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# Proficient One-pot, Multi-component Synthesis of Pyrano[2,3-c]pyrazole Derivatives Using $C_8$[DABCO]Br as Catalyst in Aqueous Medium

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## ABSTRACT

$C_8$[DABCO]Br, an ionic liquid, was demonstrated to be a highly efficient catalyst for the synthesis of a series of pyranopyrazole derivatives via a one-pot, multi-component reaction of aldehydes, hydrazine hydrate, malononitrile, and β-ketoester in water. The catalyst was found to work extremely to give the corresponding dihydropyrano[2,3-c]pyrazoles in high yields. The salient features of this new methodology are broad substrate scope conditions, short reaction times, high yields, easy work-up process, and the absence of hazardous organic solvents.

**Keywords**: Multicomponent reaction; green chemistry; Pyrano[2,3-c]pyrazole; [$C_8$dabco]Br; One pot reaction

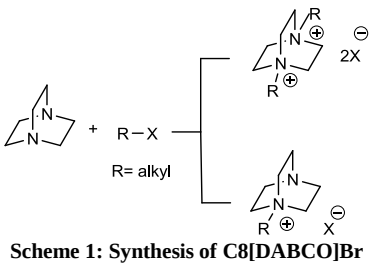
## INTRODUCTION

2-Amino-4-substituted pyrano[2,3-c]pyrazole-3-carbonitriles play a significant role in pharmaceutical field and biologically active compounds. Compounds bearing pyranopyrazole system have been found to have various biological activities, for instance antimicrobial [1], analgesic [2], vasodilator [3], anticancer [4], antiinflammatory [5], inhibitors of human Chk1 kinase [6], molluscicidal [7], antifungicidal [8] and also as biodegradable agrochemicals [9]. Furthermore, some of these compounds are commonly used as cosmetics and pigments [10].

Pyranopyrazoles were first obtained by reaction between 3-methyl-1-phenylpyrazolin-5-one and tetracyanoethylene [11]. The 2-amino-4-substituted pyrano[2,3-c]pyrazole-3-carbonitriles were obtained by addition of malononitrile to 4-arylidene-3-methyl-2-pyrazolin-5-one [12]. Several other methods include one-pot three-component condensation of pyrazolones, malononitrile, and aromatic aldehydes; [13] three-component cyclocondensation of substituted piperidin-4-ones, pyrazol-5-ones, and malononitrile; [14] four-component reaction of aldehydes, ethyl acetoacetate, malononitrile with hydrazine hydrate [15].

For these reactions, a variety of catalysts have been used such as $Et_3N$ [13a], ammonium acetate [13b], triethylbenzylammonium chloride [13c], β-cyclodextrin [15a], imidazole [15b], piperidine [15c], cinchona alkaloid organocatalysts [16], per-6-amino-β-cyclodextrin [17], Brønsted-acidic ionic liquid [18], [bmim]OH [19], L-proline and γ-alumina [20], $H_4[SiW_{12}O_{40}]$ [21], glycine [22], NaOH [23], dodecyltrimethylammonium bromide [24], iodine [25], L-proline [26], silica in water [27], MgO nanoparticle [28], $Ba(OH)_2$ [29] and cetyltrimethylammonium chloride [30].

During the last few years, ionic liquids have gained attention in many organic syntheses and various organic transformations because of their catalytic effect and their very interesting chemical and physical properties. 1, 4-Diazobicyclo-(2,2,2-octane (DABCO) ionic liquids, showed good catalytic activity and attracted the scientific community because of its ease of preparation from commercially available and relatively inexpensive materials (Scheme 1). Pretti Carlo et al. [31] reported that ionic liquids based on N-alkyl-1,4-diazabicyclo[2,2,2]octane show less toxicity and biodegradability which is similar to imidazolium base. Among the syntheses that have used DABCO's ionic liquids as catalysts, have included the synthesis of quinoxalines, phtalazinetrione and tetrahydroauinolines that involves the $C_8$[DABCO]Br (Scheme 1) [32].




**Scheme 1: Synthesis of C8[DABCO]Br**

Water for the time indicated (the reaction was monitored by TLC, eluent hexane/ethyl acetate: 2/1). At the end of the reaction, the mixture was cooled to room temperature and then poured onto ice water. The solid obtained is filtered, washed with ice water and purified by recrystallization from ethanol. The obtained products were identified by spectroscopic methods IR, $^1$H-NMR, $^{13}$C-NMR, HRMS as well as by their melting points. Selected spectroscopic and analytical data are presented below.

*6-Amino-4-(biphenyl)-3-methyl-2,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (6l)*

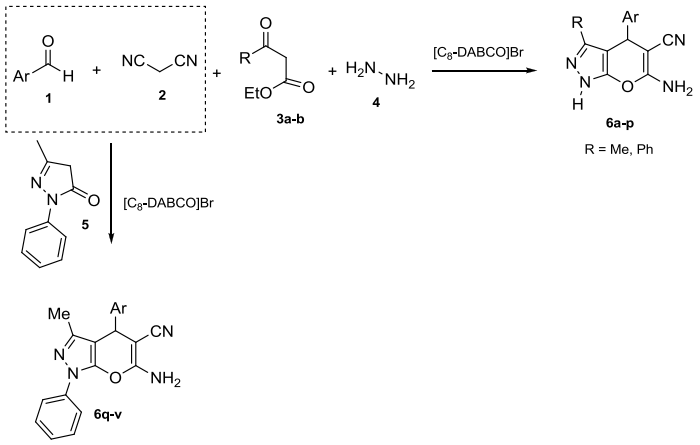
Yield. 96%. Yellow solid. mp. >250°C. IR spectrum (KBr), ν, cm$^{-1}$: 3425 ($NH_2$), 2191 (C=N). $^1$H NMR spectrum (250 MHz, DMSO-$d_6$), $\delta$, ppm (*J*, Hz): $^1$H NMR (250 MHz, DMSO-$d_6$) $\delta$ (ppm): 12.10 (br s, 1H, NH); 7.74 (d, *J*=8.0, 2H Ar); 7.61 (t, *J*=8.0, 2H Ar); 7.50 (t, *J*=7.7, 1HAr); 7.34 (d, *J*=7.0, 2H Ar); 7.26 (d, *J*=8.0, 2H Ar); 6.85 (br s, 2H, $NH_2$); 4.63 (s, 1H, $C_4$-H); 1.84 (s, 3H, $CH_3$). $^{13}$C NMR spectrum (62.9 MHz, DMSO-$d_6$), $\delta$, ppm:159.2, 155.1, 141.9, 138.2, 136.9, 133.8, 127.1, 126.3, 125.5, 125.0, 124.8, 119.1, 95.7, 55.4, 34.3, 8.1. HRMS (EI+): found, *m/z*: 328.1269 $[M]^{+\cdot}$. $C_{20}H_{16}N_4O$. Calculated *m/z*: 328.1324.

*6-amino-4-(3-nitrophenyl)-3-phenyl-1,4-dihydropyrano[2,3-c]pyrazole-5-carbonitrile (6n)*

Yield. 72%. Brown solid. mp. > 250°C. IR Spectrum (KBr), ν, cm$^{-1}$: 3429 (N-H), 2191 (C≡N), 1596 (C=N), 1523 $(C=C)_{Ar}$, 1149 (C-O), 1342-1423 ($NO_2$). $^1$H NMR (400 MHz, DMSO-$d_6$), $\delta$, ppm, (*J*, Hz): 12.26 (s, 1H, NH); 8.07 (d, *J*=8.0, 1H Ar); 7.92 (s, 1H Ar); 7.58 (t, *J*=8.0, 1H Ar); 7.51 (d, *J*=8.0, 2H Ar); 7. 38 (t, *J*= 7.2 Hz, 1H Ar); 7. 21 (t, *J*= 8.0 Hz, 2H Ar); 7.16 (s, 2H, $NH_2$); 7.15 (d, *J*=7.2, $2H_{Ar}$); 5.17 (s, 1H, $C_4$-H). $^{13}$C NMR (100 MHz, DMSO-$d_6$), $\delta$, ppm: 147.8, 145.3, 143.3, 134.0, 129.7, 128.8, 127.7, 121.5, 121.2, 102.9, 65.0, 32.0.

## RESULTS AND DISCUSSION

In this study, we will interested in the synthesis of pyranopyrazoles 6 by a multicomponent reaction from an aromatic aldehyde 1 with malonitrile 2, the 1,3-dicarbonyl compounds in this case ethyl acetoacetate or ethyl 3-oxo-3-phenylpropanoate 3a-b and hydrazine hydrate 4 or by the use of 3-methyl-1-pohenylpyrazol-5-one 5 in the presence of $C_8$[DABCO]Br as a catalyst (Scheme 2).




**Scheme 2: Synthesis of pyranopyrazoles 6 catalyzed by $C_8$[DABCO]Br**

In order to establish the optimal reaction conditions and obtain the desired pyranopyrazoles derivatives, we used a model reaction in which we reacted benzaldehyde 1a, malonitrile 2, ethyl acetoacetate 3a with hydrazine hydrate 4 using different DABCO's based ionic liquids as catalysts for this condensation with the proportions 1/1/1/1/0.1 under different reaction conditions. As we mentioned above, we tested first the effect of different catalysts then we evaluated the amount of catalyst required to promote this condensation, and finally we tested the effect of different solvents at different temperatures.

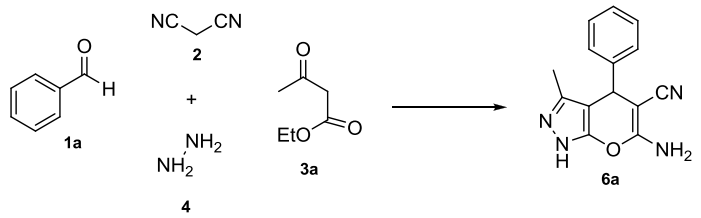
To choose an effective catalyst for the success of the reaction and obtain good returns, we tried several reactions in water with some catalysts such as DABCO, $C_8$[DABCO]Br, $C_{10}$[DABCO]Br and $C_{14}$[DABCO]Br. From the results collected in Table 1 it is observed that compound 6a is obtained in good yields regardless of the used catalyst. Indeed, $C_{10}$[DABCO]Br and $C_{14}$[DABCO]Br as well as DABCO gave yields ranging from 60-68%, however $C_8$[DABCO]Br proved to be the catalyst of choice for this type of reaction that gave better yield of pyranopyrazole 6a (83%) (Table 1 and Entry 2).

The nature of the solvent appears to play a major role in this multi-condensation. Indeed, the use of a polar aprotic solvent such as acetonitrile or in the absence of solvent, the reactions leading to the formation of the pyranopyrazole 6a with low yields ranging between 32 and 36% (Table 1, entries 7 and 8), while the use of polar solvents such as EtOH or EtOH/$H_2O$ (1/1) gave acceptable yields between 43 and 59% (entries 5 and 6). The use of water as a solvent for this condensation was found to be more appropriate in terms of yield and reaction time (Entries 1-4).

It appears from reactions which we tested at different temperatures, that this latter is an important factor for the success of this type of condensation. Indeed, the reactions carried out in water at room temperature and at 60°C give the desired product in good yields of 68% and 71%, respectively, however, this requires a prolonged reaction time (Entries 9 and 10). When we raised the temperature to reflux of water, the reaction was complete after 1 h and the yield improved to 83% (Entry 2).

We also studied the amount of $C_8$[DABCO]Br required to effect the reaction. From the feedback we tested, it was found that when the catalyst's amount decreases from 50 to 20 or 5 mol%, the yield decreases from 64 to 60 and 50% (Entries 11-13). The best result is that obtained with 10mol% of $C_8$[DABCO]Br reflux water (Entry 3).

**Table 1: Synthesis of pyranopyrazole 6a catalyzed with $C_8$[DABCO]Br : Effect of catalysts[a]**



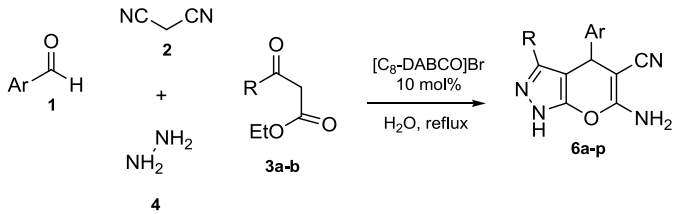

| Entry | Catalyst | Amount of catalyst (mol%) | Solvent | Time (h) | T (°C) | Yield[b] (%) |
|---|---|---|---|---|---|---|
| 1 | DABCO | 10 | $H_2O$ | 2 | Reflux | 68 |
| 2 | $C_8$[DABCO]Br | 10 | $H_2O$ | 1 | Reflux | 83 |
| 3 | $C_{10}$[DABCO]Br | 10 | $H_2O$ | 1.5 | Reflux | 65 |
| 4 | $C_{14}$[DABCO]Br | 10 | $H_2O$ | 3 | Reflux | 60 |
| 5 | $C_8$[DABCO]Br | 10 | EtOH | 3 | Reflux | 43 |
| 6 | $C_8$[DABCO]Br | 10 | EtOH-$H_2O$ | 3.5 | Reflux | 59 |
| 7 | $C_8$[DABCO]Br | 10 | $CH_3CN$ | 8 | Reflux | 36 |
| 8 | $C_8$[DABCO]Br | 10 | - | 7 | 80 | 32 |
| 9 | $C_8$[DABCO]Br | 10 | $H_2O$ | 2 | R.t | 68 |
| 10 | $C_8$[DABCO]Br | 10 | $H_2O$ | 1.5 | 60 | 71 |
| 11 | $C_8$[DABCO]Br | 50 | $H_2O$ | 1 | Reflux | 64 |
| 12 | $C_8$[DABCO]Br | 20 | $H_2O$ | 1 | Reflux | 60 |
| 13 | $C_8$[DABCO]Br | 5 | $H_2O$ | 1 | Reflux | 50 |

[a]Reactions were carried out with a mixture of benzaldehyde 1a (1 eqv.), malonitrile 2 (1 eqv.), ethyl acetoacetate 3a (1eqv.) hydrazine hydrate 4 (1 eqv.) in the presence of 10 mol % of catalyst; [b]solated yields

To investigate the generality of the reaction catalyzed by the $C_8$[DABCO]Br, the same above reaction was extended under similar conditions using a variety of aromatic or heteroaromatic aldehydes 1, malononitrile 2, ethyl acetoacetate 3a and hydrazine hydrate 4. As expected, satisfactory yields of pyranopyrazoles 6 were observed. All the results obtained are summarized in Table 2.

The condensations carried out with various aromatic or heteroaromatic aldehydes 1 (1 eqv.) with malononitrile 2 (1 eqv.), ethyl acetoacetate 3a (1 eqv.) and hydrazine hydrate 4 (1 eqv.) in the presence of $C_8$[DABCO]Br (10 mol%) give the desired pyranopyrazoles 6 in good yields ranging between 46 and 90%. The presence of electron-withdrawing or electron-donating groups on the aromatic ring does not have a great effect on the yield; however, the reaction with 4-hydroxy-benzaldehyde, 4-bromo-benzaldehyde, 4-methyl-benzaldehyde, 2-methoxy-benzaldehyde, and 4-methoxy-benzaldehyde were more efficients giving higher yields of 90% (Entries 5, 6, 9, 10 and 11). Similarly, the use of 4-phenyl-benzaldehyde gave also very good yield (Entry 12).

**Table 2: Synthesis of pyranopyrazoles 6a-p catalyzed with $C_8$[DABCO]Br[a]**



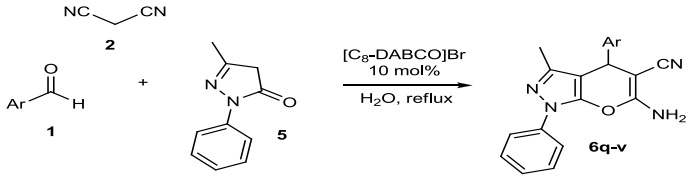

| Entry | Ar | R | Product | Time (h) | Yield[b] (%) | Mp (°C) |
|---|---|---|---|---|---|---|
| 1 | $C_6H_5$ | $CH_3$ | **6a** | 1 | 83 | 240-242 (244-245) [34] |
| 2 | 4-$NO_2$- $C_6H_4$ | $CH_3$ | **6b** | 3 | 76 | 244-246 (249) [35] |
| 3 | 3-$NO_2$- $C_6H_4$ | $CH_3$ | **6c** | 3 | 84 | 230-232 (232-234) [35] |
| 4 | 4-Cl- $C_6H_4$ | $CH_3$ | **6d** | 2 | 72 | 236-238 (233-234) [35] |
| 5 | 4-Br-$C_6H_4$ | $CH_3$ | **6e** | 2 | 92 | 182-184 (180-183) [37] |
| 6 | 4-OH- $C_6H_4$ | $CH_3$ | **6f** | 2.5 | 90 | 224-228 (224-226) [35] |
| 7 | 4-Et- $C_6H_4$ | $CH_3$ | **6g** | 2 | 72 | > 250 |
| 8 | 4-$(CH_3)_2$N-$C_6H_4$ | $CH_3$ | **6h** | 2.5 | 80 | 220-222 (219-222) [37] |
| 9 | 4- $CH_3$-$C_6H_4$ | $CH_3$ | **6i** | 2 | 94 | 209-210 (203-204) [38] |
| 10 | 2-$CH_3O$-$C_6H_4$ | $CH_3$ | **6j** | 1 | 90 | > 250 (249-250) [34] |
| 11 | 4-$CH_3O$-$C_6H_4$ | $CH_3$ | **6k** | 1 | 95 | 225-226 (210-212) [34] |
| 12 | 4-$C_6H_5$-$C_6H_4$ | $CH_3$ | **6l** | 1 | 96 | > 250 |
| 13 | $C_6H_5$ | $C_6H_5$ | **6m** | 5 | 62 | > 250 (262-263) [36] |
| 14 | 3-$NO_2$-$C_6H_4$ | $C_6H_5$ | **6n** | 3.5 | 72 | > 250 |
| 15 | 4-Cl-$C_6H_4$ | $C_6H_5$ | **6o** | 5 | 68 | 240-242 (242-244) [36] |
| 16 | 4-$CH_3$-$C_6H_4$ | $C_6H_5$ | **6p** | 5 | 60 | 242-244 (245-247) [36] |

[a]Reactions were carried out with a mixture of aldehydes 1 (1 eqv.), malonitrile 2 (1 eqv.), β-ketoesters 3 (1 eqv.) hydrazine hydrate 4 (1 eqv.) in the presence of 10 mol % of $C_8$[DABCO]Br in water at reflux; [b]Isolated yields

In order to extend the scope of our method, we have extended this condensation under the same conditions previously optimized, using benzaldehyde and some of its derivatives 1 and malononitrile 2, ethyl 3-oxo-3-phenylpropanoate 3b as a β-ketoester and hydrazine hydrate 4. Satisfactory yields were performed for products 6(m-p) (Table 2, entries 13-16). The condensations carried out with various aromatic or heteroaromatic aldehydes 1 (1 eqv.) with malononitrile 2 (1 eqv.), Ethyl 3-oxo-3-phenylpropanoate 3b (1 eqv.) And hydrazine hydrate 4 (1 eqv.) in the presence of $C_8$[DABCO]Br (10 mol%) give the expected products with yields ranging between 60 and 72%. The presence of electron-withdrawing groups on the aryl moiety such as 3-nitro-benzaldehyde or 4-chlorobenzaldehyde give higher yields, with respect to aldehydes bearing electron donating groups which give the corresponding products with moderate yields (Entry 8).

Under the same conditions, we extended the reaction by 3-methyl-1-phenyl-pyrazole-5-one 5. Satisfactory yields were observed for products 6q-v. The results are summarized in Table 6 below. It is noted from Table 3 that the use of an aromatic aldehyde 1 with malononitrile 2 (1 eqv.), and 3-methyl-1-pheny-lpyrazol-5-one 5 (1 eqv.) give satisfactory yields between 62 and 98%, but in a longer time than the first series of products. We note also that the substitution of aldehydes with electron-donating or withdrawing groups has no effect on the yield of the reaction. Good yields are obtained with the monosubstituted aldehydes but within longer time except for 4-hydroxybenzaldehyde which provides yields of 84% after 1 h only.

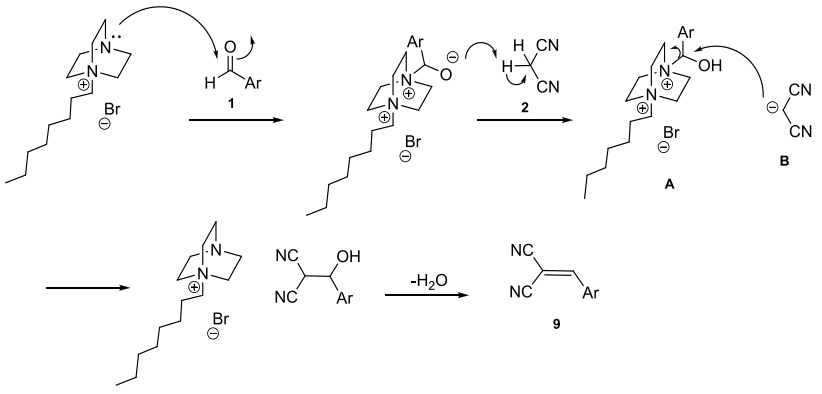
**Table 3: Synthesis of pyranopyrazoles 6q-v catalyzed with $C_8$[DABCO]Br.[a]**




| Entry | Ar | Product | Time (h) | Yield[b] (%) | Mp (°C) |
|---|---|---|---|---|---|
| 1 | $C_6H_5$ | **6q** | 3 | 62 | 172-174 (170-171)[35] |
| 2 | 4-$NO_2$-$C_6H_4$ | **6r** | 3 | 97 | 192-194 (190-192)[35] |
| 3 | 3-$NO_2$- $C_6H_4$ | **6s** | 5 | 98 | 196-198 (190-191)[35] |
| 4 | 4-Et | **6t** | 3.5 | 84 | 219-222 |
| 5 | 4-OH- $C_6H_4$ | **6u** | 1 | 84 | 216-218 (210-212) [35] |
| 6 | 2-Indolyl | **6v** | 5 | 72 | 230-232 |

[a]Reactions were carried out with a mixture of aldehydes 1 (1 eqv.), malonitrile 2 (1 eqv.), 3-methyl-1-phenylpyrazol-5-one 5 (1 eqv.) in the presence of 10 mol % of $C_8$[DABCO]Br in water at reflux; [b]Isolated yields

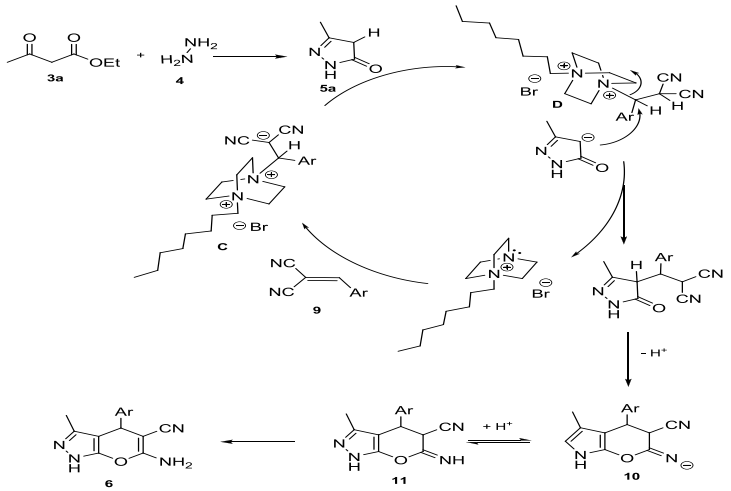
The proposed mechanism for this reaction can be divided theoretically into two steps: The first step of this mechanism is the formation of a first intermediate 9 obtained from the Knovenagel condensation. Indeed, the preparation of 2-arylidènemalononitriles 9 begins by the addition of the catalyst to aldehydes 1 to furnish nucleophilic spices which can easily extract a labile proton of malononitrile 2. The condensation between the entities A and B gives rise to the formation of 2-(hydroxy(aryl)methyl)malononitriles intermediates. Dehydration of the latter's provides access to 2-arylidènemalononitriles 9 (Scheme 3).




**Scheme 3: The synthesis of 2-arylidènemalononitriles 9 catalyzed by $C_8$[DABCO]Br**

The second step of this mechanism starts with the formation of 3-methyl-1H-pyrazol-5(4H)-one 5a by the condensation of ethyl acetoacetate 3a and hydrazine hydrate 4.

In the other hand, the condensation of the catalyst with 2-arylidènemalononitriles 9 give rise to a nucleophilic spices C, which deprotonate the obtained pyrazole. The condensation between deprotonated pyrazole and spices D result in the liberation of the catalyst. While the formation of Michael products is followed by an intramolecular cyclization resulting in the generation of intermediate 10. Protonation of 10 gives intermediates 11 which ultimately produce the desired compounds 6 after tautomerization (Scheme 4).



**Scheme 4: Mechanism for the synthesis of pyranopyrazoles 6 catalyzed by $C_8$[DABCO]Br**

## CONCLUSION

In conclusion, we have developed a simple and green method for the synthesis of pyrano[2,3-c]pyrazole derivatives from aldehydes, malonitrile, β-ketoesters, and hydrazine hydrate (or 3-methyl-1-phenylpyrazol-5-one) based on the catalytic efficiency of bromide DABCO in an efficient one-pot multi-component condensation. The merits for the presente methodology are its wide scope of substrates, high yield, short reaction time, simplicity, cleaner reaction profile, and agreement with the green chemistry protocols.

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