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$H_6P_2W_{18}O_{62}\cdot 18H_2O$: A green and reusable catalyst for one-pot synthesis of pyrano[4,3-b]pyrans in water

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ABSTRACT

A convenient, efficient and environmentally benign procedure has been developed for the synthesis of pyrano[4,3-b]pyran derivatives *via* a one-pot, three-component reaction of 4-hydroxy-6-methylpyran-2-one, aldehydes and malononitrile in water using $H_6P_2W_{18}O_{62}\cdot 18H_2O$ as catalyst. Reusability of the catalyst and reaction media, short reaction times and easy isolation of products are some added advantages of the present methodology.

1. Introduction

In recent years, heteropolyacids have attracted much attention as environmentally benign catalysts for organic synthetic processes. They possess unique physicochemical properties, such as super-acidity, high thermal and chemical stability, ability to accept and release electrons, high proton mobility, and the possibility of varying their acidity and oxidizing potential [1]. Their significantly higher Brønsted acidity makes them more effective catalysts than conventional acid catalysts, such as mineral acids, ion exchange resins and mixed oxides zeolites [2]. They are non-corrosive, inexpensive and reusable and require less waste disposal [3]. They are used as industrial catalysts for several liquid phase reactions [4–7].

Multicomponent reactions (MCRs), due to their operational simplicity, high bond forming efficiency, reduced waste and rapid access to structural diversity, have attracted much attention of synthetic organic chemists for building highly functionalized organic molecules and pharmacologically important heterocyclic compounds [8–11]. Developing MCR protocols in aqueous medium is an active area of research in this direction. Water is recognized as an attractive medium for many organic reactions because it is the lowest cost, most abundantly available solvent. Water, as a green solvent, is highly polar and therefore immiscible with most organic compounds. Moreover, the water soluble catalyst resides and operates in the aqueous phase and separation of organic materials is thus easy. Also, dramatic rate enhancements have been achieved in water in many organic reactions [12,13]. Reactions in aqueous media are generally environmentally safe, devoid of any carcinogenic effects, simple to handle, comparatively more economic and especially important in industry.

It is well known that fused pyran derivatives exhibit a wide spectrum of pharmacological activities and biological activities, such as insecticidal [14], antiviral and antileishmanial [15,16], anticonvulsant and antimicrobial activities [17]. Also, many of them are non-peptide human immunodeficiency virus (HIV) protease inhibitors [18–20]. A literature survey revealed that comparatively few methods have been reported for the preparation of pyrano[4,3-b]pyran derivatives. Recently, a one-pot, three-component reaction of 4-hydroxy-6-methylpyran-2-one with malononitrile and aromatic aldehydes has enjoyed wider utilization in the synthesis of these compounds. A variety of reagents, such as piperidine [21,22], triethylbenzyl ammonium chloride [23], KF/Al_2O_3 [24], magnesium oxide [25], ionic liquids [16,26], DBU [27], and also without any catalyst [28] have been employed to accomplish this transformation. Some of the reported methods suffer from serious limitations, such as long reaction times, complex synthetic pathways, tedious work-up, use of organic solvents, lower product yields and non-reusability of the catalyst. Therefore, it is still necessary to develop clean, efficient and convenient methods to construct such significant heterocyclic compounds.

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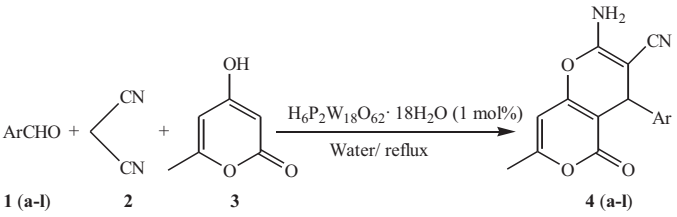

Scheme 1. $H_6P_2W_{18}O_{62}\cdot 18H_2O$ catalyzed synthesis of 2-amino-4-aryl-3-cyano-5-oxo-4*H*,5*H*-pyrano[4,3-b]pyrans in water.

Based on the previous studies on the use of heteropolyacids as catalysts, and in a continuation of our endeavors for the development of simple and highly expedient methods for the synthesis of polyfunctionalized heterocycles of biological importance [29], we examined the possibility of using $H_6P_2W_{18}O_{62}\cdot 18H_2O$, a Wells-Dawson type heteropolyacid, as a catalyst for the one-pot synthesis of pyrano[4,3-b]pyran derivatives by condensing aromatic aldehydes, malononitrile and 4-hydroxy-6-methylpyran-2-one in water under reflux (Scheme 1).

2. Experimental

All the chemicals were purchased from Merck and Sigma–Aldrich and used without further purification. Melting points were determined in open glass capillaries and are uncorrected. IR spectra were recorded on a Perkin Elmer-1430 spectrophotometer using potassium bromide discs. ^{1}H NMR and ^{13}C NMR spectra were obtained at 400 MHz with a Bruker WM-400 spectrometer using DMSO-d_6 as solvent and TMS as an internal standard. MS spectra were measured at Micromass ZMD ESI (70 eV) system.

2.1. General procedure for the synthesis of 2-amino-4-aryl-5-oxo-4H, 5H-pyrano[4,3-b]pyran-3-carbonitriles

A mixture of 4-hydroxy-6-methylpyran-2-one (1 mmol), aromatic aldehyde (1 mmol), malononitrile (1.2 mmol) and $H_6P_2W_{18}O_{62}\cdot 18H_2O$ (1 mol%) in 20 mL of water was stirred under reflux for appropriate time. After completion of the reaction as monitored by TLC, the reaction mixture was cooled to room temperature. The solid product was collected by filtration, washed with aqueous ethanol (1:1) and recrystallized from ethanol to yield the pure product. All products were characterized by their spectral and physical data.

2.2. Characterization data for the representative compounds

2.2.1. 2-Amino-7-methyl-5-oxo-4-phenyl-4H,5H-pyrano[4,3-b]pyran -3-carbonitrile (**4a**, $C_{16}H_{12}N_2O_3$)

Yellow crystals; yield: 92%; Mp 234–236 °C (236–238 °C) [22]; IR (KBr, cm^{-1}): ν 3458, 3260, 3131, 3088, 2293, 1649, 1555, 1342, 1053, 790; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.56 (s, 3H, CH_3), 4.76 (s, 1H, CH), 6.43 (s, 1H, =CH), 7.20–7.22 (dd, 2H, ArH, J_a = 3.9 Hz, J_b = 1 Hz), 7.27 (s, 2H, NH_2), 7.42 (d, 1H, ArH, J = 3.5 Hz), 7.63–7.65 (dd, 2H, ArH, J_a = 4.2 Hz, J_b = 0.9 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.15, 31.94, 57.84, 103.97, 116.22, 118.94, 122.51, 124.27, 124.58, 124.67, 127.72, 140.90, 152.95, 153.84, 158.40, 159.49.

2.2.2. 2-Amino-4-(4-methoxyphenyl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**4h**, $C_{17}H_{14}N_2O_4$)

Yellow crystals; yield: 86%; Mp 202–205 °C (205–207 °C) [22]; IR (KBr, cm^{-1}): ν 3472, 3365, 2925, 2212, 1637, 1540, 1296, 1039, 824; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.57 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 5.13 (s, 1H, CH), 6.35 (s, 1H, =CH), 6.65–6.66 (m, 2H, ArH); 7.41 (m, 2H, ArH), 7.57 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.27, 30.49, 55.87, 101.64, 111.55, 112.90, 116.17, 118.86, 122.44, 124.11, 150.92, 151.67, 152.05, 153.94, 158.71, 159.50.

2.2.3. 2-Amino-4-(furan-2-yl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**4i**, $C_{14}H_{10}N_2O_4$)

Pink crystals; yield: 95%; Mp 223–225 °C (223–224 °C) [29]; IR (KBr, cm^{-1}): ν 3208, 3085, 2195, 1620, 1384, 1258, 1139, 1013, 980, 754; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.25 (s, 3H, CH_3), 4.47 (s, 1H, CH), 6.10 (s, 1H, =CH), 6.16 (d, 1H, ArH, J = 3.1 Hz); 6.30 (dd, 1H, ArH, J_a = 1.8, J_b = 1.2 Hz); 6.97 (s, 2H, NH_2), 7.37 (d, 1H, ArH, J = 1.0 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.43, 29.88, 55.36, 97.95, 98.40, 105.90, 110.17, 118.89, 141.55, 154.12, 158.58, 158.75, 161.13, 162.36. MS (m/z): 270.0 (M^+).

2.2.4. 2-Amino-7-methyl-5-oxo-4-(thiophen-2-yl)-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**4j**, $C_{14}H_{10}N_2O_3S$)

Colorless crystals; yield: 92%; Mp 242–244 °C (242–244 °C) [29]; IR (KBr, cm^{-1}): ν 3081, 2857, 2196, 1717, 1614, 1375, 1254, 1189, 1044, 777; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.23 (s, 3H, CH_3), 4.66 (s, 1H, CH), 6.13 (s, 1H, =CH), 6.91 (dd, 1H, ArH, J_a = 3.5 Hz, J_b = 1.5 Hz); 6.97 (d, 1H, ArH, J = 2.9 Hz); 7.13 (s, 2H, NH_2), 7.25 (d, 1H, ArH, J = 3.9 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.40, 31.26, 57.81, 97.94, 100.89, 119.03, 124.44, 124.63, 126.61, 147.78, 157.72, 158.44, 161.22, 162.57. MS (m/z): 286.1 (M^+).

2.2.5. 2-Amino-7-methyl-4-(5-methyl-thiophen-2-yl)-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**4k**, $C_{15}H_{12}N_2O_3S$)

Brown crystals; yield: 93%; Mp 176–177 °C (175–177 °C) [29]; IR (KBr, cm^{-1}): ν 3471, 3363, 3119, 2923, 2211, 1639, 1549, 1296, 1039, 743; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.24 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 4.57 (s, 1H, =CH), 6.04 (s, 1H, =CH), 6.55 (d, 1H, ArH, J = 1.6 Hz), 6.74 (d, 1H, ArH, J = 3.3 Hz), 6.84 (s, 2H, NH_2); ^{13}C NMR (100 MHz, DMSO-d_6): δ 14.97, 19.44, 31.30, 58.19, 97.89, 101.02, 118.97, 124.29, 124.47, 138.17, 140.64, 157.51, 158.28, 161.30, 162.10. MS (m/z): 301.1 (M^++1).

2.2.6. 2-Amino-4-(5-chlorothiophen-2-yl)-7-methyl-5-oxo-4H,5H-pyrano[4,3-b]pyran-3-carbonitrile (**4l**, $C_{14}H_9ClN_2O_3S$)

Yellow crystals; yield: 89%; Mp 226–227 °C (228–229 °C) [29]; IR (KBr, cm^{-1}): ν 3322, 3191, 3112, 2196, 1671, 1606, 1514, 1344, 1262, 1037, 732; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.22 (s, 3H, CH_3), 4.24 (s, 1H, CH), 6.13 (s, 1H, =CH), 6.84 (d, 1H, ArH, J = 2.7 Hz), 6.93 (s, 2H, NH_2), 7.11 (d, 1H, ArH, J = 1.5 Hz); ^{13}C NMR (100 MHz, DMSO-d_6): δ 19.35, 35.47, 58.28, 97.89, 101.18, 119.19, 123.95, 128.44, 133.26, 135.34, 159.97, 161.28, 162.07, 164.28. MS (m/z): 320.0 (M^+).

3. Results and discussion

We report herein a green approach for the synthesis of pyrano[4,3-b]pyrans catalyzed by $H_6P_2W_{18}O_{62}\cdot 18H_2O$ in water under reflux. In our initial study, the reaction of 4-hydroxy-6-methylpyran-2-one, benzaldehyde and malononitrile was used as a model reaction to optimize the reaction conditions. The model reaction was carried out in the presence of a variety of catalysts and solvents under different conditions. The results obtained are summarized in Table 1 and determined that the best results in terms of reaction time, cost and yield were obtained with 1 mol% of $H_6P_2W_{18}O_{62}\cdot 18H_2O$ as catalyst in water under reflux. Higher loading of the catalyst did not improve the product yield to a great extent (Table 1, entry 9). The product formation was also observed under reaction conditions at room temperature. However, the yield was unsatisfactory (62%) and the reaction was incomplete even after 4 h (Table 1, entry 8). Thus, refluxing all the components in presence of 1 mol% of $H_6P_2W_{18}O_{62}\cdot 18H_2O$ in water proved to be the optimum conditions for this reaction.

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Table 1
Optimization of the reaction conditions for the synthesis of **4a**.

Entry	Catalyst (mol%)	Solvent	*T* (°C)	Time (min)	Yield[a] (%)
1	$H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (1)	EtOH	Reflux	60	87
2	$H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (1)	CH_2Cl_2	Reflux	180	42
3	$H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (1)	CH_3CN	Reflux	120	56
4	$H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (1)	H_2O	Reflux	45	94
5	$H_4SiW_{12}O_{40}$ (1)	H_2O	Reflux	60	86
6	Sulfamic acid (10)	H_2O	Reflux	90	72
7	*p*-Toluenesulfonic acid (10)	H_2O	Reflux	90	74
8	$H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (1)	H_2O	r.t.	240	62
9	$H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (5)	H_2O	Reflux	45	95

[a] Isolated yield.

Table 2
Synthesis of 2-amino-4-aryl-3-cyano-5-oxo-4H,5H-pyrano[4,3-b]pyrans in water using $H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (1 mol%) as catalyst under reflux.

Entry	Ar	Product	Time (min)	Yield (%)	Mp (°C) found (reported)
1	C_6H_5	**4a**	45	94	234–236 (236–238) [22]
2	4-$O_2NC_6H_4$	**4b**	45	87	215–218 (216–218) [22]
3	3-$O_2NC_6H_4$	**4c**	50	91	232–233 (234–235) [24]
4	4-ClC_6H_4	**4d**	45	94	228–230 (230–231) [24]
5	2,4-$Cl_2C_6H_3$	**4e**	60	88	232–235 (230–231) [24]
6	4-BrC_6H_4	**4f**	50	93	226–227 (223–224) [24]
7	4-$CH_3C_6H_4$	**4g**	50	90	224–225 (223–225) [23]
8	4-$CH_3OC_6H_4$	**4h**	60	86	202–205 (205–207) [22]
9	2-Furanyl	**4i**	45	95	223–225 (223–224) [29]
10	2-Thienyl	**4j**	45	92	242–244 (242–244) [29]
11	5-Me-2-Thienyl	**4k**	60	93	176–177 (175–177) [29]
12	5-Cl-2-Thienyl	**4l**	50	89	226–227 (228–229) [29]

Table 3
Comparison of the present method with other reported protocols for the synthesis of **4a**.

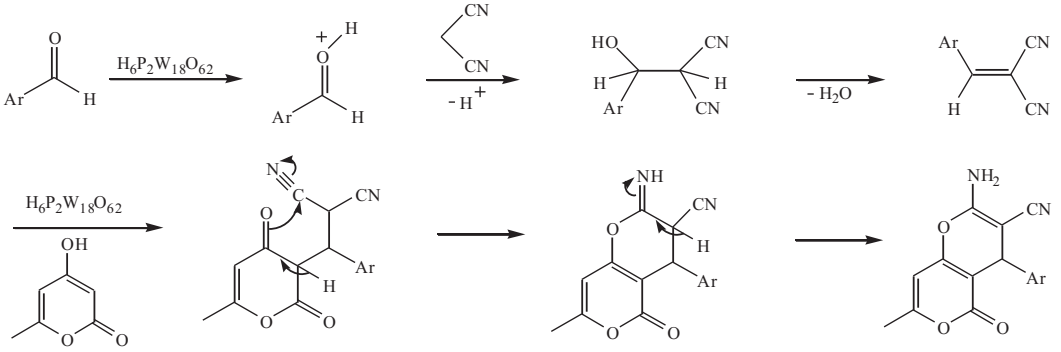
Entry	Catalyst	Conditions	Time (h)	Yield (%)
1	Piperidine (1–2 drops)	MeOH, reflux	1	79 [22]
2	TMGT (1 mol%)	100 °C	1	77 [26]
3	–	H_2O, 80 °C	10.5	65 [28]
4	MgO	H_2O/EtOH, reflux	0.5	89 [25]
5	$H_6P_2W_{18}O_{62}{\cdot}18H_2O$ (1 mol%)	H_2O, reflux	1	94[a]

[a] This work.

Using these optimized reaction conditions, a series of pyrano[4,3-b]pyran derivatives (**4a–l**) were prepared in high to excellent yields from different aromatic aldehydes having electron-donating as well as electron-withdrawing groups. These results are listed in Table 2. It is noteworthy to mention that the methodology worked well for heteroaromatic aldehydes (Table 2, entries 9–12).

A plausible mechanism for the above reaction is depicted in Scheme 2. The reaction may proceed *via* an *in situ* initial formation of the arylidenenitrile from the Knoevenagel condensation of an aldehyde with malononitrile. The unsaturated nitrile then undergoes subsequent reactions with 4-hydroxy-6-methylpyran-2-one to give the final product.

Recovery and reuse of the catalyst and reaction medium was investigated by using the model reaction. After the reaction was completed, the product was collected by simple filtration and the aqueous filtrate containing $H_6P_2W_{18}O_{62}{\cdot}18H_2O$ was used as such for the next reaction run. Again, the product **4a** was obtained in comparative yield. Following four consecutive reaction cycles, there was a slight decrease in yield (94%, 92%, 87% and 84%). Since



Scheme 2. Probable reaction pathway for the formation of pyrano[4,3-b]pyrans.

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the solvent containing catalyst is reused 'as is', we believe that any organic impurities generated in each run may cause the decrease in yield observed after each use.

Furthermore, to show the advantages of this methodology in comparison with previously reported procedures, we selected the synthesis of **4a** as a representative example. As can be seen from Table 3, the reaction catalyzed by $H_6P_2W_{18}O_{62}\cdot 18H_2O$ in water gave a comparable yield and requires less time than other protocols.

4. Conclusion

In conclusion, we have developed a green, efficient and convenient approach for the synthesis of pyrano[4,3-b]pyran derivatives using $H_6P_2W_{18}O_{62}\cdot 18H_2O$ as a catalyst in water. Reusability of the catalyst and reaction media, use of a non-toxic and inexpensive catalyst with operational simplicity makes this method an attractive choice for the preparation of pyrano[4,3-b]pyrans.

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