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Diammonium hydrogen phosphate: An efficient catalyst for the one pot synthesis of pyrano[2,3-c]pyrazoles derivatives in aqueous medium

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Abstract: Diammonium hydrogen phosphate $(NH_4)_2HPO_4$, was used as a catalyst for one pot four-component synthesis of 6-amino-4-alkyl/aryl-3-methyl-2,4-dihydropyrano[2,3-*c*]pyrazole-5-carbonitriles.It is synthesized by using ethylacetoacetate, hydrazine hydrate, malononitrile, and aromatic aldehydes in water as a solvent under mild reaction conditions. This method has several advantages such as high yield, mild reaction condition, operational simplicity, less toxic, low cost chemical and easy work-up procedure with environment friendly nature.

Keywords*:* Pyranopyrazoles, Diammonium hydrogen phosphate (DAHP) Aqueous medium, Multicomponent reactions.

Introduction

Multicomponent reactions have more advantages of great synthesis of various novel organic compounds, In recent years, there has been tremendous development in four component reactions and great work has been done in multi-component reactions (MCRs). By using readily available,economically viable starting materials maximum yield of product with environmental friendly methods has been investigated reently.[1-3] In this sense, multi-component reactions (MCRs) in aqueous medium is one of the method for synthetic transformation due to their easy handling, experimental simplification, less hazardous and minimum side product with high yield of desired product.[1-3]

Many organic solvents are harmful and therefore there is a need to minimized the use of such chemicals as far as possible .As a reaction medium use as a water .It has several advantages such as environmentally benign, reduce in the formation of by-products and direct isolation of products by precipitation and filtration as they are often insoluble. Furthermore, We have also developed another method for the synthesis of pyrano[2,3-c] pyrazole by using TBAB 10mol% Tetra butyl ammonium bromide was a catalyst. The procedure is same for both catalyst but DAHP catalyst shows rate of reaction more faster than TBAB catalyst as well as improvement in the yield of product.[2-5]

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In our earlier work, we have reported the synthesis of pyrano[2,3-c] pyrazole by using TBAB 10mol% Tetra butyl ammonium bromide as a catalyst. we wish to report the catalytic efficiency of Diammonium hydrogen phosphate for the synthesis of 6-amino-5-cyano-4-aryl-4*H*-pyrazolo[3,4 *b*]pyran derivatives **5** *via* the four-component reaction of hydrazine hydrate**1**, ethylacetoacetate **2**, aromatic aldehydes **3** and malononitrile **4** in aqueous medium (Scheme 1).[4]

In recent years, Diammonium hydrogen phosphate $(NH_4)_2HPO_4$ has immerged as an extremely useful homogeneous catalyst in various organic transformation including conjugate addition of thiols to electron deficient alkenes, transthioacetalisation of acetals, trimethylsilylation of alcohols, synthesis of aryl-14H-dibenzoxanthene. This reagent used in various industry like pharmaceuticals, chemical, textiles etc. DAHP is an inexpensive readily available with inherent properties like environmental compatibility, greater selectivity, operational simplicity non-corrosive nature and ease of reusability.[7]

The Diammonium hydrogen phosphate (DAHP) is recently used for the synthesis of pyrano[2,3d]pyrimidinone[5],Tetrahydrobenzo[b]pyran[7],1,8Dioxo-octahydroxanthene[6], 5-Arylidenerhodanines[8]

Materials and Methods:

All chemicals were used of laboratory grade and used without purification. Reactions were monitored by thin layer chromatography (TLC), visualizing with ultraviolet. Melting points were determined in open capillary tubes and are uncorrected. IR spectra were recorded on FT IR jasco 4100 KBr pellets with absorptions in cm−1. 1H NMR and 13C NMR spectra were recorded on a BRUKER AVANCE DPX spectrometer using DMSO-d6 as solvent and TMS as an internal standard. Chemical shifts (δ) are expressed in ppm, downfield from internal standard TMS and *J* values in hertz (Hz).

General procedure for the preparation of 6-Amino-4-aryl-3-methyl-2,4-dihydropyrano[2,3-C] pyrazole-5-carbonitriles or carboxylate (5a-m)

To start with, we took a mixture of hydrazine hydrate 1 (0.107 g, 2.0 mmol), ethyl acetoacetate 2 (0.260 g, 2.0 mmol),in water(5 ml) and allowed to stir for 5 min. To this mixture aromatic aldehyde derivatives 3 (2.0 mmol) and malononitrile 4 (0.132 g, 2.0 mmol) were added and allowed to refluxed under stirring for 20 min in the presence of Diammonium hydrogen phosphate (DAHP) (10 mol %). The precipitated solid was filtered, washed with water. The product obtained monitored by TLC . However, the products were further purified by recrystallization from ethanol.

All the synthesized compounds are reported in Table 3 and were confirmed by their physical constants and characterized by IR, 1H and 13C NMR and Mass. The spectroscopic data were in full agreement with the literature values.

Spectral data for prepared compounds

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6-Amino-3-methyl-4-phenyl-2,4-dihydropyrano [2, 3-c] pyrazole-5-carbonitrile **(4a)**
White crystals, mp. 250–255 °C;Vmax (KBr): 3366, 3162 (NH2), 2186 (CN), 1644 (C=N), 1592,1516 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.10 (s, 1H, NH), 7.33–7.16 (m, 5H, atom), 6.88 (s, 2H, NH2), 4.59 (s, 1H, 4-H), 1.78 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ161.3 (C6), 155.2 (C3), 144.9 (C8), 136.1 (C1'), 129.4 (C2',C6'), 128.9 (C3',C5') 127.2 (C4'), 121.2 (CN), 98.1 (C7), 57.6 (C5), 36.7 (C4), 10.2(CH3) ppm. Mass:$C_{14}H_{12}N_4O$ MS(ESI+): m/z 253.11 $(M+H)^+$

6-Amino-4-(4-chlorophenyl)-3methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4b)**
Yellow solid, mp. 239-240 °C; Vmax (KBr): 3334, 3063 (NH2), 2125 (CN), 1665 (C=N), 1590,1520 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.15 (s, 1H, NH), 7.32–7.19 (m, 5H, arom), 6.92 (s, 2H, NH2), 4.50 (s, 1H, 4-H), 1.72 (s, 3H, CH3); 13C NMR (62.9 MHz,DMSO-d6) δ162.3 (C6), 155.5 (C3), 143.9 (C8), 135.1 (C1'), 129.1 (C2',C6'), 127.9 (C3',C5') 127.8 (C4'), 122.5 (CN), 98.5 (C7), 56.8 (C5), 36.9(C4), 10.8(CH3)ppm. Mass:$C_{14}H_{11}N_4OCl$ MS(ESI+): m/z 287.11 $(M+H)^+$

6-Amino-4-(4-hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5 carbonitrile **(4c)**
Yellow solid, mp. 229-230 °C; Vmax (KBr): 3263, 3102 (NH2), 2217 (CN), 1685 (C=N), 1540,1565 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.05 (s, 1H, NH), 7.55–7.22 (m, 5H, atom), 6.77 (s, 2H, NH2), 4.51 (s, 1H, 4-H), 1.82 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.3 (C6), 151.2 (C3), 144.9 (C8), 135.1 (C1'), 128.9 (C2',C6'), 127.9 (C3',C5') 127.2 (C4'), 121.3 (CN), 98.1 (C7), 57.6 (C5), 36.9(C4), 10.8(CH3)ppm. Mass:$C_{14}H_{12}N_4O_2$ MS(ESI+): m/z 270.15 $(M+H)^+$

6-Amino-4-(4-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4d)**
White solid, mp.225-226 °C; Vmax (KBr): 3185, 3010 (NH2), 2205 (CN), 1715 (C=N), 1590,1520 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.56 (s, 1H, NH), 7.25–7.32 (m, 5H, arom), 6.45 (s, 2H, NH2), 4.65 (s, 1H, 4-H), 1.85 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.3 (C6), 152.2 (C3), 1445.8 (C8), 138.1 (C1'), 129.9 (C2',C6'), 125.9 (C3',C5') 125.2 (C4'), 128.3 (CN), 99.1 (C7), 59.6 (C5), 36.0(C4), 9.98(CH3) ppm. Mass:$C_{15}H_{14}N_4O2$ MS(ESI+): m/z 273.21 $(M+H)^+$

6-Amino-3-methyl-4-(4methylphenyl)-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4e)**
Yellow crystals, mp.219-220 °C; Vmax (KBr): 3204, 3047 (NH2), 2187 (CN), 1704 (C=N), 1540,1522 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.12 (s, 1H, NH), 7.47–7.08 (m, 5H, atom), 6.92 (s, 2H, NH2), 4.50 (s, 1H, 4-H), 1.72 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.3 (C6), 150.2 (C3), 144.9 (C8), 135.1 (C1'), 124.9 (C2',C6'), 129.9 (C3',C5') 128.2 (C4'), 125.8 (CN), 98.4 (C7), 57.6 (C5), 36.9(C4), 11.5(CH3)ppm Mass:$C_{15}H_{14}N_4O$ MS(ESI+): m/z 267.05 $(M+H)^+$

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6-Amino-4-(4-nitrophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4f)**
Brown crystals, mp. 249-250 °C; Vmax (KBr): 3375, 3263 (NH2), 2210 (CN), 1630 (C=N), 1570,1532 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.77 (s, 1H, NH), 7.78–7.26 (m, 5H, arom), 6.55 (s, 2H, NH2), 4.68 (s, 1H, 4-H), 1.79 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.3 (C6), 156.2 (C3), 154.9 (C8), 134.1 (C1'), 128.9 (C2',C6'), 127.9 (C3',C5') 127.2 (C4'), 122.8 (CN), 94.1 (C7), 52.6 (C5), 36.2(C4), 11.5(CH3)ppm. Mass:$C_{14}H_{11}N_5O_3$ MS(ESI+): m/z 298.14 $(M+H)^+$

6-Amino-4-(3-hydroxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4g)**
White powder, mp.248-249 °C; Vmax (KBr): 3407, 3173 (NH2), 2177 (CN), 1699 (C=N), 1595,1526 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.84 (s, 1H, NH), 7.48–7.08 (m, 5H, atom), 6.72 (s, 2H, NH2), 4.72 (s, 1H, 4-H), 1.85 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.3 (C6), 154.2 (C3), 144.9 (C8), 135.1 (C1'), 128.9 (C2',C6'), 127.9 (C3',C5') 127.2 (C4'), 121.3 (CN), 98.1 (C7), 57.6 (C5), 36.9(C4), 10.8(CH3) ppm. Mass:$C_{14}H_{12}N_4O_2$ MS(ESI+): m/z 271.11 $(M+H)^+$

6-Amino-4-(3-nitrophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4h)**
Brown powder, mp. 229-230 °C; Vmax (KBr): 3336, 3145 (NH2), 2157 (CN), 1715 (C=N), 1601,1540 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 11.85 (s, 1H, NH), 7.11–6.98 (m, 5H, atom), 7.15 (s, 2H, NH2), 4.51 (s, 1H, 4-H), 1.68 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.3 (C6), 151.8 (C3), 144.9 (C8), 135.1 (C1'), 124.9 (C2',C6'), 129.9 (C3',C5') 127.2 (C4'), 121.3 (CN), 98.0 (C7), 57.4 (C5), 37.9(C4), 10.1(CH3) ppm. Mass:$C_{14}H_{11}N_5O_3$ MS(ESI+): m/z 298.10 $(M+H)^+$

6-Amino-4-(2-methoxyphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4i)**
White powder, mp.253-254 °C; Vmax (KBr): 3305, 3063 (NH2), 2187 (CN), 1644 (C=N), 1580,1521 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.18 (s, 1H, NH), 7.66–7.29 (m, 5H, atom), 7.85 (s, 2H, NH2), 4.77 (s, 1H, 4-H), 1.62 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.3 (C6), 152.2 (C3), 144.9 (C8), 135.1 (C1'), 130.4 (C2',C6'), 121.9 (C3',C5') 124.2 (C4'), 131.3 (CN), 98.9 (C7), 57.1 (C5), 36.5(C4), 10.3(CH3) ppm. Mass:$C_{15}H_{14}N_4O2$ MS(ESI+): m/z 273.11 $(M+H)^+$.

6-Amino-4-(2-nitrophenyl)-3-methyl-2, 4-dihydropyrano [2, 3-c] pyrazole-5-carbonitrile **(4j)**
Blackish powder,mp. 246-247 oC; Vmax (KBr): 3363, 3036 (NH2), 2214 (CN), 1649 (C=N), 1590,1520 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.68 (s, 1H, NH), 7.31–7.11 (m, 5H, atom), 7.25 (s, 2H, NH2), 4.78 (s, 1H, 4-H), 1.89 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ172.3 (C6), 151.4 (C3), 146.9 (C8), 138.1 (C1'), 138.9 (C2',C6'), 135.9 (C3',C5') 133.2 (C4'), 121.3 (CN), 94.1 (C7), 55.6 (C5), 36.9(C4), 10.8(CH3) ppm. Mass:$C_{14}H_{11}N_5O_3$ MS(ESI+): m/z 298.17 $(M+H)^+$

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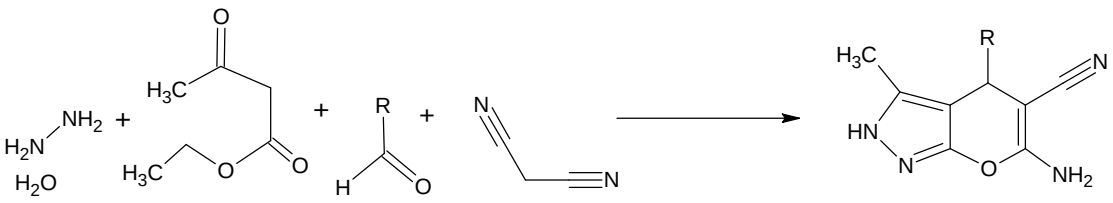
6-Amino-4-(4-bromophenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile **(4k)** Vmax (KBr): 3362, 3182 (NH2), 2185 (CN), 1651 (C=N), 1621,1585 (Ar) cm-1; 1H NMR(250 MHz, DMSO-d6) δ 12.18 (s, 1H, NH), 7.32–7.15 (m, 5H, atom), 6.91 (s, 2H, NH2), 4.55 (s, 1H, 4-H), 1.75 (s, 3H, CH3); 13C NMR (63.9 MHz,DMSO-d6) δ162.5 (C6), 151.8 (C3), 145.9 (C8), 135.8 (C1'), 127.9 (C2',C6'), 127.9 (C3',C5') 131.2 (C4'), 131.3 (CN), 97.1 (C7), 54.6 (C5), 37.7(C4), 9.95(CH3) ppm. Mass:$C_{14}H_{11}N_4OBr$ MS(ESI+): m/z 333.15 $(M+H)^+$

Result and Discussion

The reaction (Scheme 1) between hydrazine hydrate, ethyl acetoacetate, malononitrile, and benzaldehyde (R = C6H5) was chosen as a model condensation reaction for optimizing the various reaction parameters: solvent, temperature, catalyst.



1 2 3 4 5

Scheme 1

Initially, the reaction was tried without any catalyst in solvent-free conditions at ambient temperature, but the reaction could not complete even after 24 h stirring (Table 1,entry 1). Interestingly, when 5 ml of water was added to the reaction mixture, an oily product was obtained (Table 1, entry 2) . To increase the reaction rate and minimize the consumption of energy, we performed the model Diammonium hydrogen phosphate (DAHP) as catalysts in aqueous media under reflux conditions. From these preliminary studies, it was observed that the rate of the catalyzed reaction is higher than the corresponding uncatalyzed one at the same temperature. Table 1. entry 3)

Table 1 The Influence of temperature on one-pot condensation of ethylacetoacetate, hydrazine hydrate, benzaldehyde and malnonitrile**.**

Entry	Catalyst	Solvent	Temp °C	Time min	Yield%
1	Cat free	Neat	Room Temperature	120	-
2	Cat free	Water	Room Temperature	120	Nil
3	DAHP (10mol%)	Water	Reflux	20	95

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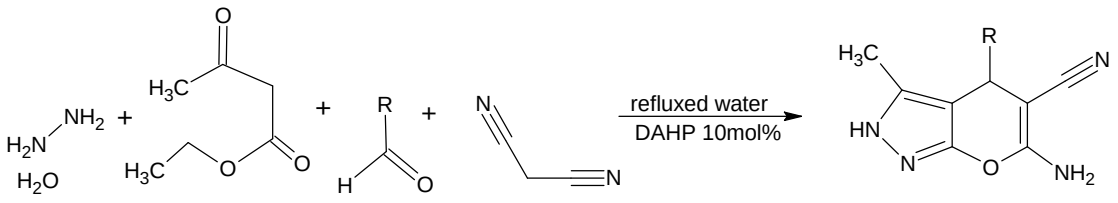
The choice of a solvent is a crucial factor for multicomponent reactions, so different organic solvents were examined for the reaction (Table 2, entries 2-4) and we found that water was the solvent of choice which provided the highest rate and yield (Table 2, entry 4). Similar yield was also obtained under solvent free conditions but relatively longer reaction time was needed (Table 2, entry 1).

Table 2. The Influence of solvent on the model reaction in the presence of Diammonium hydrogen phosphate (DAHP) (10 mol%)

Entry	Catalyst	Temperature °C	Time ,h	Yield%
1	Solvent free	90°C	4	88
2	CH3CN	Reflux	5	51
3	DMSO	Reflux	1	45
4	H2O	Reflux	20 min	95

Reaction conditions: ethyl acetoacetate (2.0 mmol), hydrazine hydrate(2.0 mmol), benzaldehyde (2.0mmol) and malononitrile (2.0 mmol). Isolated yield

With the optimized reaction conditions in hand and to study the efficiency of this catalyst, we extended our study with different aromatic aldehydes to prepare a series of pyranopyrazoles in good to excellent yields (Scheme 2, Table 3, 4a-m).



1 **2** **3** **4** **5**

Scheme 2. Synthesis of pyranopyrazoles (4a-k)

Table 3. One-pot synthesis of pyranopyrazoles catalyzed by Diammonium hydrogen phosphate (DAHP) (10 mol%)

Entry	Aldehyde	Time min	Product	Yield %	Melting point °c

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					Found	Reported
1	C6H5	20	**4a**	95	240-242	243-245
2	4-Cl-C6H4	20	**4b**	95	232-238	233-236
3	4-OH-C6H4	20	**4c**	95	229-230	224-226
4	4-MeO-C6H4	20	**4d**	90	224-226	208-211
5	4-CH3-C6H4	20	**4e**	95	215-216	210-212
6	4-NO2-C6H4	20	**4f**	94	248-251	245-248
7	3-OH-C6H4	20	**4g**	85	248-250	247-249
8	3-NO2-C6H4	20	**4h**	89	215-218	214-217
9	2-MeO-C6H4	20	**4i**	96	253-254	248-251
10	2-NO2-C6H4	20	**4j**	96	243-246	243-244
11	4-Br-C6H4	20	**4k**	92	180-182	182-185

Reactions were performed on a 2.0 mmol scale of all reactants with 10 mol % of Diammonium hydrogen phosphate (DAHP) in refluxed water (5 ml)

On the basis of the chemistry of pyranopyrazoles, we propose the possible foll owing mechanism: One molecule of hydrazine derivative **1** was firstly condensed with ethyl acetoacetate **2** to yield pyrazolone derivative **6**. On the other hand, aromatic aldehyde **3** condensed with malononitrile **4** to give α-cyanocinnamonitrile derivative **7**. The next step may involve Michael addition of the active methylene of **6** to an electron deficient carbon of dicyanoalkene **7**, which gives an intermediate **8** tautomerization to the intermediate followed by the nucleophilic attack of OH group on the cyano (CN) moiety to give the cyclic intermediate **9**, which is tautomerized to target pyranopyrazoles **4a-k**. In this process, Tetra n-butyl ammonium bromide (TBAB) could promote these reactions as phase transfer catalyst (Scheme 3).

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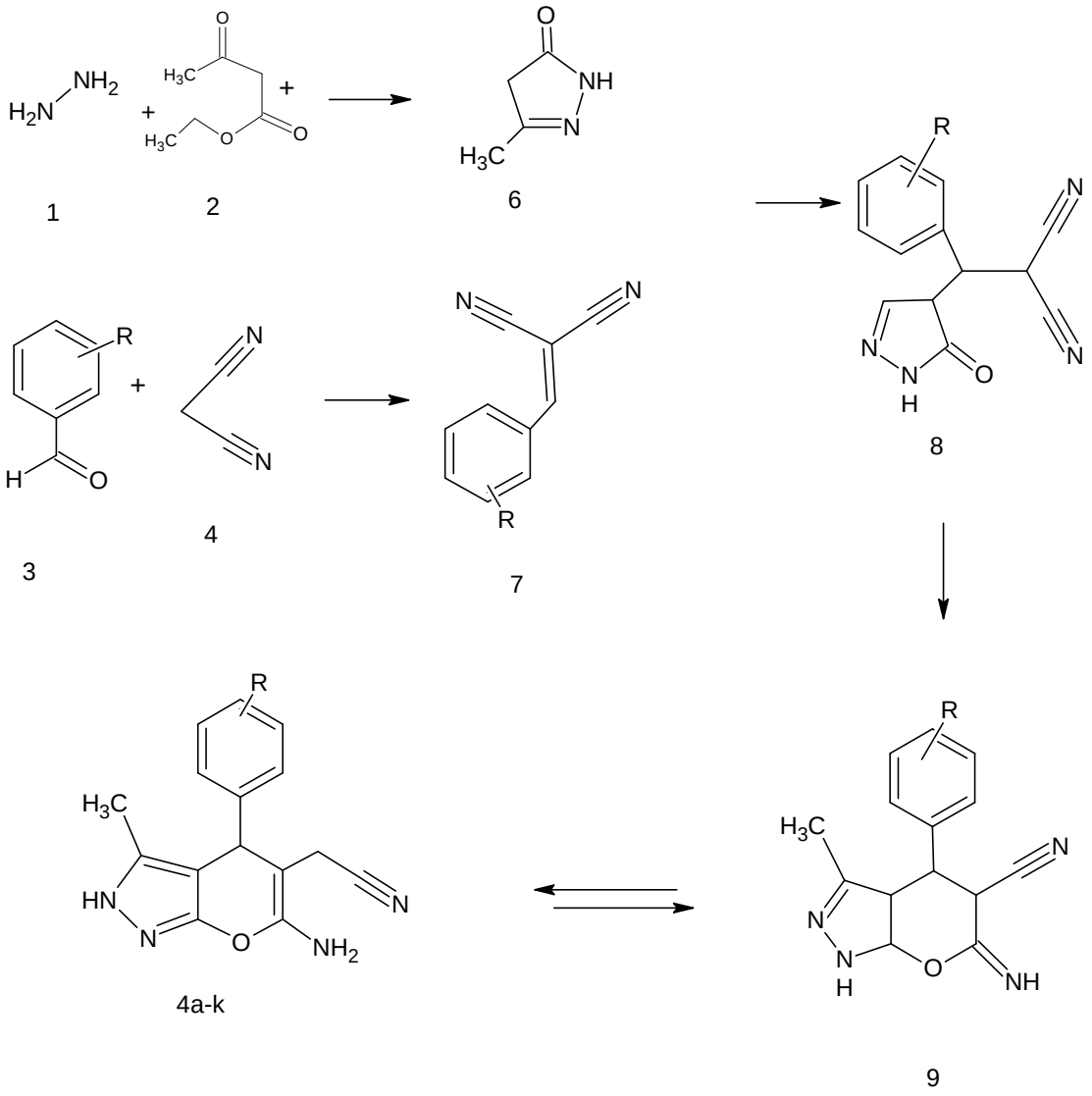

Scheme 3. Plausible mechanism of pyranopyrazoles synthesis

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Conclusion

We have developed a novel, efficient and ecofriendly method for the synthesis of pyrano [2,3-C] pyrazole derivative using (DAHP) Diammonium hydrogen phosphate is an easily available, inexpensive, environment friendly and efficient catalyst by multicomponent condensation in aqueous media. The present method gives product very quickly and non-hazardous to environment.

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