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Rapid One-pot, Four Component Synthesis of Pyranopyrazoles Using Heteropolyacid Under Solvent-free Condition

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A series of pyranopyrazoles, was efficiently synthesized *via* one-pot, four component reaction of ethyl acetoacetate, hydrazine hydrate, aldehydes and malononitrile in the presence of catalytic amount silicotungstic acid under solvent free condition. NOE experiments confirmed that the product exist exclusively in the 2*H* form. The present protocol offers the advantages of clean reaction, short reaction time, high yield, easy purification and economic availability of the catalyst.

Key Words : Pyranopyrazoles, Multicomponent, Heteropolyacid, Solvent-free, NOE

Introduction

An increase in regulatory restrictions on the use, manufacture and disposal of organic solvents has focused attention on the development of non-hazardous alternatives such as solvent-free syntheses, multicomponent reactions and reusable heterogeneous catalysts for the sustainable development of chemical enterprise. These organic reactions possess advantages over traditional reactions in organic solvents. For example, solvent-free, multicomponent reactions with reusable heterogeneous catalysts reduce the consumption of environmentally hazardous solvents and utilize scaled-down reaction vessels. In the recent years, the use of solid acids as heterogeneous catalyst has received considerable attention in different areas of organic synthesis.[1] Heteropolyacids (HPAs) have several advantages, including high flexibility on modification of the acid strength, ease of handling, environmental compatibility, non toxicity and experimental simplicity.[2] They are known to possess a strong purely Brönsted acidity, and found to be very efficient in catalyzing reactions that conventionally use Lewis acids. Thus, the use of HPAs as a catalyst makes the process convenient and environmentally benign.

Heteropolyacids found to exhibit excellent catalytic properties in the dehydration of diols,[3] rearrangements,[4] tetrahydropyranylation of alcohols,[5] Friedel-Craft alkylation,[6] Prins reaction,[7] synthesis of dihydroquinolines,[8] pyrimidine synthesis,[9] Biginelli reaction[10] and Dakin-West reaction.[11]

Pyranopyrazoles are an important class of biologically active heterocycles. They are reported to possess a multiplicity of pharmacological properties including anticancer,[12a] antimicrobial,[12b] antiinflammatory,[12c] insecticidal, and molluscicidal activities.[12d,e] They are also potential inhibitors of human Chk1 kinase.[12f] They also find applications as pharmaceutical ingredients and biodegradable agrochemicals.[13]

In a view of great importance of pyranopyrazoles various methods for synthesis of 6-amino-5-cyanodihydro-pyrano-[2,3-c]pyrazoles has been reported. These compounds may be readily obtained from the reaction of 4-arylmethylene-5-pyrazolone and malononitrile, or 2-pyrazolin-5-ones and benzylidenemalononitriles.[14] The first reported pyranopyrazole was synthesized from the reaction between 3-methyl-1-phenylpyrazolin-5-one and tetracyanoethylene.[15] Various 6-amino-5-cyanodihydro-pyrano[2,3-c]pyrazoles were synthesized by the reaction of arylidienemalononitrile with 3-methylpyrazoline-5-ones or by the condensation of 4-arylidienepyrazoline-5-one with malononitrile.[16]

Sharanin *et al.*,[17] have developed a three-component reaction between pyrazolone, an aldehyde and malononitrile in ethanol using triethylamine as the catalyst. Vasuki and co-workers reported an efficient four-component reaction protocol for the synthesis of pyranopyrazole derivatives in the presence of bases such as piperidine, pyrrolidine, morpholine and triethylamine at ambient temperature.[18] Kappusami *et al.* have developed solvent-free multicomponent synthesis of pyranopyrazoles using per-6-amino-β-cyclodextrin as a catalyst.[19] More recently Myrboh *et al.* reported the synthesis of pyranopyrazoles using L-proline and γ-alumina as catalyst.[20] As a part of ongoing program on

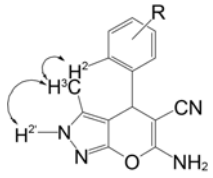
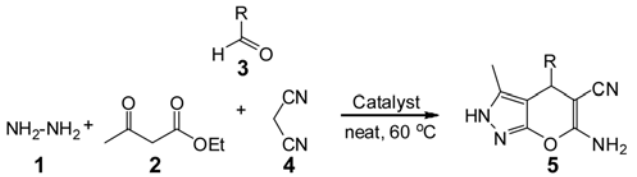


Figure 1. Observed NOE enhancements between CH (CH_3) and N^2H as well as CH (CH_3) and C^2H.



Scheme 1

the development of novel methods in organic synthesis,[21] we report herein a simple, rapid and high yielding one pot four-component reaction protocol for the synthesis of pyrano-pyrazole derivatives employing environmentally friendly silicotungstic acid ($H_4[SiW_{12}O_{40}]$) as a catalyst under solvent free condition (Scheme 1).

Experimental

General Procedure for the Synthesis of the Pyrano-pyrazoles (5a-t). In a 25 mL round-bottom flask, hydrazine hydrate 96% (0.107 g, 2 mmol), ethyl acetoacetate (0.26 g, 2 mmol), 3-nitro benzaldehyde (0.30 g, 2 mmol) malononitrile (0.13 g, 2 mmol) and silicotungstic acid (2 mol %) were taken. The reaction mixture was heated at 60 ºC under solvent free conditions for 10 min. After completion, the reaction mixture was cooled to room temperature, and acetonitrile was added and shaken well for 5 min, then poured over crushed ice, stirred for 10 min, precipitated product was filtered, washed with water, dried and re-crystallized from methanol.

Spectral and Analytical Data of Some Representative Compounds.

6-Amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-*c*]-pyrazole-5-carbonitrile (5a): White powder, mp 244-246 °C, yield 95%; IR (KBr): ν 3371, 3248, 2192, 1613, 1445 cm^{-1}; ^1H NMR (300, $CDCl_3$): δ 1.79 (s, 3H), 4.85 (s, 1H), 6.91 (s, 2H), 7.18-7.35 (m, 5H), 12.13 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 10.1, 36.8, 58.1, 121.0, 126.9, 127.9, 128.7, 136.5, 146.5; MS (ESI): *m/z* = 252 (M^+); Anal. Calcd. for $C_{14}H_{12}N_4O$: C, 66.65; H, 4.79; N, 22.21. Found: C, 66.54; H, 4.68; N, 22.13.

6-Amino-3-methyl-4-(3-nitro-phenyl)-2,4,dihydro-pyrano-[2,3-*c*]pyrazole-5-carbonitrile (5c): Brown solid, mp 214-216 °C, yield 96%; IR (KBr): ν 3385, 3278, 2189, 1622, 1456 cm^{-1}; ^1H NMR (300, $CDCl_3$): δ 1.83 (s, 3H), 4.98 (s, 1H), 6.95 (s, 2H), 7.84 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.42-7.45 (m, 2H), 12.16 (s, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 9.78, 32.5, 59.6, 120.2, 121.4, 124.7, 127.6, 130.0, 134.1, 135.3, 141.8, 146.2, 148.8, 175.9; MS (ESI): *m/z* = 297 (M^+); Anal. Calcd. for $C_{14}H_{11}N_5O_3$: C, 56.56; H, 3.73; N, 23.56. Found: C, 56.14; H, 3.62; N, 23.35.

6-Amino-4-(2,4-dichlorophenyl)-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5f): White solid, mp 196-198 °C, yield 95%; IR (KBr): ν 3422, 3240, 2190, 1610, 1424, 1062 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.82 (s, 3H), 4.80 (s, 1H), 7.05 (s, 2H), 7.18 (d, J = 8.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.86 (s, 1H), 12.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.2, 35.2, 58.6, 118.5, 119.8, 126.9, 128.3, 133.1, 135.8, 136.3, 142.6, 148.4, 149.9, 178.1; MS (ESI): *m/z* = 321 (M^+); Anal. calcd for $C_{14}H_{10}Cl_2N_4O$: C, 52.36; H, 3.14; Cl, 22.08; N, 17.45; O, 4.98; Found: C, 52.02; H, 2.99; Cl, 21.92; N, 17.38; O, 4.83.

6-Amino-4-(2,6-dichlorophenyl)-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5g): White solid, mp 188-190 °C, yield 92%; IR (KBr): ν 3428, 3250, 2195, 1614, 1422, 1066 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.83 (s, 3H), 4.85 (s, 1H), 7.10 (s, 2H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 12.17 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.3, 36.4, 59.8, 118.9, 119.6, 128.7, 134.2, 137.8, 143.5, 148.9, 148.6, 178.2; MS (ESI): *m/z* = 321 (M^+); Anal. calcd for $C_{14}H_{10}Cl_2N_4O$: C, 52.36; H, 3.14; Cl, 22.08; N, 17.45; O, 4.98; Found: C, 52.08; H, 2.95; Cl, 21.98; N, 17.30; O, 4.88.

6-Amino-4-(2,4-difluorophenyl)-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitrile (5k): Yello solid, mp 176-178 °C, yield 90%; IR (KBr): ν 3427, 3242, 2191, 1612, 1428, 1060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.81 (s, 3H), 4.86 (s, 1H), 7.09 (s, 2H), 7.22 (d, *J* = 8.2 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.88 (s, 1H), 12.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0, 36.5, 58.2, 118.9, 120.6, 127.4, 128.8, 133.7, 136.7, 137.6, 143.0, 148.9, 150.1, 178.7; MS (ESI): *m/z* = 288 (M^+).

6-Amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydro-pyrano[2,3-*c*]pyrazole-5-carbonitrile (5n): White solid, mp 210-212 °C, yield 95%; IR (KBr): ν 3485, 3258, 2185, 1608, 1442 cm^{-1}; ^1H NMR (300, $CDCl_3$): δ 1.77 (s, 3H), 3.82 (s, 3H), 4.62 (s, 1H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 7.15 (s, 2H), 12.10 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.0, 36.2, 55.1, 57.9, 107.4, 113.4, 114.2, 118.5, 136.8, 144.2, 155.8, 156.3, 160.5; MS (ESI): *m/z* = 175 (M^+); Anal. Calcd. for $C_{15}H_{14}N_4O_2$: C, 63.82; H, 5.10; N, 19.85. Found: C, 63.42; H, 4.98; N, 19.79.

6-Amino-4-(2,4-dimethoxyphenyl)-2,4-dihydropyrano-[2,3-*c*]pyrazole-5-carbonitrile (5o): White solid, mp 222-224 °C, yield 92%; IR (KBr): ν 3382, 3240, 2168, 1608, 1450 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.78 (s, 3H), 3.76 (s, 3H), 3.77 (s, 3H), 4.77 (s, 1H), 6.46 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 12.06 (s, 1H); MS (ESI): *m/z* = 312 (M^+).

6-Amino-4-(2,4,6-trimethoxyphenyl)-2,4-dihydropyrano-[2,3-*c*]pyrazole-5-carbonitrile (5p): White solid, mp 228-230 °C, yield 90%; IR (KBr): ν 3381, 3246, 2170, 1610, 1455 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.76 (s, 3H), 3.71 (s, 3H), 3.72 (s, 6H), 4.74 (s, 1H), 6.31 (s, 2H), 6.84 (s, 2H), 12.03 (s, 1H); MS (ESI): *m/z* = 342 (M^+).

6-Amino-4-(furan-2-yl)-3-methyl-2,4-dihydropyrano-[2,3-*c*]pyrazole-5-carbonitrile (5s): White solid; mp 218-220 °C, yield 88%; IR (KBr): ν 3362, 3275, 2180, 1610, 1450 cm^{-1}; ^1H NMR (300, $CDCl_3$): δ 1.80 (s, 3H), 4.77 (s, 1H), 6.14 (s, 2H), 6.22 (d, *J* = 1.8 Hz, 1H), 6.42 (dd, *J* = 1.8, *J* = 3.4 Hz, 1H), 7.53 (d, *J* = 3.4 Hz, 1H), 12.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 10.23, 30.11, 54.06, 95.18, 105.34, 111.23, 120.66, 136.28, 146.22, 154.82, 155.92, 162.18; MS (ESI): *m/z* = 242 (M^+); Anal. Calcd. for $C_{12}H_{10}N_4O_2$: C,59.50; H, 4.16; N, 23.13. Found: C, 59.40; H, 4.05; N, 23.07.

Results and Discussion

Our initial experiments were focused on the one pot, four component reactions of ethyl acetoacetate, hydrazine hydrate, 3-nitro benzaldehyde and malononitrile using different catalysts under solvent free conditions, and the results are listed in Table 1.

Table 1. Screening of catalysts for one-pot condensation of ethyl acetoacetate, hydrazine hydrate, 3-nitro benzaldehyde and malononitrile[a]

Entry	Catalyst	Catalyst (mol %)	Time (min)	Yield (%)[b]
1	none	-	180	-
2	$FeCl_3$	2	10	20
3	$SnCl_4$	2	10	38
4	$ZnCl_2$	2	10	25
5	P_2O_5	2	10	32
6	CAN	2	10	15
7	$H_4[SiW_{12}O_{40}]$	2	10	96
8	$H_4[SiW_{12}O_{40}]$	0.5	10	34
9	$H_4[SiW_{12}O_{40}]$	1	10	68
10	$H_4[SiW_{12}O_{40}]$	5	10	95

[a]Reaction conditions: ethyl acetoacetate (2.0 mmol), hydrazine hydrate (2.0 mmol), 3-nitro benzaldehyde (2.0 mmol), and malononitrile (2.0 mmol), solvent free, 60 °C (oil bath). [b]Isolated yield.

Table 2. Effect of solvent on the reaction of ethyl acetoacetate, hydrazine hydrate, 3-nitro benzaldehyde and malononitrile catalysed by $H_4[SiW_{12}O_{40}]$

Entry	Solvent	Temp (^oC)	Time (min)	Yield (%)
1	acetone	reflux	60	35
2	dichloromethane	reflux	60	27
3	tetrahydrofuran	reflux	60	36
4	ethanol	reflux	60	40
5	methanol	reflux	60	52
6	acetonitrile	reflux	60	68
7	none	60	10	96

It was found that silicotungstic acid ($H_4[SiW_{12}O_{40}]$) showed better catalytic activity among other catalysts such as $FeCl_3$, $SnCl_4$, $ZnCl_2$, P_2O_5 and ceric ammonium nitrate (CAN). When 2 mol % silicotungstic acid was used, the reaction proceeded smoothly and gave the product **5c** in 96% yield (Table 1, entry 7). Moreover, we found that the yields were obviously affected by the amount of silicotungstic acid loaded. When 0.5 mol %, 1 mol % and 5 mol % of silicotungstic acid were used, the yields were 34%, 68%, and 95%, respectively (Table 1, entries 8-10). Therefore, 2 mol % of silicotungstic acid was sufficient to push the reaction forward, and further increasing the amount of silicotungstic acid did not increase the yields. In addition, no desired product was detected in the absence of the catalyst (Table 1, entry 1). The above results showed that silicotungstic acid was essential in the reaction, and the best results were obtained when the reaction was carried out with 2 mol % of silicotungstic acid under solvent free conditions at 60 °C.

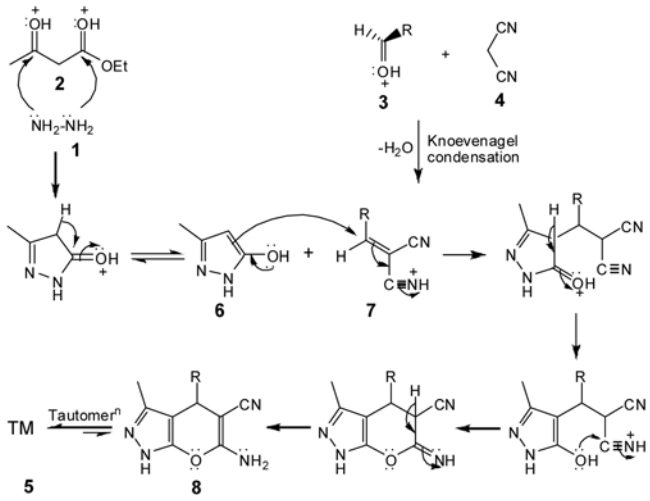
Then, we examined the effect of solvents for above reaction. The results of Table 2 indicate that solvents affected the efficiency of the reaction. Yields were poor in dichloromethane, acetone, tetrahydrofuran and ethanol (Table 2, entries 1-4). Better yields were obtained in acetonitrile and methanol (Table 2, entry 5 and 6). However, the best results were obtained under solvent free conditions (Table 2, entry 7).

Table 3. Four-component synthesis of Pyranopyrazoles

Entry	R	Product	Yield (%)[a]
1	C_6H_5	**5a**	95
2	2'-NO_2-C_6H_4	**5b**	94
3	3'-NO_2-C_6H_4	**5c**	96
4	4'-NO_2-C_6H_4	**5d**	94
5	3'-Cl-C_6H_4	**5e**	94
6	2'-Cl,4'-Cl-C_6H_4	**5f**	95
7	2'-Cl,6'-Cl-C_6H_3	**5g**	92
8	3'-Br-C_6H_4	**5h**	96
9	4'-Br-C_6H_4	**5i**	96
10	4'-F-C_6H_4	**5j**	93
11	2'-F,4'-F-C_6H_3	**5k**	90
12	4'-Me-C_6H_4	**5l**	94
13	4'-Me_2N-C_6H_4	**5m**	95
14	4'-MeO-C_6H_4	**5n**	95
15	2'-MeO,4'-MeO-C_6H_3	**5o**	92
16	2',4',6'-$(MeO)_3$-C_6H_2	**5p**	90
17	2'-OH-C_6H_4	**5q**	90
18	4'-OH-C_6H_4	**5r**	91
19	2'-Furanyl	**5s**	88
20	2'-Thiophenyl	**5t**	86
21	Propyl	**5u**	58
21	*n*-Hexyl	**5v**	65

[a]Isolated yields.

To study the generality of this protocol, we extended our study with different aromatic and aliphatic aldehydes to prepare a series of pyranopyrazoles (**5a-v**, Table 3). In case of aromatic aldehydes, products were obtained in good to excellent yields while aliphatic aldehydes results poor yields. All the synthesized compounds were characterized by IR, ^1H NMR, ^{13}C NMR, LCMS and elemental analysis data. ^1H NMR and ^{13}C NMR indicated the presence of product **5** (the 2H form). In addition, the regiochemistry of compound **5** was also determined by an NOE study (Figure 1). NOE experiments could readily confirm the predominance of product **5** as irradiating the CH_3 signal at 1.79 δ,



Scheme 2

resulted in an enhanced NH signal at 12.13 δ along with aryl proton enhancement. Thus, we conclude that the product **5** formed in predominant form and this is also supported by the previous X-ray crystallographic investigations.[18]

Mechanistically, the reaction occurs *via* initial formation of arylidenemalononitrile **7** by the Knoevenagel condensation between **3** and **4**, and pyrazolone **6** by the reaction between **1** and **2**. Finally, Michael addition of pyrazolone **7** to arylidenemalononitrile **7**, followed by cyclization and tautomerization yield pyranopyrazole **5** (Scheme 2).

Conclusion

In conclusion, we have developed a highly efficient heteropolyacid catalyzed, one-pot, four component protocol for the synthesis of pyranopyrazoles *via* condensation of ethyl acetoacetate, hydrazine hydrate, aldehyde and malononitrile. The advantages of this method are clean reaction, short reaction time, high yield, easy purification and economic availability of the catalyst.

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