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Poly(4-vinylpyridine) efficiently catalyzed one-pot four-component synthesis of pyrano[2,3-c]pyrazoles

Jalal Albadi*[a] and Azam Mansournezhad[b]

[a]*Behbahan Khatam Alanbia University of Technology, 6361647189, Behbahan, Iran*
[b]*Department of chemistry, Islamic Azad University, 7581863886, Gachsaran, Iran*

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An efficient one-pot synthesis of pyrano[2,3-c]pyrazoles *via* four-component reaction of phenyl hydrazine, ethyl acetoacetate, malononitrile and aromatic aldehydes, catalyzed by poly(4-vinylpyridine) is reported. This method provides many advantages such as, atom-economy, easy work up, clean procedure, short reaction times and high yields of products.

1. Introduction

Multi-component reactions (MCRs) have been considered to produce biologically active compounds and have become an important area of research in organic and medicinal chemistry. [1] These reactions offer a wide range of potentials for efficient construction of highly complex molecules in a single procedure step; thus, avoiding the difficult purification operations and allowing savings of both solvents and reagents. Therefore, they are perfectly agreeable to automation for combinatorial synthesis.[2] Moreover, multi-component reactions (MCRs) due to their atom economy, simplicity, high yields of products and time-saving features provide a simple and useful route for the synthesis of various heterocyclic compounds.[3] In the past decade there have been great developments in three- and four-component reactions and great effort continue to be made to develop new MCRs. Pyranopyrazoles, are an important class of heterocyclic compounds that received significant attention from many pharmaceutical and organic chemists essentially because of the broad spectrum of their biological and pharmaceutical properties.[4] Compounds including pyranopyrazoles have been found to have various biological activities, for instance antimicrobial, analgesic, vasodilator, anticancer,

* Corresponding author. Tel/Fax: +986712229969
E-mail address: chemalbadi@bkatu.ac.ir; Albadi@bkatu.ac.ir (J. Albadi)

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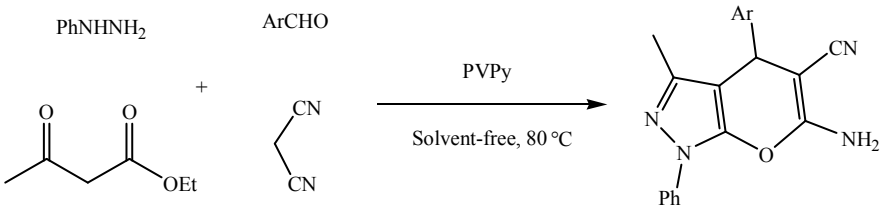
antiinflammatory, molluscicidal, antifungicidal, and also as biodegradable agrochemicals. [5-8] Furthermore, these compounds are used as cosmetics and pigments. [9] Several procedures for the synthesis of pyranopyrazoles were reported. These procedures include one-pot three-component condensation of pyrazolone derivatives, malononitrile, and aromatic aldehydes,[10] three-component cyclocondensation of substituted piperidin-4-ones, pyrazol-5-ones, and malononitrile,[11] four-component reaction of aldehydes, ethyl acetoacetate, malononitrile with hydrazine hydrate,[12-15] two-component reaction of 3-methyl-2-pyrazolin-5-one with benzylidenemalononitriles,[16] and four-component reaction involving aromatic aldehydes, Meldrum's acid, hydrazine hydrate, and ethyl acetoacetate.17 In order to improve the efficiency of these procedures, various catalysts have been developed. [18-30] In recent years, practical applications of solid basic catalysts in organic synthesis have increased. Solid base catalysts are noncorrosive, environmentally benign and presenting fewer disposal problems while allowing easier separation and recovery of the products. Therefore, solid base catalyst is one of the economically and ecologically important fields in catalysis and the replacement of liquid bases with heterogeneous catalysts is becoming more and more important in the chemical industry. Recently, we have reported that poly(4-vinylpyridine) (PVPy), as a green and basic catalyst, could catalyze the synthesis of chromenes and tetrahydrobenzo[*b*]pyran derivatives. [31-32] PVPy, is a cheap and commercially available. In comparison with other commercially available catalysts, poly(4-vinylpyridine) is safe, easy to handle and environmentally benign. In continuation of these researches, herein, we wish to report the applicability of poly(4-vinylpyridine) (PVPy), for the synthesis of pyrano[2,3-c]pyrazoles *via* one pot-four-component reaction of phenyl hydrazine, ethyl acetoacetate, malononitrile and aromatic aldehydes, under solvent-free conditions. (Scheme 1).



Scheme 1. One-pot four-component synthesis of pyrano[2,3-c]pyrazolescatalyzed by PVPy

2. Results and Discussion

Initially, in order to optimize the reaction conditions, the reaction of benzaldehyde, phenyl hydrazine, malononitrile and ethyl acetoacetate in the presence of PVPy, was studied under a variety of conditions (Table 1). In the absence of the catalyst, the reaction did not carry on, and no product was achieved, which indicated that the catalyst should be necessary for this reaction. Thus, the reaction was studied in the presence of different amounts of the catalyst. The results are summarized in Table 1. It was found that using 0.05 gr of PVPy, under solvent-free conditions was sufficient for the reaction to complete after 22 min.

Table 1. Optimization of the reaction conditions [a]

Entry	Conditions	Amounts of catalyst (gr)	Time (min)	Yield (%) [b]
1	Solvent-free/80 °C	-	120	-
2	Solvent-free/80 °C	0.02	65	75
3	Solvent-free/80 °C	0.05	22	93
4	H_2O/reflux	0.05	120	Trace
5	CH_3CH_2OH/reflux	0.05	120	Trace
6	CH_3OH/reflux	0.05	120	Trace
7	CH_2Cl_2/reflux	0.05	120	-
8	Acetone /reflux	0.05	120	-
9	CH_3CN /reflux	0.05	120	-

[a] Reaction conditions: Benzaldehyde (1 mmol), malononitrile (1 mmol), phenyl hydrazine (1 mmol), ethyl acetoacetate (1 mmol) in the presence of of PVPy. [b] Isolated yield.

The model reaction in water, EtOH, MeOH, MeCN, dichloromethane and acetone in the presence of 0.05 gr of catalyst was studied and results are revealed in Table 1. Finally, it was found that the best result was achieved by carrying out the reaction of benzaldehyde, phenyl hydrazine, malononitrile and ethyl acetoacetate (1: 1: 1: 1: mol/ratio) in the presence of 0.05 gr of PVPy under solvent-free conditions (Table 1, entry 3).

In order to evaluate the generality of this procedure, after optimization of conditions, reaction of various aromatic aldehydes was studied. In all cases, aromatic aldehydes containing electron-donating and electron-withdrawing groups reacted effectively and desired compounds achieved in good to high yields. It can be observed that the group on aromatic ring has no significant effect on the reaction. Aliphatic aldehydes stay intact under the similar reaction conditions. Thus, this procedure can be useful for the chemoselective synthesis of pyrano[2,3-c]pyrazoles from aromatic aldehydes in the presence of aliphatic ones.

Table 2. One pot four-component synthesis of pyrano[2,3-c]pyrazoles catalyzed by PVPy [a]

Entry	Aldehyde	Time (min)	Yield (%) [b]	M.p (ºC)	
				Found	Reported
1	C_6H_5CHO	18	92	168-170	169-171[18]
2	2-ClC_6H_4CHO	22	91	144-146	144-146[18]
3	3-ClC_6H_4CHO	20	91	149-151	148-150[24]
4	4-ClC_6H_4CHO	12	92	173-175	175-177[18]
5	2,4-ClC_6H_3CHO	12	91	182-184	185-187[18]
6	3-$O_2NC_6H_4CHO$	15	91	191-193	190-191[18]
7	4-$O_2NC_6H_4CHO$	10	93	197-199	196-198[18]
8	4-BrC_6H_4CHO	20	91	177-178	176-177[24]
9	4-$MeOC_6H_4CHO$	42	89	172-174	174-176[18]
10	4-MeC_6H_4CHO	20	90	174-176	177-179[18]
11	4-HOC_6H_4CHO	65	90	208-210	211-212[18]
12	4-CNC_6H_4CHO	18	90	217-218	217-219[20]
13	4-FC_6H_4CHO	15	91	167-168	167-168[22]

[a] Reaction conditions: Aldehyde (1 mmol), malononitrile (1 mmol), phenyl hydrazine (1 mmol), ethyl acetoacetate (1 mmol), in the presence of PVPy. [a]Isolated pure products.

The experimental procedure with PVPy is very easy and it can be easily recovered by filtration. This catalyst is cheap, easy to handle and commercially available. Moreover, all products were cleanly isolated with simple filtration and evaporation of solvent. The solid products were easily recrystallized from hot ethanol and were obtained in good to high yields during short reaction times. The activity of the recovered catalyst was also studied under the optimized conditions and the desired product was obtained in high yields after 1-5 runs (Table 3). To examine this property, the reaction of benzaldehyde, phenyl hydrazine, malononitrile and ethyl acetoacetate was selected again as a model (Table 3). After reaction completion, PVPy was filtered, washed with hot ethanol and after dryness was reused in the next similar process. This process repeated for 5 runs and it was observed that corresponding product was achieved in high yields after 1-5 runs.

Table 3. Recyclability study of PVPy

Run	1	2	3	4	5
Time (min)	18	20	20	25	35
Yield (%)[a]	92	90	90	87	87

[a] Isolated pure products.

3. Conclusions

In conclusions, an efficient one-pot synthesis of pyrano[2,3-c]pyrazoles was developed *via* four-component reaction of phenyl hydrazine, ethyl acetoacetate, malononitrile and aromatic aldehydes, in the presence of PVPy under solvent-free conditions. PVPy as a commercially available and basic recyclable catalyst, can be reused at least 5 times without significant decrease of its catalytic activity.

Moreover, environmental friendly reaction condition, simplicity of the reaction, short reaction times, high yields of products and ease of work up are the most important advantages of this method which make this procedure a useful addition to the available procedures. We are exploring further applications of PVPy for the other types of organic reactions in our laboratory.

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4. Experimental

4.1. Materials and Methods

Chemicals were purchased from Fluka and Merck chemical companies. Products were characterized by comparison of their spectroscopic data (NMR, IR) and physical properties with those reported in the literature. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. All the NMR spectra were recorded on a Bruker Advance 400 MHz. Yields refer to isolated pure products.

4.2. General procedure

A mixture of aromatic aldehydes (1 mmol), malononitrile (1 mmol), phenyl hydrazine (1 mmol), ethyl acetoacetate (1 mmol) and PVPy (0.05 gr), was heated in an oil bath (80 $^{\circ}$ C) for the appropriate times according to Table 2. After completion of the reaction as followed by TLC, the resulting mixture was cooled, ethylacetate (10 mL) was added and the catalyst was recovered by filtration to be reused subsequently. Evaporation of the solvent from the filtrate and recrystallization of the solid residue from hot ethanol afforded the pure products in high yields.

4.3. Physical and Spectral Data

Table 2, entry 1: IR (KBr) ν_{max}/cm^{-1}: 3395, 3315, 3200, 2905, 2195, 1655, 1405, 1300, 1015. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.78 (s, 3H), 4.77 (s, 2H), 5.29 (s, 1H), 7.22-7.27 (m, 3H), 7.31 (t, 2H, *J* =7.8 Hz), 7.31 (s, 2H), 7.34 (m, 1H), 7.47 (m, 2H), 7.76 (d, 2H, J=7.8 Hz), ^{13}C NMR (100 MHz, $CDCl_3$), δ: 12.76, 32.39, 60.78, 96.67, 117.36, 120.34, 125.87, 127.11, 128.36, 129.28, 130.41, 132.75, 136.33, 136.80, 142.90, 145.26, 158.66.
Table 2, entry 2: IR (KBr) ν_{max}/cm^{-1}: 3310, 3300, 3195, 2900, 2190, 1645, 1400, 1300. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.89 (s, 3H), 4.83 (s, 2H), 5.31 (s, 1H), 7.17-7.39 (m, 5H), 7.43-7.45 (m, 2H), 7.57 (m, 1H), ^{13}C NMR (100 MHz, $CDCl_3$), δ: 12.74, 32.74, 60.97, 97.45, 117.23, 120.25, 125.75, 126.85, 128.35, 128.92, 130.50, 132.76, 136.35, 136.34, 141.92, 145.56, 158.57.
Table 2, entry 3: IR (KBr) ν_{max}/cm^{-1}: 3300, 3290, 3190, 2195, 1660, 1640, 1200, 1050. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.84 (s, 3H), 4.82 (s, 2H), 5.32 (s, 1H), 7.19-7.25 (m, 5H), 7.31-7.67 (m, 5H), 7.73 (m, 1H, Ar). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 13.24, 35.50, 57.95, 97.32, 110.41, 117.68, 120.60, 120.72, 126.33, 128.34, 129.65, 131.77, 136.15, 144.11, 145.85, 148.23, 159.42.
Table 2, entry 4: IR (KBr) ν_{max}/cm^{-1}: 3290, 3085, 2205, 1675, 1580, 1515, 1390, 1230, 1075, 1030. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.75 (s, 3H), 4.81 (s, 1H), 7.25-7.31 (m, 3H), 7.46-7.52 (m, 4H), 7.75 (d, 2H, J= 8.6 Hz,), 7.82 (d, 2H, J= 8.4 Hz,). ^{13}C NMR (DMSO-d_6,125 MHz): δ: 13.36, 37.50, 57.85, 97.91, 110.82, 118.88, 120.62, 120.92, 127.13, 129.76, 130.11, 133.53, 137.96, 144.85, 146.10, 150.11, 160.26.
Table 2, entry 5: IR (KBr) ν_{max}/cm^{-1}: 3400, 3310, 3205, 2900, 2200, 1645, 1405, 1305. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 1.91 (s, 3H), 4.82 (s, 2H), 5.30 (s, 1H), 7.17 (d, 1H, J=8.4 Hz), 7.27 (s, 1H), 7.37 (t, 1H, J = 7.2 Hz), 7.46-7.52 (m, 3H), 7.67 (d, 2H, J=8). 13C NMR (100 MHz, CDCl3), δ: 12.76, 33.48, 61.92, 97.56, 118.66, 121.28, 126.97, 128.06, 129.37, 129.67, 131.50, 133.94, 137.41, 137.87, 143.95, 146.06, 158.88.

Table 2, entry 6: IR (KBr) νmax/cm-1: 3320, 3095, 2205, 1675, 1590, 1475, 1335, 1250, 1020. 1H NMR (DMSO-d6, 500 MHz), δ: 1.78 (s, 3H), 4.81 (s, 1H), 7.30-7.55 (m, 5H), 7.40-7.81 (m, 5H), 7.91 (m, 1H, Ar). ^{13}C NMR (DMSO-d_6,125 MHz), δ: 13.41, 37.52, 57.92, 99.52, 111.22, 119.60, 121.62, 121.87, 127.21, 129.50, 130.20, 132.87, 137.75, 144.51, 146.85, 150.22, 160.35.

Table 2, entry 7: IR (KBr) ν_{max}/cm^{-1}: 3320, 3085, 2200, 1675, 1595, 1455, 1335, 1125, 107. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.76 (s, 3H), 4.73 (s, 1H), 7.45-7.56 (m, 3H), 7.62-7.70 (m, 4H), 7.81 (d, 2H, J= 8.6 Hz), 7.87 (d, 2H, J= 8.0 Hz). ^{13}C NMR (DMSO-d_6,125 MHz): δ: 13.50, 37.52, 58.13, 98.51, 110.81, 119.66, 119.95, 120.91, 126.94, 129.81, 130.13, 133.76, 138.55, 144.96, 145.9, 150.07, 160.47.

Table 2, entry 8: IR (KBr) ν_{max}/cm^{-1}: 3285, 3090, 2200, 1670, 1585, 1510, 1220, 1100, 1025. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.74 (s, 3H), 4.83 (s, 1H), 7.15-7.22 (m, 3H), 7.32-7.40 (m, 4H), 7.65 (d, 2H, J= 8.6 Hz,), 7.71 (d, 2H, J= 8.4 Hz,). ^{13}C NMR (DMSO-d_6,125 MHz): δ: 13.37, 37.51, 56.82, 97.62, 110.22, 118.37, 119.91, 120.41, 126.65, 128.52, 129.70, 133.13, 136.85, 144.12, 145.88, 149.92, 160.22.

Table 2, entry 9: IR (KBr) ν_{max}/cm^{-1}: 3380, 3310, 2990, 2205, 1670, 1445, 1225, 1105, 1015. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.75 (s, 3H), 3.75 (3H), 4.55 (s, 1H), 6.87 (s, 2H), 7.12 (t, 1H, J=7.4 Hz), 7.19 (d, 2H, J=8 Hz), 7.22 (d, 2H, J=8 Hz), 7.29 (t, 2H, J=7.8 Hz), 7.51 (d, 2H, J=7.8Hz). ^{13}C NMR (DMSO-d_6,125 MHz), δ: 13.40, 36.65, 45.22, 56.80, 96.52, 109.64, 115.15, 118.77, 120.12, 124.74, 127.82, 129.66, 132.84, 136.55, 143.81, 145.12, 150.12, 160.20.

Table 2, entry 10: IR (KBr) ν_{max}/cm^{-1}: 3385, 3315, 3205, 2910, 2210, 1675, 1425, 1325, 1010. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.77 (s, 3H), 1.86 (3H), 4.56 (s, 1H), 7.13 (s, 2H), 7.20 (t, 1H, J=7.4 Hz), 7.22 (d, 2H, J=8 Hz), 7.29 (d, 2H, J=8 Hz), 7.35 (t, 2H, J=7.6 Hz), 7.62 (d, 2H, J=7.6Hz). ^{13}C NMR (DMSO-d_6,125 MHz), δ: 13.42, 36.67, 37.52, 56.85, 97.45, 110.12, 116.85, 119.46, 120.42, 125.25, 128.65, 130.15, 133.15, 137.35, 144.35, 145.57, 150.25, 160.22.

Table 2, entry 11: IR (KBr) ν_{max}/cm^{-1}: 3390, 3310, 2210, 1650,1405, 1300. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.78 (s, 3H), 4.56 (s, 1H), 6.72 (d, 2H, J=7.8 Hz), 7.05 (d, 2H, J=7.81Hz), 7.25 (s, 2H), 7.30 (t, 1H, J=7.03Hz), 7.47 (t, 2H, J=7.31Hz), 7.75 (d, 2H, J=7.74Hz), 9.35 (s, 1H). ^{13}C NMR (DMSO-d_6,125 MHz), δ: 13.42, 37.52, 57.90, 98.52, 110.85, 119.62, 120.62, 120.90, 127.15, 129.79, 130.12, 133.52, 138.32, 144.90, 145.90, 150.95, 160.32.

Table 2, entry 12: IR (KBr) ν_{max}/cm^{-1}: 3089, 3082, 2200, 2195, 1673, 1590, 1515, 1390, 1250, 1120, 1070, 1030. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.75 (s, 3H), 4.82 (s, 1H), 7.31-7.34 (m, 3H), 7.48-7.52 (m, 4H), 7.79 (d, J= 8.5 Hz, 2H), 7.85 (d, J= 8.0 Hz, 2H). ^{13}C NMR (DMSO-d_6,125 MHz): δ: 13.42, 37.50, 57.91, 98.57, 111.12, 118.82, 120.62, 120.85, 127.12, 129.80, 130.12, 133.45, 138.33, 144.90, 145.91, 150.42, 160.15.

Table 2, entry 13: IR (KBr) ν_{max}/cm^{-1}: 3310, 3015, 2215, 1675, 1585, 1515, 1230, 1120. ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 1.75 (s, 3H), 4.81 (s, 1H), 7.32-7.41 (m, 3H), 7.48-7.56 (m, 4H), 7.88 (d, 2H, J= 8.6 Hz,), 7.91 (d, 2H, J= 8.6 Hz,). ^{13}C NMR (DMSO-d_6,125 MHz): δ: 13.37, 37.62, 57.91, 97.95, 110.83, 118.89, 120.66, 120.96, 128.12, 129.82, 130.10, 133.52, 138.55, 145.65, 146.17, 151.16, 160.41.

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