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A Facile, Eco-friendly, Proton Donor-Acceptor Catalyzed, One-Pot, Three-Component Synthesis of Tetrahydrobenzo[b]pyrans

A. INDRASENA*, SD. RIYAZ, A. NAIDU and P.K. DUBEY

Department of Chemistry, Jawaharlal Nehru Technological University Hyderabad College of Engineering, Kukatpally, Hyderabad-500 085, India

*Corresponding author: E-mail: adisherla.indrasena@gmail.com

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Piperidinium acetate catalyzed, three-component cyclocondensation between aryl aldehydes **(1)**, malononitrile **(2)** and cyclic-1,3-diketo compounds **(3)** in the eco-friendly and universal solvent water at room temperature for 0.5 h, resulted in the formation of tetrahydro[b]pyran derivatives **(4)**. The formation of **4** could also be established in a step-wise fashion by isolating independently each of the intermediates benzylidine malononitrile **5** and benzylidine cyclohexane-1,3-dione **6** and treating them subsequently with **3** and **2**, respectively to obtain benzopyrans **4**. Mechanistic studies on the formation of **4** from **1**, **2** and **3** are reported. Further, the synthesis of **4** could also be achieved in two variable but identical end-product giving tandem syntheses by treating **1** with **2** and then with **3** giving **4** or by treating **1** with **3** and then with **2** giving **4**. All the products were suitably characterized using NMR, IR and Mass spectroscopy.

Keywords: Proton donor-acceptor catalyst, Piperidinium acetate, One-pot reaction, 4*H*-Benzo[b]pyrans.

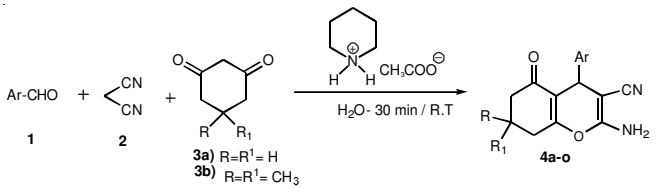
INTRODUCTION

4*H*-Benzo[b]pyrans are an important class of compounds which have received considerable attention in recent years due to their wide range of biological activities[1]. These include activities such as anticoagulant, anticancer, spasmolytic, diuretic, antiancaphylactia[2] *etc*. 4*H*-Pyrans also constitute the structural unit of a series of natural products[2]. A number of 2-amino-4*H*-pyrans are useful as photoactive materials[2]. Singh *et al*. reported[3] the synthesis of tetrahydrobenzo[b]pyrans from benzaldehyde, malanonitrile and cyclic-1,3-diketo compounds in refluxing acetonitrile containing catalytic amount of acetic acid. Kaupp *et al*. prepared[4] benzo[b]pyrans utilizing the reactants in solid or molten state without using a solvent. Other literature reported reactions has their own merits and limitations[5].

The use of piperidinium acetate as catalyst in the most eco-friendly solvent water at room temperature involving shorter reaction times giving better yields for the synthesis of benzo[b]pyrans has not been studied. Furthermore, mechanistic studies involving isolation of intermediates and reactions involving tandem syntheses of intermediates as well as end-products has not been explored so far. These studies are being reported in this communication for the first time.

Proton donor-acceptor catalysts[5-9] have been playing a vital role in the synthesis of Knoevenagel condensation derivatives since a long time. Their, ease of synthesis and easy availability makes the synthetic chemists use them as effective C-C bond forming agents. Keeping this in view, it was intended to use these proton donor acceptor catalysts in carrying out the schemes shown below. Furthermore, the use of piperidinium salts as a catalyst in the synthesis of 4*H*-benzo[b]pyrans has not been studied extensively and intensively.

As part of our continued interest in the green development[10-12] of expedient methods for the synthesis of heterocyclic compounds of biological importance, we report herein a very simple and highly efficient method for the synthesis of 4*H*-benzo[b]pyrans (**Scheme-I**).



Scheme-I

EXPERIMENTAL

Melting points are uncorrected and were determined in open capillary tubes in sulphuric acid bath. Thin-layer chromatography (TLC) was performed on silica gel G and spotting was done using iodine or UV light. IR spectra were recorded with Jasco FT-IR 5300, ^{1}H NMR on Varian 400-MHz instrument and Mass spectra on an Agilent LC-MS instrument giving only $M^{+\cdot}$ values in Q+1 mode.

General procedure for preparation of 4: A mixture of appropriate benzaldehyde (**1a**, 3.0 mmol), malononitrile (**2**, 3.0 mmol) and the appropriate 1,3-dicarbonyl compound (**3**, 3.0 mmol), piperidinium acetate (catalytic amount-10 mg) and water (25 mL) was stirred at room temperature for 20-30 min. At the end of this period, the separated solid was collected by filtration, washed with water (2 mL × 25 mL) and dried in a vaccum oven to obtain crude **4a.** The latter, were recrystallized from EtOH to get the pure **4a** (**Scheme-I**).

2-Amino-4-(3-ethoxy-4-methoxy-phenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4e): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400 MHz, DMSO-d_6/TMS): δ 0.98 (s,3H,-CH_3) 1.09 (s, 3H,-CH_3), 1.46 (t, 3H,-OCH_2-CH_3), 1.99-2.17 (m, 2H), 2.35-2.73 (m, 2H), 3.82 (s, 3H, -OCH_3), 4.07 (q, 2H, -OCH_2), 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15–7.30 (3H, m, ArH): Anal. calcd. (%) for ($C_{21}H_{24}N_2O_4$) requires C, 68.46; H, 6.57; N, 7.60; found (%) C, 68.49; H, 6.67; N, 7.50; LC-MS:*m/z*: (M^+ + 1): 367.

2-Amino-4-biphenyl-4-yl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4f): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400 MHz, DMSO-d_6/TMS): δ 0.98 (s, 3H, -CH_3) 1.05 (s, 3H, -CH_3), 2.10-2.14 (m, 2H), 2.25-2.29 (m, 2H), 7.04 (S, 2H, -NH_2, D_2O exchangeble), 7.2-7.64 (9 H, m, ArH): Anal. calcd. (%) for ($C_{24}H_{22}N_2O_2$) requires C, 77.81; H, 5.99; N, 7.56; found (%) C, 77.85; H, 5.97; N, 7.66; LC-MS *m/z*: (M^+ + 1: 371.

2-Amino-4-(4-chloro-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4g): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400MHz, DMSO-d_6/TMS): δ 1.86 -2.62 (m, 6H-(CH_2)$_3$), 4.18 (s, 1H,) 7.00 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (5 H, m, ArH): Anal. calcd. (%) for ($C_{16}H_{13}N_2O_2Cl$) requires C, 63.90; H, 4.36; N, 9.31; found (%) C, 63.60; H, 4.76; N, 9.31;LC-MS:*m/z*: (M^++1): 301.

2-Amino-4-(4-ethoxy-3-methoxy-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4h): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety,sharp); ^1H NMR (400MHz, DMSO-d_6/TMS): δ 0.98 (s,3H,-CH_3) 1.09 (s, 3H, -CH_3), 1.99-2.17 (m, 2H), 2.35-2.73 (m, 2H), 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (5 H, m, ArH): Anal. calcd. (%) for ($C_{19}H_{20}N_2O_4$) requires C, 67.05; H, 5.92; N, 8.23; found 9 %) C, 67.08; H, 5.72; N, 8.63; LC-MS:*m/z*: (M^+ + 1): 341.

2-Amino-4-(4-hydroxy-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4i): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety,sharp) ; ^1H- NMR (400 MHz, DMSO-d_6/TMS): δ 1.86 -2.62 (m, 6H-(CH_2)$_3$), 4.18 (s,1H,) 6.14 (S, 2H, -NH_2, D_2O exchangeble), 6.82 (s, 1H, -OH), 7.15–7.30 (4 H, m, ArH):, 7.15–7.30 (4H, m, ArH): Anal. calcd. (%) for ($C_{16}H_{14}N_2O_3$) requires C, 68.07; H, 5.00; N, 9.92; found (%) C, 68.27; H, 5.08; N, 9.62; LC-MS:*m/z*: (M^++1): 283.

2-Amino-4-(4-dimethylamino-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4j): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400 MHz, DMSO-d_6/TMS): δ 1.86 -2.62 (m,6H –(CH_2)$_3$), 2.95 (6H, s, 2 N-CH_3), 4.18 (s, 1H) 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (4 H, m, ArH): Anal. calcd. (%) for ($C_{18}H_{19}N_3O_2$) requires C, 69.88; H, 6.19; N, 13.58; found (%) C, 69.58; H, 6.49; N, 13.28; LC-MS: *m/z*: (M^+ + 1): 310.

2-Amino-4-(4-nitro-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4k): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400 MHz, DMSO-d_6/TMS): δ 1.86 -2.62 (m,6H -(CH_2)$_3$), 4.18 (s,1H,) 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (4 H, m, ArH): Anal. calcd. (%) for ($C_{16}H_{13}N_3O_4$) requires C, 61.73; H, 4.2 found (%) C, 61.43; H, 4.11; N, 13.60; LC-MS:*m/z*: (M^++1): 312.

2-Amino-4-(3-nitro-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4l): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety,sharp) ; ^1H NMR (400 MHz, DMSO-d_6/TMS): δ 1.86 -2.62 (m, 6H -(CH_2)$_3$), 4.18 (s,1H,) 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (4 H, m, ArH): Anal. calcd. (%) for ($C_{16}H_{13}N_3O_4$) requires C, 61.73; H, 4.21 found (%) C, 61.53; H, 4.31; N, 13.40; LC-MS:*m/z*: (M^++1): 312.

2-Amino-4-(4-methoxy-phenyl)-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile(4m): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400 MHz, DMSO-d_6/TMS): δ 1.86 -2.62 (m,6H –(CH_2)$_3$), 3.82 (s, 3H, -OCH_3), 4.18 (s,1H,) 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (4 H, m, ArH): Anal. calcd. (%) for ($C_{17}H_{16}N_2O_3$) requires C, 68.91; H, 5.44; N, 9.45; found (%) C, 68.94; H, 5.24; N, 9.55; LC-MS:*m/z*: (M^++1): 297.

2-Amino-5-oxo-4-*p*-tolyl-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4n): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (-CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400 MHz, DMSO-d_6/TMS): δ 1.86 -2.62 (m, 6H -(CH_2)$_3$), 3.82 (s, 3H, -OCH_3), 4.18 (s,1H,) 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (4 H, m, ArH): Anal. calcd. (%) for ($C_{17}H_{16}N_2O_2$) requires C, 72.84; H, 5.75; N, 9.99; found (%) C, 725.84; H, 5.45; N, 9.59; LC-MS:*m/z*: (M^++1): 281.

2-Amino-4-biphenyl-4-yl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitrile (4o): IR (KBr, ν_{max}, cm^{-1}): 3415, 3325 (unequal doublet, asymmetric and symmetric stretching of -NH_2), 2195 (- CN group, sharp), 1710 (-C=O of chromene moiety, sharp); ^1H NMR (400MHz, DMSO-d_6/TMS): δ 1.86-2.62 (m, 6H -(CH_2)$_3$), 4.18 (s,1H,) 6.14 (S, 2H, -NH_2, D_2O exchangeble), 7.15-7.30 (9 H, m, ArH): Anal. calcd. (%) for ($C_{22}H_{18}N_2O_2$) requires C, 77.17; H, 5.30; N, 8.18; found (%) C, 77.47; H, 5.10; N, 8.48; LC-MS:*m/z*: (M^+ + 1): 343.

Preparation of 5a from 1a and 2: A mixture of benzaldehyde (**1a**, 3.0 mmol), malononitrile (**2**, 3.0 mmol) and

piperidinium acetate(catalytic amount) in water (25 mL) was stirred at R.T for 20-30 min. At the end of this period, the separated solid was collected by filtration, washed water (50 mL) and dried in a vacuum oven to obtain **5a**. The latter, was used as such in the next step. The structure of the product was established on the basis of IR, NMR and Mass spectroscopy, which are in congruence with the reported method[13]. Yield (%): 93; m.p. 49-50 ºC.

Preparation of 4a from 5a: A mixture of **5a** (**1**, 3 mmol), cyclic-1,3-diketo compound (**3**, 3.0 mmol) and piperidinium acetate(catalytic amount) in water (25 mL) was stirred at room temperature for 20-30 min. At the end of this period. The separated solid was collected by filtration, washed with water (50 mL) and dried in a vaccum oven to obtain **4a.** The latter, was recrystallized from EtOH to get the pure **4a**.

Preparation of 6a from 1a and 3: A mixture of benzaldehyde (**1**, 3.0 mmol), cyclic-1,3-diketo compound (**3**, 3 mmol) and piperidinium acetate (catalytic amount) in water (25 mL) was stirred at room temperature for 20-30 min. At the end of this period, the separated solid was collected by filtration, washed with water (50 mL) and dried in a vaccum oven to obtain the **6a**. The latter was used as such in the next step. The structure of the product was established on the basis of IR, NMR and mass spectroscopy, which are in congruence with the reported method[13]. Yield (%): 93; m.p. 49-50 ºC.

Preparation of 4a from 6a: A mixture of **6a** (**1a**, 3 mmol), malononitrile (**2**, 3.0 mmol) and piperidinium acetate (catalytic amount -10 mg) and water (25 mL) was stirred at room temperature for 20-30 min. At the end of this period, the separated solid was collected by filtration, washed with water (50 mL) and dried in a vaccum oven to obtain crude **4a**. The latter, was recrystallized from EtOH to get the pure **4a**.

Preparation of 4a *via* first tandem synthesis: A mixture of benzaldehyde (**1a**, 3.0 mmol), malononitrile (**2**, 3 mmol), piperidinium acetate(catalytic amount-10 mg) and water (25 mL) was stirred at room temperature for 20-30 min. The completion of the reaction was monitored by the TLC for the disappearance of **1a**. To the same reaction mixture was added cyclic-1,3-diketo (3 mmol) compound and continued stirring for another 15-20 min. At the end of this period, the separated solid was collected by filtration, washed with water (50 mL) and dried in a vaccum oven to obtain the **4a**. The latter, require no further recrystallization.

Preparation of 4a *via* second tandem synthesis: A mixture of benzaldehyde (**1a**, 3.0 mmol), cyclic-1,3-diketo (**2**, 3 mmol), piperidinium acetate(catalytic amount, 10 mg) and water (25 mL) was stirred at room temperature for 20-30 min. The completion of the reaction was monitored by the TLC for the disappearance of **1a**. To the same reaction mixture was added malononitrile (3 mmol) and the mixture was stirred for additional 15-20 min. At the end of this period, the separated solid was collected by filtration, washed with water (50 mL) and dried in a vaccum oven to obtain the **4a**. The latter, require no further recrystallization.

RESULTS AND DISCUSSION

A mixture of aromatic aldehyde (**1**), malononitrile (**2**) and 5,5-dimethyl-1,3-cyclohexanedione (**3**) in the most eco-friendly and universal solvent *i.e.*, water, was stirred together, for 20-30 min, in the presence of catalytic amount of piperidinium acetate (10 mg) at room temperature. The corresponding 4*H*-benzo[b]pyrans (**4a-o**) were obtained in excellent yields.The results are summarized in Table-1.

As shown in Table-1, the reaction seems to go well with a range of benzaldehydes containing electron-withdrawing groups (such as nitro, halide *etc*.) or even those containing electron-donating groups (such as hydroxyl, alkoxy, dimethylamino *etc*.).

The catalyst plays a vital role in determining the success of the reaction in terms of rate and yields. In the absence of catalyst, there was hardly any progress in the reaction even after stirring the reactants for 2-3 h. Various proton donor-acceptor catalysts have been screened for this reaction in the present work. These include piperidinium benzoate, piperidinium *p*-toluenesulfonate and pyridine *p*-toluenesulfonate. Among all the catalysts used in the present work piperidinium acetate proved to be most effective as far as completion of reaction in short time and yields are concerned (Fig. 1).

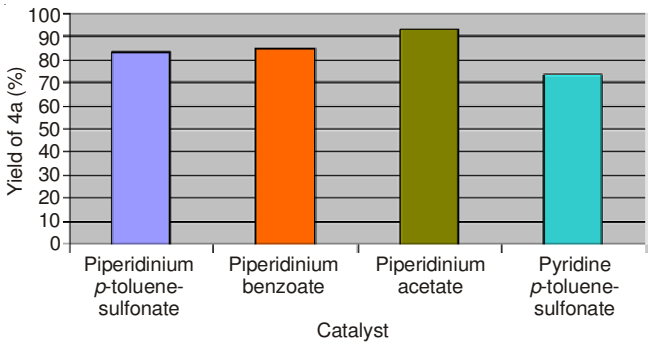
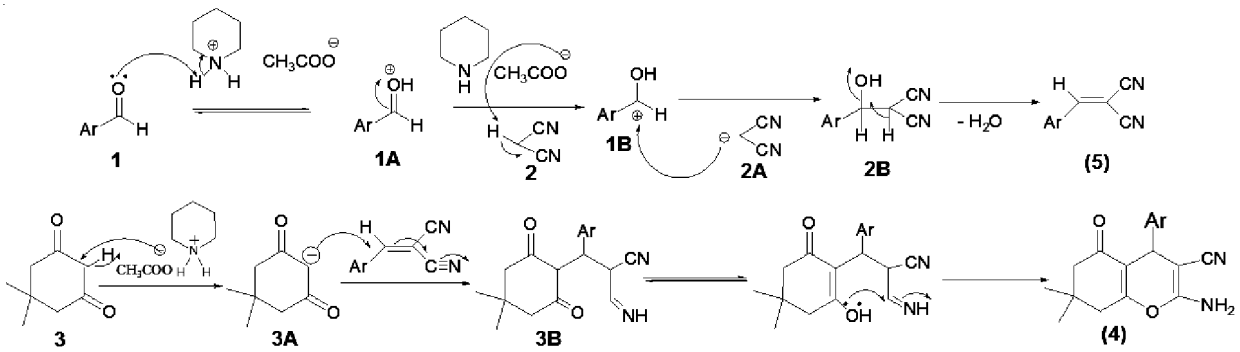


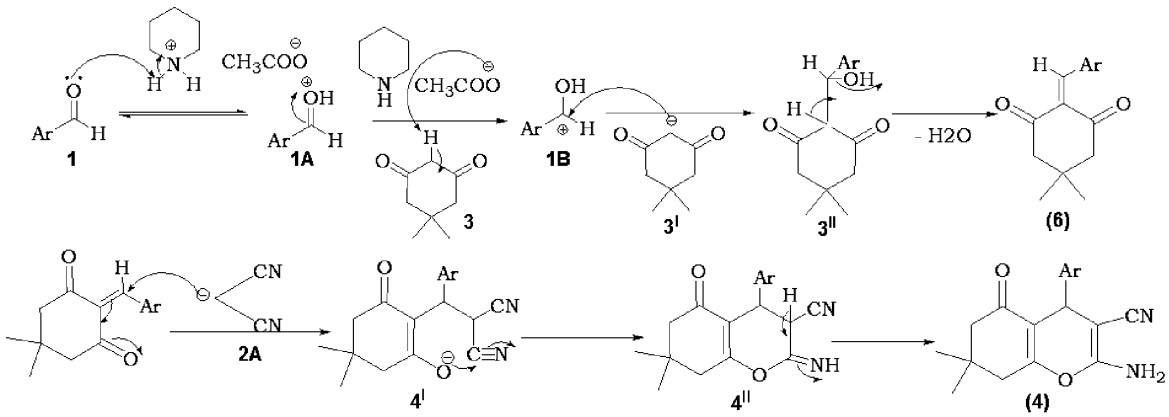
Fig. 1. Reaction of **1a** with **2** and **3a** in water at room temperature for 0.5 h

Two possible mechanisms have been proposed to account for the formation of **4** from **1, 2** and **3**. In the first possible mechanism (**Scheme-II**), initially, piperidinium acetate protonates the carbonyl group of **1** to form reversibly **1A**. Then, the acetate anion of piperidinium acetate abstracts a proton from the active methylene group of **2** to afford **2A**. **2A** attacks the carbocation species **1B** to form the intermediate **2B** which loses a molecule of water to form the α,β-unsaturated cyano compound **5**. The cyclic-1,3-diketo compound **3** reacts through its carbanion **3A** with **5** to form the intermediate **3B**. Then, the intermediate **3B** is cyclized by nucleophilic attack of OH group on to the cyano moiety to afford the target molecule **4**. Evidence for the above mechanism comes from the fact that, the intermediate **5** [condensation product of reaction between aromatic aldehyde **(1)** and malononitrile **(2)**] was prepared separately, isolated, characterized and treated with **3** subsequently to obtain the target moiety *i.e*. **4.**

In the second possible mechanism (**Scheme-III**), initially, piperidinium acetate protonates the carbonyl group of **1** to form reversibly **1A**. Then, the acetate anion of piperidinium acetate abstracts a proton from the active methylene group of **3** to afford **3′**. **3′** attacks the carbocation species **1B** to form the intermediate **3″** which loses a molecule of water to form the α,β-unsaturated cyano compound **6**. The di cyano compound



Scheme-II



Scheme-III

TABLE-1
PIPERIDINIUM ACETATE CATALYZED REACTION OF **1** WITH **2** AND **3** GIVING **4**

S. No.	1 Used	3 Used		Product obtained	Yield (%)	m.p. (ºC)
		R^1	R^2			
1	**1a**(Ar = C_6H_5)	CH_3	CH_3	**4a**	92	225-227(Lit. m.p. 229-231)[4]
2	**1b** (Ar= 4-NO_2-C_6H_4)	CH_3	CH_3	**4b**	95	175-177 (Lit. m.p. 177-178)[4]
3	**1c** (Ar= 4-Cl-C_6H_4)	CH_3	CH_3	**4c**	90	209-211 (Lit. m.p. 208-210)[5]
4	**1d** (Ar= 4-OH -C_6CH_4)	CH_3	CH_3	**4d**	94	217-218 (Lit. m.p. 214-215)[5]
5	**1e** (Ar=(3-$OCH_3$4-C_2H_5)-C_6H_3	CH_3	CH_3	**4e**	89	208-210
6	**1f** (Ar= 4-C_6H_4-C_6H_5)	CH_3	CH_3	**4f**	91	>250
7	**1g** (Ar= 4-Cl-C_6H_4)	H	H	**4g**	93	240-242
8	**1h** (Ar=(3-$OCH_3$4-C_2H_5)-C_6H_3	H	H	**4h**	94	198-200
9	**1i** (Ar=4-OH-C_6H_4)	H	H	**4i**	95	185-187
10	**1j** (Ar= 4-$Me_2NC_6H_4$)	H	H	**4j**	95	>250
11	**1k** (Ar= 4-NO_2-C_6H_4)	H	H	**4k**	96	228-230
12	**1l** (Ar= 3-NO_2-C_6H_4)	H	H	**4l**	92	210-213
13	**1m** (Ar= 4-OCH_3-C_6H_4)	H	H	**4m**	90	196-199
14	**1n** (Ar= 4-$CH_3C_6H_4$)	H	H	**4n**	89	>188-190
15	**1o** (Ar= 4-C_6H_4-C_6H_5)	H	H	**4o**	89	220-222

2 reacts through its carbanion **2A** with **6** to form the intermediate **4′**. Then the intermediate **4′** is cyclized by the nucleophilic attack of OH group on to the cyano moiety to afford the target molecule **4**. Evidence for the above mechanism comes from the fact that, the intermediate **6** [condensation product of reaction between aromatic aldehyde **(1)** and malononitrile **(3)**] was prepared separately, isolated, characteriszed and treated with **2** subsequently to obtain the target moiety *i.e.*, **4.**

In substance, it can be said that the two mechanisms (**Schemes II** and **III**) differ from one another, in that, the **Scheme-II** involves, initial formation of an intermediate between the aldehyde **(1)** and the malononitrile **(2)** followed by Michael addition of the intermediate to the cyclic-1,3-diketo compound, whereas the **Scheme-III** involves an initial formation of intermediate between aldehyde **(1)** and the cyclic-1,3-diketo compound **(3)**, followed by Michael addition of the intermediate to the active methylene compound **2** *i.e.*, malononitrile to yield the final product **4**, in both the cases.

It appears that the reaction involving condensation of **1** with **2** and **3** giving **4** is occuring by both the mechanisms simultanesously and concurrently in the reaction vessel. This is further proved by the tandem experiments described below. The synthesis of **4** could also be achieved in two variable but

identical end-product giving tandem syntheses. Thus, a mixture of benzaldehyde (**1a)** (*i.e.*, 1, R=H), malononitrile **(2)** and piperidinium acetate was stirred in water at room temperature for 20 min. The reaction was monitored on TLC for the disappearance of **1a**. To the resulting mixture, **3** was added in a tandem way without isolating **5** and then stirred at room temperature for further 20 min. At the end of this period, the mixture was processed to obtain the final product **4**. Similarly, a mixture of benzaldehyde (**1a)** (*i.e*., 1, R=H), cyclic-1,3-diketo compound. **(3)** and piperidinium acetate was stirred in water at room temperature for 20 min. The reaction was monitored on TLC for the disappearance of **1a**.To the resulting mixture, **2** was added in a tandem way without isolating **6** and then stirred at room temperature for further 20 min. At the end of this period, the mixture was processed to obtain the final product **4.**

Conclusion

In this work, a simple and eco friendly methodology has been developed for the synthsis of benzopyrans by using a cheap and easily available proton-donor catalyst piperidinium acetate. The simple work-up and reaction condition makes this route more attractive and economically viable. Furthermore, the methodology has been extended to various other benzaldehyde derivatives resulting in high yields of the benzopyrans.

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