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Task-Specific Ionic Liquid as the Recyclable Catalyst for the Rapid and Green Synthesis of Dihydropyrano[3,2c]chromene Derivatives

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TASK-SPECIFIC IONIC LIQUID AS THE RECYCLABLE CATALYST FOR THE RAPID AND GREEN SYNTHESIS OF DIHYDROPYRANO[3,2-c]CHROMENE DERIVATIVES

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GRAPHICAL ABSTRACT



Abstract A task-specific ionic liquid, $[H_3N^+-CH_2-CH_2-OH][CH_3COO^-]$, was successfully applied as an efficient and reusable catalyst for the one-pot domino to approach to dihydropyrano[3,2-c]chromene derivatives with atom economy in a condensation reaction of 4-hydroxycoumarin, aldehydes, and malononitrile in a combinatorial fashion. The reaction gave excellent yields within short reaction times at room temperature under solvent-free grinding conditions. The products and ionic liquid could be conveniently separated from the reaction mixture, indicating that the whole process was performed as a green chemical transformation.

Keywords Dihydropyrano[3,2-c]chromene; ionic liquid; multicomponent reaction; recyclable catalyst; solvent-free

INTRODUCTION

Multicomponent^[1] (MCR) and domino reaction^[2] offer significant advantages compared to the classical step-by-step formation of individual bonds because of their greater synthetic efficiency. The resulting reduced number of synthetic and purification steps for a given target molecule increases the attractiveness and practicality of the process. As a special benefit, often MCRs also enhance structural diversity in an unprecedented way. Because of the wide variation of the starting materials, various opportunities arise for the synthesis of compound libraries. Recently, research in academia and industry has increasingly emphasized the use of MCRs as well as domino reaction sequences for a broad range of products.^[3]

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Scheme 1. Three-component synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carboni-trile derivatives.

Ionic liquids (ILs), when used for replacing classical organic solvents, offer a new, cost-effective, and environmentally benign approach toward modern chemical green processes.^[4] ILs have been considered ecofriendly alternatives to volatile organic media because of their negligible vapor pressure and nonflammable nature.^[5] Additionally, the incorporation of functional groups can render a particular capability to the ionic liquids, enhancing their function, which may lead to increased reusability stability of ILs compared with unfunctionalized counterparts. Moreover, specific functional groups can also be incorporated for task-specific purposes.^[6] The implementation of task-specific ILs further enhances the versatility of ILs for the cases where both reagent and medium are coupled.^[7] Task-specific room-temperature ILs (TSILs) have emerged as a powerful alternative to conventional molecular organic solvents or catalysts because of their particular properties, such as low vapor pressure, thermal stability, wide liquid range, and ease of recovery and reuse.^[8]

Pyrano[3,2-c]chromene derivatives are important heterocycles with a wide range of biological properties^[9] such as spasmolytic, diuretic, anticoagulant, anticancer, and antianaphylactic activities.^[10] In addition, 2-aminochromene derivatives exhibit a wide spectrum of biological activities including antihypertensive and anti-ischemic behavior.^[11] Also, a number of 2-amino-4*H*-pyrans are useful as photoactive materials.^[12] 2-Amino-4-aryl-5-oxo-4*H*,5*H*-pyrano[3,2-c]chromene-3-carbonitriles have already been prepared in the presence of organic bases such as piperidine or pyridine in a large volume of organic solvents such as absolute ethanol under thermal conditions.^[13] These compounds have also been prepared in the presence of diammonium hydrogen phosphate, (NH₄)₂HPO₄ (DAHP), in aqueous ethanol^[14] and a saturated solution of potassium carbonate in water under microwave irradiation.^[15] Some of the reported procedures require long reaction times, multistep reactions, expensive and toxic reagents, complex synthetic workup pathways, modest yields, and nonreusable catalyst.^[16]

In continuation of our research on the synthesis and new applications of homogenous and heterogeneous catalysts in organic chemistry,^[17] here we use the RTIL 2-hydroxyethanaminium acetate (HEAA), $[H_3N^+-CH_2-CH_2-OH][CH_3COO^-]$, as an efficient and reusable catalyst for the one-pot synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile derivatives by three-component condensation of 4-hydroxycoumarin, aldehydes, and malononitrile at room temperature under solvent-free grinding conditions (Scheme 1).

RESULTS AND DISCUSSION

We characterize the ionic liquid^[18,19] by NMR and infrared (IR) spectroscopy for the first time. We interpret the results as follows: ¹H NMR (DMSO- d_6 , 500 Hz): δ

1.70 (s, 3H, CH₃–COO), 2.77 (t, J = 5.38 Hz, 2H, $-O-CH_2-$), 3.53 (t, J = 5.38 Hz, 2H, $-CH_2-N$), 7.1–7.8 (broad singlet, 4H, $-NH_3^+$, ^-OH) ppm. The Fourier transform (FT)–IR spectrum showed a broad band in the 3600–2400 cm⁻¹ range, which exhibits zwitterionic quaternary ammonium carboxylate character. The OH stretching vibration is embedded in this band. The broad band centered at 1567 cm⁻¹ is a combined band of the carbonyl stretching and N–H plane-bending vibrations. A literature survey confirms this interpretation of [H₃N⁺–CH₂–CH₂–OH][HCOO⁻].^[20]

To optimize the amount of catalyst, the reaction of benzaldehyde (3 equiv), malononitrile (3 equiv), and 4-hydroxycoumarin (3 equiv) under grinding conditions was selected as a model. The best result was obtained by carrying out the reaction using six drops (0.120 g) of 2-hydroxyethanaminium acetate (HEAA) at room temperature.

Using these optimized reaction conditions, the scope and efficiency of the reaction were explored for the synthesis of a wide variety of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitriles using various aldehydes, 4-hydro-xycoumarin, and malononitrile in excellent yields and short reaction times. The results are summarized in Table 1.

As shown in Table 1, the direct three-component reactions performed well with aliphatic aldehydes (entry 13), heterocyclic 2-pyridinecarbaldehyde (entry 16), and a variety of aryl aldehydes including those bearing electron-withdrawing and electron-donating groups such as OMe, OH, Cl, F, and NO₂. The desired products were obtained in good to excellent yields in short reaction times. We also have prepared five new analogs of this class of compound (Table 1, Entries 13–17).

Entry	Aldehyde(s)	Time (min)	Yield (%) ^a	Mp (°C)	Lit. Mp	[Ref]
1	Benzaldehyde	8	93	255-256	256-258	[14]
2	2-Chlorobenzaldehyde	6	83	263-264	266-268	[21]
3	3-Chlorobenzaldehyde	7	92	243-244	247-248	[22]
4	4-Chlorobenzaldehyde	10	93	263-264	263-265	[14]
5	3-Nitrobenzaldehyde	8	94	261-262	262-264	[14]
6	4-Nitrobenzaldehyde	8	90	261-262	258-260	[14]
7	4-Fluorobenzaldehyde	13	94	263-264	260-262	[21]
8	4-Hydroxybenzaldehyde	8	72	259-260	261-262	[22]
9	4-Methylbenzaldehyde	8	83	258-259	254-255	[23]
10	4-Methoxybenzaldehyde	8	90	229-230	226-228	[24]
11	2,3-Dichlorobenzaldehyde	11	74	282-283	280-282	[14]
12	2,4-Dichlorobenzaldehyde	14	71	255-256	257-259	[14]
13	3-Phenylpropanal	11	95	$187 - 188^{b}$		
14	3-Fluorobenzaldehyde	8	94	243–244 ^b		
15	2-Methylbenzaldehyde	9	75	264–265 ^b		
16	Pyridine-2-carboxaldehyde	10	70	246–247 ^b		
17	2,5-Dimethoxybenzaldehyde	8	93	247–248 ^b		

 Table 1. Synthesis of dihydropyrano[3,2-c]chromen derivatives in the presence of 2-hydroxyethanaminium acetate (HEAA)

^{*a*}Yields refer to the isolated pure products. All of the desired product(s) were characterized by comparison of their physical and spectroscopic data with those of known compounds.^[14,23–25]

^bThe spectral patterns of the new products showed similar peaks and fragmentations according to analogous compounds reported in the literature.



Scheme 2. The suggested mechanism for the preparation of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]-chromene-3-carbonitrile derivatives.

The suggested mechanism of the HEAA-catalyzed transformations is shown in Scheme 2. As reported in the literature,^[18] the Knoevenagel coupling of aldehydes with malononitrile gave intermediate (I). Then, the subsequent 1,4-conjugate addition of 4-hydroxycoumarin to the intermediate (I) followed by cyclization affords the corresponding products.^[24,25]

The reusability of the catalyst was tested in the synthesis of 2-amino-5-oxo-4-phenyl-4,5-dihydropyrano[3,2-c]chromene-3-carbonitrile from the reaction of benzaldehyde, malononitrile, and 4-hydroxycoumarin, as shown in Fig. 1. The catalyst was recovered after each run, dried, and used for the subsequent run to check its activities. The catalyst was tested for four runs. The catalyst displayed good reusability. In addition, the IR of the reused TSIL was compared with that of the new synthesized IL, and the difference was small. The reason for the decreasing yields



Figure 1. Investigation on the reusability of 2-hydroxyethanaminium acetate (HEAA) as the catalyst.

Table 2.	Comparison of results of 2-hydroxyethanaminium acetate (HEAA) with other catalysts reported

Entry	Conditions	Time	Yield (%)
1	HEAA (0.04 g), solvent-free, rt	6–14 min	70–95; present work
2	DAHP (10 mol%), H ₂ O/EtOH (1:1), rt	4 h	81–95
	(S)-Proline (10 mol%), $H_2O/EtOH$ (1:1), reflux	3 h	72-88
3	$H_6[P_2W_{18}O_{62}] \cdot 18H_2O$ (1 mol%), H_2O EtOH (1:1), reflux	30-85 min	86–90
4	TBAB (10 mol%), H_2O , reflux	45-60 min	84–93
	TBAB (10 mol%), solvent-free, 120 °C	40 min	75-89
5	KF-Al ₂ O ₃ (0.125 g), EtOH, 80 °C	4–7 h	80-90
6	Piperidine (0.5 ml), EtOH, Δ	30 min	70–90
7	TEBA (0.07 g), H ₂ O, 90 °C	7–18 h	85–96

could be that in the course of removing water from the TSIL by heating, a little of the catalyst decomposed.

To demonstrate the merit of the present work in comparison with previously reported results, we compared results of diammonium hydrogen phosphate and (S)-proline,^[14] H₆[P₂W₁₈O₆₂] · 18H₂O,^[24] tetrabutylammonium bromide,^[25] KF-Al₂₋O₃,^[22] piperidine,^[23] and triethylbenzylammonium chloride^[21] in the synthesis of 2-amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitriles derivatives. As shown in Table 2, HEAA can act as an effective catalyst with respect to reaction times, yield, and the obtained products.

CONCLUSION

in the literature

In summary, an efficient protocol for the one-pot preparation of 2-amino-5oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitriles excellent yields and short reaction times from the three-component condensation reaction of 4-hydroxycoumarin, aldehydes, and malononitrile using a TSIL HEAA, as an efficient and reusable catalyst at room temperature under grinding conditions was described. Five new desired products were synthesized and characterized for the first time. The safe catalytic system offers several advantages, including operational simplicity, environmental friendliness, and green chemical transformation.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and used without further purification. All yields refer to isolated products after purification. Products were characterized by comparison of spectroscopic data (IR, ¹H NMR spectra) and melting points with those of authentic samples. The NMR spectra were recorded on a Bruker Avance DPX 500-MHz instrument. The spectra were measured in dimethyl-sulfoxide (DMSO- d_6) relative to tetramethylsilane (TMS, 0.00 ppm). IR spectra were recorded on a Jasco FT-IR 460 plus spectrophotometer. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyzer. Melting points were determined in open

capillaries with a Buchi 510 melting-point apparatus. Thin-layer chromatography (TLC) was performed on silica gel polygram SIL G/UV 254 plates.

General Procedure for the Synthesis of 2-Amino-5-oxo-4,5-dihydropyrano[3,2-c]chromene-3-carbonitriles

A mixture of aldehydes (3 mmol), malononitrile (3 mmol), and 4-hydroxycoumarin (3 mmol) in the presence of six drops (0.120 g) of 2-hydroxyethanaminium acetate (HEAA) were pulverized in a mortar at room temperature for the appropriate time (Table 1). The reaction was monitored by TLC. After completion of the reaction, water was added, and the precipitated mixture was filtered off for separation of crude products. The IL is soluble in water, and after washing the solid products with water completely, the water was evaporated under reduced pressure and the IL was recovered and reused (Fig. 1). For further purification, the solid product was recrystallized by aqueous ethanol give the pure products. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds.^[14,21–23] Spectral data for five novel compounds are given.

Selected Data

2-Amino-4-(phenethyl)-3-cyano-4H,5H-pyrano[3,2-c]chromene-5-one (Table 1, Entry 13). ¹H NMR (DMSO- d_6 , 500 Hz): δ 1.81–1.88 (m, 1H, CH₂), 2.08–2.17 (m, 1H, CH₂), 2.44–2.62 (m, 2H, CH₂), 3.50 (t, J=4.3 Hz, 1H, CH), 7.00 (t, J=8.1, 1H, Ar), 7.08 (d, J=7.0 Hz, 2H, Ar), 7.13 (t, J=7.5 Hz, 3H, Ar), 7.34–7.45 (m, 4H, NH₂ & Ar), 7.62–7.67 (m, 1H, Ar), 7.76 (dd, J=5.9, 1.2 Hz, 1H, Ar) ppm; ¹³C NMR (DMSO- d_6 , 125 Hz): δ 30.3, 30.7, 34.6, 54.8, 103.7, 112.9, 116.3, 119.5, 122.1, 124.3, 125.5, 127.9, 128.1, 132.5, 141.2, 152.0, 154.0, 159.4, 159.8 ppm; IR (KBr, cm⁻¹): 3382, 3315, 3189, 2198, 1694, 1671, 1608, 1396, 1315, 1179, 1211, 1112, 759; MS (EI, 70 eV) m/z (%) = 344 (M⁺, 7), 240 (20), 239 (100), 187 (8), 138 (21), 91 (10), 43 (17). Anal. calcd for C₂₁H₁₆N₂O₃: C, 73.24; H, 4.68; N, 8.13%. Found: C, 73.28; H, 4.70; N, 8.20%.

2-Amino-4-(3-flourophenyl)-3-cyano-4H,5H-pyrano[3,2-c]chromene-5one (Table 1, Entry 14). ¹H NMR (DMSO- d_6 , 500 Hz): δ 4.50 (s, 1H, CH), 7.01–7.14 (m, 3H, Ar), 7.31–7.41 (m, 5H, NH₂ & Ar), 7.63–6.69 (m, 1H, Ar), 7.87 (dd, J = 7.9, 1.2 Hz, 1H, Ar) ppm; ¹³C NMR (DMSO- d_6 , 125 Hz): δ 36.6, 57.5, 103.2, 112.9, 113.8, 113.9, 114.4, 114.5, 116.4, 119.0, 122.5, 123.7, 124.5, 130.3, 130.3, 132.8, 146.1, 146.2, 152.1, 153.6, 157.9, 159.5, 161.2, 163.1 ppm; IR (KBr, cm⁻¹): 3375, 3315, 3191, 2195, 1711, 1675, 1619, 1489, 1370, 1252, 1062, 763; MS (EI, 70 eV) m/z (%) = 334 (M⁺, 22), 267 (13), 239 (100), 121 (21), 92 (8). Anal. calcd. for C₁₉H₁₁FN₂O₃: C, 68.26; H, 3.32; N, 8.38%. Found: C, 68.35; H, 3.30; N, 8.40%.

2-Amino-4-(2-methylphenyl)-3-cyano-4H,5H-pyrano[3,2-c]chromene-5one (Table 1, Entry 15). ¹H NMR (DMSO- d_6 , 500 Hz): δ 2.48 (s, 3H, CH₃), 4.73 (s, 1H, CH), 6.90–7.20 (m, 4H, Ar), 7.34 (s, 2H, NH₂), 7.41 (d, J = 8.3 Hz, 1H, Ar), 7.46 (t, J = 7.6 Hz, 1H, Ar), 7.66–7.73 (m, 1H, Ar), 7.89 (d, J = 7.8 Hz, 1H, Ar) ppm; ¹³C NMR (DMSO- d_6 , 125 Hz): δ 19.0, 32.4, 57.9, 104.5, 122.8, 116.4, 119.1, 122.3, 124.6, 126.6, 126.7, 127.8, 130.0, 132.7, 135.2, 142.2, 152.0, 153.4, 157.7, 159.5 ppm; IR (KBr, cm⁻¹): 3400, 3283, 3179, 2202, 1709, 1675, 1637, 1603, 1490, 1457, 1377, 1171, 1059, 957, 753; MS (EI, 70 eV) m/z (%) = 330 (M⁺, 18), 249 (24), 240 (17), 239 (100), 121 (21). Anal. calcd. for C₂₀H₁₄N₂O₃: C, 72.72; H, 4.27; N, 8.48%. Found: C, 72.80; H, 4.30; N, 8.50%.

2-Amino-4-(pyridin-2-yl)-3-cyano-4H,5H-pyrano[3,2-c]chromene-5-one (Table 1, Entry 16). ¹H NMR (DMSO-d₆, 500 Hz): δ 4.61 (s, 1H, CH), 6.26 (d, J = 3.0 Hz, 1H, Ar), 6.32–6.39 (m, 1H, Ar), 7.42–7.50 (m, 5H, NH₂ & Ar), 7.52 (s, 1H, Ar), 7.69 (t, J = 7.5 Hz, 1H, Ar), 7.85 (d, J = 7.7 Hz, 1H, Ar) ppm; ¹³C NMR (DMSO-d₆, 125 Hz): δ 30.6, 55.3, 101.5, 106.4, 110.6, 112.8, 116.6, 118.9, 122.3, 124.6, 133.0, 142.3, 144.5, 152.1, 153.8, 154.1, 158.7, 159.3 ppm; IR (KBr, cm⁻¹): 3368, 3282, 3169, 2201, 1704, 1672, 1604, 1376, 1268, 1171, 1111, 1056, 957, 757; MS (EI, 70 eV) m/z (%) = 317 (M⁺, 0.2), 306 (60), 278 (100), 239 (54), 158 (41), 121 (67), 92 (13), 63 (11). Anal. calcd. for C₁₈H₁₁N₃O₃: C, 68.14; H, 3.49; N, 13.24%. Found: C, 68.20; H, 3.54; N, 13.35%.

2-Amino-4-(2,5-dimethoxyphenyl)-3-cyano-4H,5H-pyrano[3,2-c]chromene-5-one (Table 1, Entry 17). ¹H NMR (DMSO-d₆, 500 Hz): δ 3.63 (s, 3H, CH₃), 3.64 (s, 3H, CH₃), 4.64 (s, 1H, CH), 6.66 (d, J=2.3 Hz, 1H, Ar), 6.75-6.79 (m, 1H, Ar), 6.90 (d, J=8.8 Hz, 1H, Ar), 7.25 (s, 2H, NH₂), 7.41-7.49 (m, 2H, Ar), 7.67 (t, J=7.7 Hz, 1H, Ar), 7.89 (d, J=7.7 Hz, 1H, Ar) ppm; ¹³C NMR (DMSO-d₆, 125 Hz): δ 32.6, 55.2, 56.4, 56.8, 103.1, 112.2, 112.9, 113.1, 115.7, 116.4, 119.2, 122.2, 124.5, 131.9, 132.6, 151.5, 152.0, 153.1, 153.9, 158.5, 159.4 ppm; IR (KBr, cm⁻¹): 3403, 3322, 3192, 2195, 1708, 1672, 1605, 1501, 1380, 1224, 1054, 959, 620; MS (EI, 70 eV) m/z (%) = 376 (M⁺, 23), 361 (14), 345 (42), 279 (100), 239 (26), 215 (13), 121 (24). Anal. calcd. for C₂₁H₁₆N₂O₅: C, 67.82; H, 4.28; N, 7.44%. Found: C, 67.92; H, 4.36; N, 7.55%.

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