Facile, Efficient, and Eco-Friendly Synthesis of Benzo[b] pyran-2-imines over MgO and Transformation to the Coumarin Derivatives
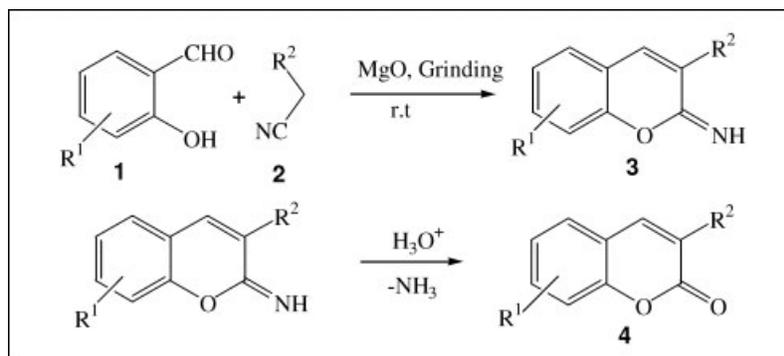
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Room temperature synthesis of benzo[b]pyran-2-imine derivatives *via* the Knoevenagel condensation of malononitrile and cyanoacetates with salicylaldehyde derivatives over MgO and their transformation to the known coumarins is described. The satisfactory results were obtained with good yields, short reaction time, and simplicity in the experimental procedure.
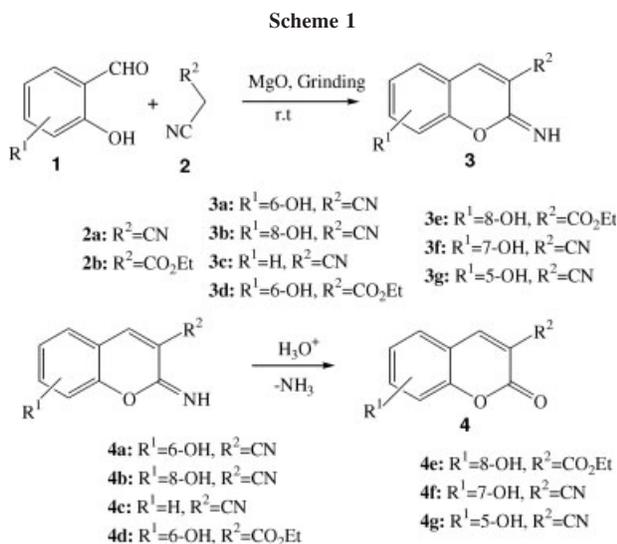
INTRODUCTION

Organic reactions under solvent-free [1] and aqueous [2] conditions have increasingly attracted chemists' interests, particularly from the viewpoint of green chemistry [3]. As an important carbon-carbon bond forming reaction, Knoevenagel condensation has been extensively studied. Generally, this type of reaction is catalyzed by base or Lewis acid in the liquid-phase system. In recent years, chemists paid more and more attention to the clean synthesis of alkenes by Knoevenagel condensations. Alkali metal hydroxides (e.g., NaOH and KOH), pyridine, and piperidine are the traditional catalysts used in these reactions. However, basic zeolites, such as Cs-exchanged NaX (CsNaX) and GeX, as well as cesium and cesium-lanthanum impregnated mesoporous MCM-41 are also able to catalyze the Knoevenagel condensation under mild reaction conditions [4]. The Knoevenagel condensations between aldehydes and malononitrile in dry media catalyzed by silica gel [5], ammonium acetate (NH₄OAc)-basic alumina [6], and zinc dichloride [7] have been reported. We described the same reactions, which could proceed efficiently in NH₄Cl aqueous solution [8]. Recently, we reported a convenient method for the preparation of coumarins *via* the Knoevenagel reaction in ionic liquids [ILs] [9].

Magnesium oxide has been used for benzylation of aromatic compounds [10], transesterification [11], Michael addition of sulfonamides to α,β-unsaturated esters [12], synthesis of chiral epoxy ketones, chiral nitro alcohols, and Michael adducts [13], etc. More recently, we reported the efficient synthesis of nitrones over MgO under solvent-free conditions [14]. In continuation of our recent interest to use solid supports, ILs, water, or solventless systems as a green reaction medium and microwave (MW)-mediated reactions [15], we wish to report here the synthesis of several benzopyran-2-imines over MgO in solventless system followed by their transformation to the coumarin derivatives without using MW and conventional heating technique in solventless system over MgO solid support (Scheme 1).

The use of ILs has received more attention as eco-friendly, reusable, and alternative reaction media in organic synthesis because of their unique properties [16–21]. A number of organic reactions, including hydrogenation, oxidation, and C—C bond forming reactions, have already been demonstrated in ILs [22–25]. We first examined the reaction of 2,5-dihydroxysalicylaldehyde with active methylene compounds **2a–b** over a variety of solid supports at room temperature (Table 1). As shown in Table 1, we found that the

Scheme 1

2a: R^2=CN
2b: R^2=CO$_2$Et

3a: R^1=6-OH, R^2=CN
3b: R^1=8-OH, R^2=CN
3c: R^1=H, R^2=CN
3d: R^1=6-OH, R^2=CO$_2$Et

3e: R^1=8-OH, R^2=CO$_2$Et
3f: R^1=7-OH, R^2=CN
3g: R^1=5-OH, R^2=CN

4a: R^1=6-OH, R^2=CN
4b: R^1=8-OH, R^2=CN
4c: R^1=H, R^2=CN
4d: R^1=6-OH, R^2=CO$_2$Et

4e: R^1=8-OH, R^2=CO$_2$Et
4f: R^1=7-OH, R^2=CN
4g: R^1=5-OH, R^2=CN

reaction using MgO as a solid support was accelerated to produce the related 3-cyano-2H-1-benzopyran-2-imines **3a** and **3d** in 93% and 91% yields, respectively, at room temperature for 25 min by grinding.

In another experiment, for the same reaction, several butylmethylimidazolium-based ILs, [bmim]X, with varying anions, such as Cl⁻, BF$_4$⁻, and PF$_6$⁻, were examined in the presence of KHCO$_3$ at room temperature. The observation shows that the reaction in ILs was carried out slower with lower yields in comparison with the reaction by hand grinding of reactants over MgO and all ILs examined gave similar results (entries 5–7). The reactions in ILs were conducted at higher temperatures for optimizing the conditions and no significant improvements were observed in yields or reaction times. There is no significance difference in the results using different bases such as Na$_2$CO$_3$, K$_2$CO$_3$, NaHCO$_3$, NH$_4$OAc, NaOH, NH$_4$Cl, and piperidine as the catalyst

in this procedure. It should be noted that in the absence of any catalyst, the condensation reaction failed to give the desired 2H-1-benzopyran-2-imines.

From the results obtained as shown in Table 1, it is clear that the reaction over MgO should be the method of choice for synthesizing 2H-1-benzopyran-2-imines, because a comparatively higher yield was achieved in a shorter reaction time. Under identical conditions, a variety of salicylaldehydes were reacted with active methylene compounds to afford the related benzo[b]pyran-2-imine derivatives in good to high yield, which hydrolyzed in acidic conditions to afford the related coumarins (Table 2). A plausible mechanism for the Knoevenagel condensation reaction catalyzed by MgO is outlined in Scheme 2.

In summary, we have successfully applied MgO as efficient support and catalyst for the synthesis of benzo[b]pyran-2-imine derivatives in solventless system. This methodology is highly profitable in terms of convenient, fast, and safe synthesis of benzo[b]pyran-2-imines in pure form and good yields. The products were purified by column chromatography using hexane/ethyl-acetate mixtures as eluent and were characterized by ¹H NMR, ¹³C NMR, IR, and elemental analysis.

EXPERIMENTAL

General information. All reagents were purchased from Merck Company (Germany) and used without further purification. ¹H NMR spectra were obtained in CDCl$_3$ solution from Bruker Avance AC-400MHz or 300MHz and ¹³C NMR spectra at 100MHz or 75MHz on the aforementioned instrument using TMS as internal standard. Elemental analyses were carried out on a Perkin–Elmer 240C elemental analyzer and are reported in percent atomic abundance.

Preparation of benzo[b]pyran-2-imine in ILs, general procedure. The selected arylaldehyde (10 mmol), the active methylene compound (11 mmol), KHCO$_3$ (10 mmol), and IL

Table 1

Effect of different solid supports and ionic liquids on synthesis of 2H-1-benzopyran-2-imines **3a** and **3d**.[a]

Entry	Solid support[b]/base	Ionic liquid[c]	Time (min)	Yield[d](%) 3a	3d
1	MgO	–	25	93	91
2	Alumina/KHCO$_3$	–	30	62	58
3	Molecular sieves 3A°/KHCO$_3$	–	35	59	60
4	Silica gel/KHCO$_3$	–	45	50	54
5	–	[bmim]Cl/KHCO$_3$	120	58	55
6	–	[bmim]PF$_6$/KHCO$_3$	120	55	58
7	–	[bmim]BF$_4$/KHCO$_3$	120	61	64

[a] Reaction conditions: 10 mmole of salicylaldehyde, 11 mmole of active methylene compound, and 10 mmole of base.
[b] Reactants were carried out by Hand-Grinding over solid support at room temperature.
[c] Reactants were carried out by stirring of the mixture of reactants in ionic liquids (2 mL) at room temperature.
[d] Isolated yields after column chromatography.

Table 2

Synthesis of benzo[b]pyran-2-imine derivatives by hand-grinding over MgO and their transformation to coumarins.[a]

Entry	R^1	R^2	Product **3**		Product **4**
			Time (min)	Yield[b] (%)	Yield[b] (%)
1	6-OH	CN	25	93	92
2	8-OH	CN	25	91	89
3	H	CN	30	93	90
4	6-OH	CO$_2$Et	28	91	90
5	8-OH	CO$_2$Et	28	89	88
6	7-OH	CN	22	94	92
7	5-OH	CN	22	95	94

[a] Reaction conditions: 10 mmole of salicylaldehyde, 11 mmole of active methylene compound, and 10 mmole of base.
[b] Isolated yields after column chromatography.

(2 ml) were stirred at room temperature for appropriate time (Table 1). The completion of reaction was monitored by thin layer chromatography (TLC) using (ethylacetate/n-hexane:1/5) as eluent. After completion of the reaction, the mixture was extracted with ethylacetate. The extracts were concentrated on a rotary evaporator, and the crude mixture was purified by silica gel (Merck 230–240 mesh) column chromatography using (ethylacetate/n-hexane:1/5) mixtures as eluent.

Preparation of benzo[b]pyran-2-imine over solid supports, general procedure. The selected aldehyde (10 mmol), the active methylene compound (11 mmol), KHCO$_3$ (10 mmol), and solid support (1 g) were co-grinded in a mortar at room temperature for appropriate time (Table 2). The completion of reaction was monitored by TLC using (ethylacetate/petroleum:1/5) as eluent. After completion of the reaction, the mixture was extracted with ethylacetate. The extracts were concentrated on a rotary evaporator, and the crude mixture was purified by silica gel (Merck 230–240 mesh) column chromatography using (ethylacetate/n-hexane:1/5) mixtures as eluent.

3-Cyano-6-hydroxy-benzo[b]pyran-2-imine (3a). IR (KBr, λ_{max} = cm^{-1}: 3411 (broad, OH), 3302 (NH), 2222 (CN), 1660 (C=NH), 1612 (C=C); ^{1}H NMR: δ 8.40 (s, 1H), 7.51 (dd, 1H, J = 8.12, 1.43 Hz), 7.39 (d, 1H, J = 1.43 Hz), 7.36 (d, 1H, J = 8.12 Hz); ^{13}C NMR: δ 161.1, 151.2, 132.3, 125.7, 124.5, 117.8, 116.4, 115.1, 114.1, 104.4; Anal. Calcd. for C$_{10}$H$_6$N$_2$O$_2$: C,64.52; H,2.25; N,15.05. Found: C,64.55; H,2.22; N,15.12.

3-Cyano-8-hydroxy-benzo[b]pyran-2-imine (3b). IR (KBr, λ_{max} = cm^{-1}: 3383 (broad, OH), 3310 (NH), 2219 (CN), 1658 (C=NH), 1608 (C=C); ^{1}H NMR: δ 8.15 (s, 1H), 7.57 (dd, 1H, J = 8.12, 8.08 Hz), 7.49 (dd, 1H, J = 8.12, 1.67 Hz), 7.41 (dd, 1H, J = 8.08, 1.67 Hz); ^{13}C NMR: δ 160.5, 150.9, 140.1, 131.08, 123.6, 120.2, 116.1, 115.8, 112.7, 105.5; Anal. Calcd. for C$_{10}$H$_6$N$_2$O$_2$: C,64.52; H,2.25; N,15.05. Found: C,64.59; H,2.20; N,15.09.

3-Cyano benzo[b]pyran-2-imine (3c). IR (KBr, λ_{max} = cm^{-1}: 3308 (NH), 2218 (CN), 1658 (C=NH), 1610 (C=C); ^{1}H NMR: δ 8.12 (s, 1H), 7.61 (dd, 1H, J = 8.10, 1.42 Hz), 7.43 (m, 2H), 7.40 (dd, 1H, J = 8.12, 1.45 Hz); ^{13}C NMR: δ 161.0, 150.4, 138.4, 131.5, 128.5, 119.5, 118.8, 117.0, 116.9, 105.1; Anal. Calcd. for C$_{10}$H$_6$N$_2$O: C, 70.58; H, 3.55; N, 16.46. Found: C, 71.01; H, 3.51; N, 16.50.

3-Carb-ethoxy-6-hydroxy-benzo[b]pyran-2-imine (3d). IR λ_{max} = cm^{-1}: 3370 (broad, OH), 3315 (NH), 2225 (CN), 1712 (C=O), 1652 (C=NH), 1613 (C=C); ^{1}H NMR δ 8.64 (s, 1H), 7.79 (d, 1H, J = 1.51 Hz), 6.84 (dd, 1H, J = 8.19, 1.51 Hz), 6.73 (d, 1H, J = 8.19 Hz), 4.23 (q, 2H, J = 7.23 Hz), 1.29 (t, 3H, J = 7.23 Hz); ^{13}C NMR δ 166.1, 153.4, 145.4, 141.0, 138.2, 121.3, 120.4, 119.8, 117.5, 116.1, 62.0, 17.2; Anal. Calcd. for C$_{12}$H$_{11}$NO$_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 61.95; H, 4.61; N, 6.08.

3-Carbethoxy-8-hydroxy-benzo[b]pyran-2-imine (3e): IR λ_{max} cm^1. 3365 (broad, OH), 3311 (NH), 2221 (CN), 1710 (C=O), 1660 (C=NH), 1609 (C=C); ^{1}H NMR δ 8.67 (s, 1H), 7.57 (dd, 1H, J = 8.10, 7.98 Hz), 7.49 (dd, 1H, J = 8.10, 1.50 Hz), 7.41 (dd, 1H, J = 7.98, 1.53 Hz), 4.19 (q, 2H, J = 7.20 Hz), 1.26 (t, 3H, J = 7.20 Hz); ^{13}C NMR δ 168.6, 154.0, 147.0, 143.1, 140.1, 123.2, 120.0, 121.1, 116.6, 118.3, 63.1, 16.1; Anal. Calcd. for C$_{12}$H$_{11}$NO$_4$: C, 61.80; H, 4.75; N, 6.01. Found: C, 62.02; H, 4.63; N, 6.09.

3-Cyano-7-hydroxy-benzo[b]pyran-2-imine (3f). IR (KBr, λ_{max} = cm^{-1}: 3357 (broad, OH), 3310 (NH), 2216 (CN), 1659 (C=NH), 1616 (C=C); ^{1}H NMR: δ 8.24 (s, 1H), 7.61 (dd, 1H, J = 7.88, 1.28 Hz), 7.31 (d, 1H, J = 7.88 Hz), 7.29 (d, 1H, J = 1.28 Hz); ^{13}C NMR: δ 159.1, 154.3, 141.7, 135.4, 128.8, 122.0, 119.8, 118.4, 118.02, 105.5; Anal. Calcd. for C$_{10}$H$_6$N$_2$O$_2$: C, 64.52; H, 2.25; N, 15.05. Found: C, 64.60; H, 2.21; N, 15.07.

3-Cyano-5-hydroxy-benzo[b]pyran-2-imine (3g). IR (KBr, λ_{max} = cm^{-1}: 3360 (broad, OH), 3300 (NH), 2219 (CN), 1706 (C=O), 1612 (C=C); ^{1}H NMR: δ 8.18 (s, 1H), 7.59 (dd, 1H, J = 7.80, 1.32 Hz), 7.30 (d, 1H, J = 7.80 Hz), 7.26 (d, 1H, J = 1.32 Hz); ^{13}C NMR: δ 157.9, 153.2, 140.0, 136.4, 127.7, 123.4, 119.8, 117.7, 116.5, 106.8; Anal. Calcd. for

Scheme 2
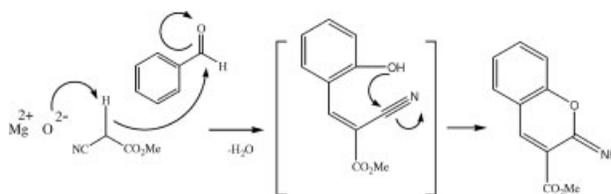
$C_{10}H_6N_2O_2$: C, 64.52; H, 2.25; N, 15.05. Found: C, 64.58; H, 2.19; N, 15.11.

Hydrolysis of the freshly prepared benzo[b]pyran-2-imines under acidic conditions afforded to related coumarins.

6-Hydroxy-2-oxo-2H-chromene-3-carbonitrile (4a). IR (KBr, $\lambda_{max} = cm^{-1}$: 3415 (broad, OH), 2229 (CN), 1712 (C=O), 1604 (C=C); ^{1}H NMR: δ 8.28 (s, 1H), 7.70 (dd, 1H, $J = 7.88, 1.28$ Hz), 7.39 (d, 1H, $J = 7.85$ Hz), 7.32 (d, 1H, $J = 1.28$ Hz); ^{13}C NMR: δ 159.5, 154.0, 136.5, 130.8, 126.5, 118.5, 118.3, 117.9, 115.2, 103.8; Anal. Calcd. for $C_{10}H_6NO_3$: C, 64.18; H, 2.69; N, 7.48. Found: C, 64.28; H, 2.66; N, 7.39.

8-Hydroxy-2-oxo-2H-chromene-3-carbonitrile (4b). IR (KBr, $\lambda_{max} = cm^{-1}$: 3371 (broad, OH), 2223 (CN), 1708 (C=O), 1610 (C=C); ^{1}H NMR: δ 8.24 (s, 1H), 7.68 (dd, 1H, $J = 8.15, 8.10$ Hz), 7.49 (dd, 1H, $J = 8.15, 1.75$ Hz), 7.41 (dd, 1H, $J = 8.10, 1.70$ Hz); ^{13}C NMR: δ 160.1, 151.4, 139.7, 132.1, 125.1, 119.0, 117.2, 115.4, 114.02, 101.1; Anal. Calcd. for $C_{10}H_6NO_3$: C, 64.18; H, 2.69; N, 7.48. Found: C, 64.28; H, 2.66; N, 7.39.

2-Oxo-2H-chromene-3-carbonitrile (4c). IR (KBr, $\lambda_{max} = cm^{-1}$: 2229 (CN), 1711 (C=O), 1608 (C=C); ^{1}H NMR: δ 8.19 (s, 1H), 7.65 (dd, 1H, $J = 7.89, 1.22$ Hz), 7.49 (m, 2H), 7.44 (dd, 1H, $J = 8.10, 1.34$ Hz); ^{13}C NMR: δ 162.5, 154.0, 136.5, 130.8, 126.5, 118.5, 118.3, 117.9, 115.2, 103.8; Anal. Calcd. for $C_{10}H_5NO_2$: C, 70.18; H, 2.94; N, 8.18. Found: C, 70.23; H, 2.91; N, 8.21.

Ethyl 6-Hydroxy-2-oxo-2H-chromene-3-carboxylate (4d). IR $\lambda_{max} = cm^{-1}$: 3313 (broad, OH), 3030, 2989, 1739 (C=O), 1672 (C=O), 1612 (C=C); ^{1}H NMR (300 MHz, DMSO-d6) δ 8.52 (s, 1H), 7.61 (dd, 1H, $J = 8.13, 1.30$ Hz), 7.30 (d, 1H, $J = 1.32$ Hz), 7.32 (d, 1H, $J = 8.09$ Hz), 4.20 (q, 2H, $J = 7.21$ Hz), 1.29 (t, 3H, $J = 7.21$ Hz); ^{13}C NMR (75MHz, DMSO-d6) δ 164.3, 152.2, 146.0, 142.6, 137.8, 119.53, 118.6, 116.1, 115.5, 115.1, 63.0, 18.6.

Ethyl 8-Hydroxy-2-oxo-2H-chromene-3-carboxylate (4e). IR $\lambda_{max} = cm^{-1}$: 3313 (broad, OH), 3030, 2989, 1739 (C=O), 1672 (C=O), 1672 (C=O); ^{1}H NMR (300 MHz, DMSO-d6) δ 8.01 (s, 1H), 7.60 (t, 1H, $J = 7.91$ Hz), 7.38 (dd, 1H, $J = 7.91, 1.95$ Hz), 7.32 (dd, 1H, $J = 7.91, 1.95$Hz), 4.15 (q, 2H, $J = 7.18$ Hz), 1.21 (t, 3H, $J = 7.18$ Hz); ^{13}C NMR (75MHz, DMSO-d6) δ 165.9, 156.4, 148.4, 145.9, 141.2, 123.4, 121.1, 121.0, 118.5, 117.3, 61.9, 18.4.

7-Hydroxy-2-oxo-2H-chromene-3-carbonitrile (4f). IR (KBr, $\lambda_{max} = cm^{-1}$: 3370 (broad, OH), 2220 (CN), 1709 (C=O), 1613 (C=C); ^{1}H NMR(300 MHz, DMSO-d6): δ 8.19 (s, 1H), 8.07 (s, 1H), 7.69 (dd, 1H, $J = 7.81, 1.29$ Hz), 7.43 (d, 1H, $J = 7.81$ Hz), 7.29 (d, 1H, $J = 1.29$ Hz); ^{13}C NMR: δ 160.1, 156.5, 143.8, 136.6, 129.1, 123.1, 120.5, 119.8, 118.3, 108.8; Anal. Calcd. for $C_{10}H_6NO_3$: C, 64.18; H, 2.69; N, 7.48. Found: C, 64.30; H, 2.61; N, 7.50.

5-Hydroxy-2-oxo-2H-chromene-3-carbonitrile (4g). IR (KBr, $\lambda_{max} = cm^{-1}$: 3383 (broad, OH), 2223 (CN), 1719 (C=O), 1611 (C=C); ^{1}H NMR(300 MHz, DMSO-d6): δ 8.14 (s, 1H), 7.61 (dd, 1H, $J = 8.11, 1.31$ Hz), 7.31 (dd, 1H, $J = 7.98, 1.31$ Hz), 7.29 (dd, 1H, $J = 7.98, 8.11$ Hz); ^{13}C NMR: δ 165.0, 156.7, 143.2, 136.8, 130.8, 124.4, 120.2, 119.4, 118.5, 109.1; Anal. Calcd. for $C_{10}H_6NO_3$: C, 64.18; H, 2.69; N, 7.48. Found: C, 64.27; H, 2.64; N, 7.52.

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