La_{0.7}Sr_{0.3}MnO_3$ [27], and Palladium(0) [28] nanoparticules, lime juice [29], and cetyltrimethylammonium chloride [30]. Some methods without catalysts have also successfully applied to the synthesis of this class of compounds such as in water at reflux [31], in a water:ethanol mixture at 100°C [3], under ultrasonic [32] and microwave [33] irradiations.

Some of these methods are effective, elegant, with good yields and environmentally friendly but others suffer from one or more drawbacks such as the use of organic solvents or toxic reagents, strong acid or base catalysts, unsatisfactory yields, prolonged reaction time, requirement of special apparatus (e.g. microwave and ultrasound

irradiations) and harsh reaction conditions procedures. These facts prompted us towards further investigation in search for environmentally friendly, more effective procedure accompanied with higher yields, for the preparation of this kind of compounds.

Boronic acids have been used as catalysts in several chemical transformations [34-37]. As a consequence of our interest in the synthesis of heterocyclic compounds via green chemical methodologies, and to further enlarge the application of phenylboronic acid as catalyst in MCRs [38-40], we wish to report herein the one-pot synthesis of pyrano[2,3-c]pyrazole derivatives **5** via a four-component reaction of aryl aldehydes, malononitrile, hydrazine hydrate and ethyl acetoacetate catalysed by phenylboronic acid in aqueous media (Scheme 1).



Scheme 1. The synthesis of pyrano[2,3-c]pyrazole derivatives 5

MATERIALS AND METHODS

2.1 Chemicals and Materials

All chemicals were used without further purification. Melting points were determined on Banc Kofler apparatus and are uncorrected. IR spectra were recorded on Chimadzu FT IR 8201 PC spectrometer in KBr with absorptions in cm^{-1}. ^1H NMR and ^{13}C NMR spectra were obtained at 250.13 and 62.9 MHz respectively with a Bruker DPX-250 (AVANCE) spectrometer using DMSO-d_6 as solvent and TMS as an internal standard. *J* values are in *Hz*. Chemical shifts are expressed in *ppm* downfield from internal standard TMS.

2.2 Synthesis and characterization

The mixture of aldehyde (2 mmol), malononitrile (2 mmol), ethyl cyanoacetate (2 mmol), hydrazine hydrate (2 mmol) and $PhB(OH)_2$ (5 mol%) in water (5 ml) was refluxed for an appropriate time (Table **1**). After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature, the formed solid was filtered, washed with a mixture of ethyl acetate/hexane (2/8). The crude products were purified by crystallization from ethanol/water (1/1) to afford the pure products **5**.

All the compounds were characterized by spectroscopic and physical data, which were found to be identical to those described in the literature.

Spectral analyses for all synthesized compounds

6-amino-5-cyano-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c]pyrazole (5a): IR (KBr): ν: 3373; 3310; 3172; 2172; 2192; 1648; 1489; 1401. ^1H NMR: 12,09 (s,1H); 7,10-7,30 (m, 5H) ;6,80 (s, 2H); 4,6 (s, 1H) ; 1,8 (s, 3H) . ^{13}C NMR: 161.31; 155.21; 144.89; 136.03; 128.89; 127.91; 127.19; 121.24; 98.09; 57.64; 36.67; 10.17.

6-amino-5-cyano-3-methyl-4-(4-bromophenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5b):IR (KBr): ν: 3394; 2187; 1600; 1502; 1488; 1260; 1056. ^1H NMR: 12.15 (s, 1H), 7.41 (d, 2H, *J* = 7.2), 7.11 (d, 2H, *J* = 7.2), 6.82 (s, 2H), 4.57 (s, 1H), 1.78 (s, 3H). ^{13}C NMR: 161.17, 154.95, 143.87, 136.16, 131.57, 129.92, 120.98, 120,17 ; 97.26, 57.11, 36.06, 10.04.

6-amino-5-cyano-3-methyl-4-(4-methoxyphenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5c): IR (KBr): ν: 3359; 2191; 1639; 1600; 1504; 1392; 1257. ^1H NMR: 12.11 (s, 1H), 7.03 (d, 2H, *J* = 8.2), 6.78 (d, 2H, *J* = 8.2), 6.60 (s, 2H), 4.45 (s, 1H), 3.68 (s, 3H), 1.75 (s, 3H). ^{13}C NMR: 160.7; 158.0; 154.8, 136.3; 135.6; 128.5; 120.9; 113.6; 97.7; 57.9; 54.9; 35.7; 9.8.

6-amino-5-cyano-3-methyl-4-(4-hydroxyphenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5d): IR (KBr): ν: 3390; 3300; 3140; 2176; 1646; 1599; 1408. ^1H NMR: 12 (s, 1H) ; 9,30 (s, 1H) ; 6,8 (s, 2H) ; 6,9 (d, 2H, *J* = 8,4) ; 6,7 (d, 2H, *J* = 8,4) ; 4,4 (s, 1H) ; 1,8 (s, 3H). ^{13}C NMR: 161.07; 156.45; 155.19; 135.97; 135.20; 128.88; 121.35; 115.55; 98.5; 58.22; 35.91; 10.2.

6-amino-5-cyano-3-methyl-4-(2-hydroxyphenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5e): IR (KBr): ν: 3352; 3217; 2187; 1658; 1527; 1483; 1400; 1049. ^{1}H NMR: 11.18 (s, 1H), 8.90 (s, 1H), 7,20-7,30 (m, 4H) 6.42 (s, 2H), 4.64 (s, 1H), 1.77 (s, 3H). ^{13}C NMR: 163.6; 159.9; 158.9; 148.3; 132.9; 131.5; 127.2; 123.9; 119.3; 116.4; 104.7; 56.3; 28.5; 9.8.

6-amino-5-cyano-3-methyl-4-(2-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5f): IR (KBr): ν: 3413; 2187; 1654; 1600; 1527; 1411; 1153. ^{1}H NMR: 12.13 (s, 1H), 7.76 (d,1H, *J* = 8), 7.59 (t, 1H, *J* = 7.5), 7.41 (t, 1H, *J* = 7.6), 7.27 (d, 1H, *J* = 8.3) 6.79 (s, 2H), 5.15 (s, 1H), 1.77 (s, 3H). ^{13}C NMR: 159.7; 153.5; 136.6; 134.2; 129.8; 126.4; 121.9; 118.8; 94.9; 54.9; 29.6; 8.1.

6-amino-5-cyano-3-methyl-4-(3-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5g): IR (KBr): ν: 3471; 3116; 2970; 2285; 2194; 1651; 1600; 1527; 1404; 1350. ^{1}H NMR: 9 (s,1H) ; 8,4-7.8 (m, 4H) ;6,35 (s, 2H) ; 4,9 (s, 1H) ; 1,9 (s, 3H) . ^{13}C NMR: 161.5; 147.7 ; 135.3 ; 135.1 ; 130.8 ; 123.1 ; 122.8; 117.2; 98.0; 55.9; 37.3 ; 10.1. *6-amino-5-cyano-3-methyl-4-(4-nitrophenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5h)*: IR (KBr): ν: 3475; 3228; 3112; 2194; 1651; 1596; 1404; 1350. ^{1}H NMR: δ : 12,2 (s,1H) ; 8,2 (d, *J* = 8.6, 2H) ; 7.4 (d, *J* = 8.6, 2H) ; 6,9 (s, 2H) ; 4,9 (s, 1H) ; 1,8 (s, 3H). ^{13}C NMR: 159.6; 153.3 ;150.4 ; 144.9 ; 134.4 ; 127.2 ; 122.2 ; 118.9 ; 94.9 ; 54.7 ; 34.7 ; 8.2.

6-amino-5-cyano-3-methyl-4-(4-chlorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5i): IR (KBr): ν: 3475; 3232; 3112; 2191; 1600; 1492; 1400. ^{1}H NMR : 9,8 (s, 1H) ; 8,4 (d, 2H, *J* = 8,3) ; 8.2 (d, 2H, *J* = 8,3) ; 7,3 (s, 2H) ; 5,7 (s, 1H) ; 2,9 (s, 3H). ^{13}C NMR: 160.0; 154.2 ;142.0 ; 1353 ; 131.2 ; 128.9 ; 128.3 ; 120.0 ; 99.2 ; 57.4 ; 35.3 ; 9.2.

6-amino-5-cyano-3-methyl-4-(2-chlorophenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5j): IR (KBr): ν: 3355; 2187; 1651; 1604; 1407; 1045. ^{1}H NMR : 11.93 (s, 1H), 7.10-7.46 (m, 4H), 6.59 (s, 2H), 5.03 (s, 1H),1.76 (s, 3H). ^{13}C NMR: 159.9; 153.6; 139.6; 134.1; 131.2; 129.4; 128.6; 126.8; 125.8; 119.2; 95.6; 55.1; 31.7; 8.33.

6-amino-5-cyano-3-methyl-4-(4-dimethylaminophenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5k): IR (KBr): ν: 3390; 2930; 1620; 1523; 1477; 1392. ^{1}H NMR: 9.8(s,1H) ; 8.2 -7.8(m, 4H) ; 6,7 (s, 2H) ; 4,6 (s, 1H) ; 3,1 (s, 6H) ; 2,3 (s, 3H). ^{13}C NMR: 160.9; 152.2 ; 133.9 ; 129.9 ; 125.1 ; 116.1 ; 115.1; 40.3 ; 31.1 ; 11.8.

6-amino-5-cyano-3-methyl-4-(4-methylphenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5l): IR (KBr): ν: 3371; 3047; 2279; 1639; 1596; 1492; 1400; 1053. ^{1}H NMR: 12.11 (s, 1H), 7.12 (d, *J* = 8.3, 2H), 7.05 (d, *J* = 8.3, 2H), 6.89 (s, 2H), 4.55 (s, 1H), 2.27 (s, 3H),1.79 (s, 3H). ^{13}C NMR: 160.8; 154.8; 141.6; 135.1; 129.1; 127.5; 120.0; 119.4; 97.8; 57. 4; 35.9; 20.8; 9.9.
6-amino-5-cyano-3-methyl-4-(2-methylphenyl)-2,4-dihydropyrano[2,3-c]pyrazole (5m): IR (KBr): ν: 3224; 3124; 2191; 1639; 1492; 1400; 1053. ^{1}H NMR : 11.93 (s, 1H), 6.97-7.15 (m, 4H), 6.47 (s, 2H), 4.80 (s, 1H),2.30 (s, 3H), 1.68 (s, 3H). ^{13}C NMR: 159.4; 153.7; 140.2; 133.9; 133.5; 128.9; 127.4; 125.0; 124.7; 119.3; 96.0; 55.7; 31.7; 17.6; 8.1. HRMS calcd for [M+] ($C_{15}H_{14}N_4O$) 276.11676 found 266.1150.

6-amino-5-cyano-3-methyl-4-(2-thiophene)-2,4-dihydropyrano[2,3-c]pyrazole (5n): IR (KBr): ν: 3359; 2191; 1647; 1600; 1488; 1400; 1041. ^{1}H NMR (: 12.11 (s, 1H), 6.86-6.96 (m, 3H), 6.42 (s, 2H), 4.91 (s, 1H), 1.92 (s, 3H). ^{13}C NMR: 159.2; 152.9; 148.0; 134.5; 124.8; 123.1; 119.2; 95.9; 56.4; 30.2; 8.4.

4-(6-amino-5-cyano-3-methyl-2,4-dihydropyrano[2,3-c]pyrazol-4-yl)phenylboronic (5o): IR (KBr): ν: 3483; 3182; 2360; 2194; 1604; 1504; 1168; 1045;. ^{1}H NMR: 1.79 (s, 3H), 4.61 (s, 1H), 7.00 (s, 2H), 7.13 (d, *J* = 7.6, 2H), 7.75 (d, *J* = 8, 2H),8.13 (s, 2H), 12.13 (s, 1H). ^{13}C NMR: 160.9; 154.3; 146.3; 135.7; 134.4; 126.7; 120.9; 97.6; 57.1; 18.6; 9.6. HRMS calcd for $[M+Na]^+$ ($C_{14}H_{13}N_4O_3BNa$) 319.09729 found 319.0974.

3-(6-amino-5-cyano-3-methyl-2,4-dihydropyrano[2,3-c]pyrazol-4-yl)-4-methoxyphenylboronic acid (5p): IR (KBr): ν: 3741; 3274; 2356; 2198; 1652; 1604; 1525; 1253; 1029. ^{1}H NMR: 1.78 (s, 3H), 3.82 (s, 3H), 4.99 (s, 1H), 7.49 (s, 2H), 7.66 (d, J = 7.6, 2H), 7.70 (d, J = 8, 2H), 7.88 (s, 2H), 12.13 (s, 1H). ^{13}C NMR: 161.5; 158.1; 155.2; 135.1; 134.5; 130.9; 121.2; 119.1; 98.1; 56.6; 9.6. HRMS calcd for $[M+Na]^+$ ($C_{15}H_{15}N_4O_4BNa$) 349.10786 found 349.1083.

RESULTS AND DISCUSSION

To optimize the reaction conditions, the reaction of benzaldehyde, malononitrile, hydrazine and ethyl acetoacetate in the presence of 10 mol % of phenylboronic acid, regarding to the aldehyde, was used as a model reaction.

First, we conducted the reaction in various solvents, such as acetonitrile, ethanol and water, under refluxing conditions and at ambient temperature. The best yield (78%), of corresponding product, was obtained by carrying

out the reaction at reflux in water for 1h. In order to optimize the amount of $PhB(OH)_2$, used as catalyst, we have carried out the model reaction with varying amounts, i.e., 0, 5, 10, 20, 30 and 50 mol%.

Considering the yields, the optimum amount of the catalyst turned out to be 5 mol %, and above this amount, the catalyst showed no significant effect on the yield of the product.

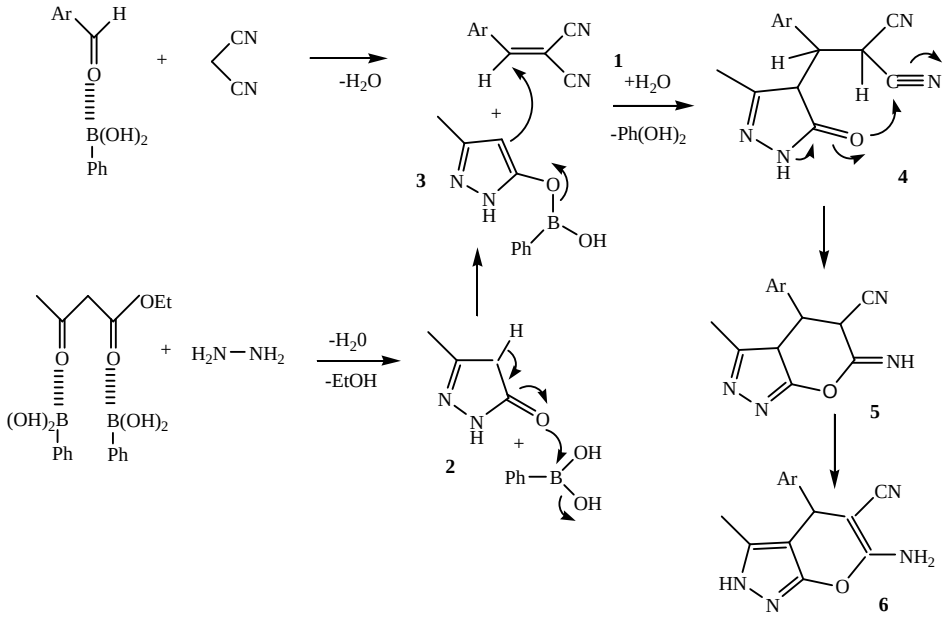
Having optimized the reaction conditions, and to generalise the scope of the present method, a series of pyrano [2,3]pyrazole derivatives **5(a–p)** were synthesized (Table **1**). As shown in Table **1**, aromatic aldehydes carrying either electron donating or withdrawing groups, at any position (*p*, *m* or *o*), underwent the reaction smoothly to give the expected products in good yields (Table **1**, entries 5 and 9). However, aldehydes substituted with electron-withdrawing or weak electron-donating groups required longer time to be converted into the corresponding substituted pyrano[3,2-c]pyrazoles (Table **1**, entries 3, 4 and 7). Hetero-aromatic aldehydes can also be successfully converted to the corresponding heteroaryl substituted pyrano[3,2-c]pyrazoles but in fair yields (Table **1**, entry 14), in contrast, the aliphatic aldehydes, such as isobutyladehyde, gave the corresponding products in poor yields (22%).

Although the detailed mechanism of this reaction has not yet been clarified, the formation of compounds **6** can be explained by the possible mechanism presented in Scheme 2.

Tableau 1: PhB(OH)$_2$-catalyzed pyrano[2,3-c]pyrazoles 5a-p synthesis[a]

Entry	Product	R	Time (h)	Yield (%)[b]	Mp (°C)	
					Found	Lit.[Ref.]
1	**5a**	C_6H_5	3	82	242-244	242-243[25]
2	**5b**	4-BrC_6H_4	1	93	248-250	248-251[30]
3	**5c**	4-$CH_3OC_6H_4$	1	75	226-228	212-213[30]
4	**5d**	4-HOC_6H_4	1	88	224-226	225-227[25]
5	**5e**	2-HOC_6H_4	2	84	210-212	208-210[41]
6	**5f**	2-$O_2NC_6H_4$	3	81	240-242	242-244[25]
7	**5g**	3-$O_2NC_6H_4$	1	84	188-190	190-192[29]
8	**5h**	4-$O_2NC_6H_4$	3	96	244-246	249-250[25]
9	**5i**	4-ClC_6H_4	1	77	232-234	230-232[25]
10	**5j**	2-ClC_6H_4	3	75	238-240	246-247[30]
11	**5k**	4-$(CH_3)_2NC_6H_4$	3	72	166-168	165-168[29]
12	**5l**	4-$H_3CC_6H_4$	3	94	206-208	204-206[29]
13	**5m**	2-$H_3CC_6H_4$	1	85	262-264	-
14	**5n**	2-thiophenyl	2	74	232-234	223-225[3]
16	**5o**	4-$(OH)_2B\,C_6H_4$	1,5	83	+300	-
17	**5p**	2-H_3CO-3-$(OH)_2B\,C_6H_4$	1,5	80	+300	-

[a]Reactions conditions: aldehyde (2 mmol), hydrazine (2 mmol), ethyl acetoacetate (2 mmol), malononitrile (2 mmol), $PB(OH)_2$ (5 mol %), water (5 ml), reflux. [b]Isolated yield of product.



Scheme 2. The proposed mechanism for the synthesis of compounds 6

First, one molecule of aromatic aldehyde, activated by $PhB(OH)_2$, was condensed with malononitrile, via Knoevenagel addition, to afford the intermediate arylidenemalononitrile derivative **1**. Ethylacetoacetate, activated also by $PhB(OH)_2$, reacted with hydrazine to yield the corresponding pyrazolone **2**. The active methylene of **3,** by reaction with the electrophilic C=C double bond of **1** via Michael type addition**,** gives the intermediate **4**, followed by intra-molecular cyclisation and tautomerisation to give the expected product **6**.

CONCLUSION

In conclusion, we have described a novel eco-friendly approach for the synthesis of pyrano[2,3-c]pyrazole derivatives in aqueous media. The use of $PhB(OH)_2$ as an inexpensive, non-toxic, non-explosive, non-volatil, easy to handle, with simple experimental and easy purification of products by simple crystallization, and the use of water as solvent combined with the exploitation of the multicomponent strategy, make the present procedure an attractive method for the preparation of these compounds.

Acknowledgments
We gratefully acknowledge the financial support from MESRS of Algeria

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