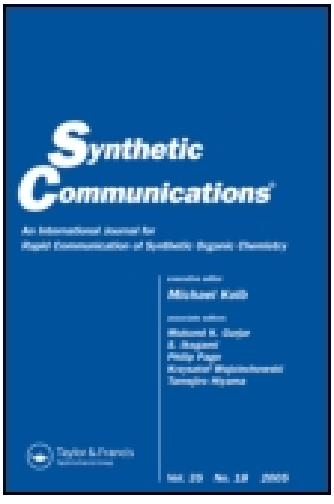

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Sequential Aldol/Michael Addition Reaction in Ionic Liquid Catalyzed by Morpholine: A Convenient Synthesis of 1,3,5-Triaryl-1,5-pentanedione

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Sequential Aldol/Michael Addition Reaction in Ionic Liquid Catalyzed by Morpholine: A Convenient Synthesis of 1,3,5-Triaryl-1,5-pentanedione

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Abstract: A series of 1,3,5-triaryl-1,5-pentanediones was obtained via a sequential aldol condensation and Michael addition reaction in ionic liquid catalyzed by morpholine, as a one-pot reaction. The significance of our findings relates to reducing the use of organic solvents, potentially toxic and hazardous materials, as well as its simplicity, good yields, mild conditions, and lower costs.

Keywords: Ionic liquid, morpholine, synthesis, 1,3,5-triaryl-1,5-pentanedione

INTRODUCTION

Kröhnke-type pyridines[1] and other substituted pyridines including the terpyridines[2,3] are prominent building blocks in supramolecular chemistry, with

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their π-stacking ability, directional H-bonding, and coordination. They are also the useful intermediates in the syntheses of pesticides, desiccants, surfactants, and so forth.[4,5]

In general, 1,3,5-triaryl-1,5-pentanedione was used as the important precursor in their synthesis. But the general methods used in the synthesis of 1,3,5-triaryl-1,5-pentanedione always use volatile organic solvents and display only moderate to low yields.[2,6,7] To adopt the principles of green chemistry,[8] Yang[9] and coworkers obtained the target molecule in water catalyzed by NaOH through two steps. Gareth[10] and coworkers developed a solvent-free route to such compounds, but the strong base NaOH was also used as catalyst.

In these syntheses, acetophenone substituted by an electron-withdrawing group (such as 4-acetylpyridine) and p-substituted ones (such as 4-methylacetophenone), which have smaller steric effects, were used. Probably because of the deactivation and steric effect of hydroxyl group on the carbonyl group, this kind of reaction (including 2′-hydroxyacetophenone) is difficult and has never been reported. As one hydroxyl group is added on the benzene ring, the yield will reduce 30%–40%.[11]

But we have to conquer this difficulty because the hydroxyl group is a general group in the structure of most natural products and often displays biological activity.[12] Our basic idea in this communication is to develop a green, cheap, conventional synthesis of 1,3,5-triaryl-1,5-pentanedione including hydroxyl groups.

Recently, there have been several reports on the new versions of Michael additions in ionic liquids; for example, Xuesen Fan and coworkers[13] reported the Knoevenagel and Michael reactions using the ionic liquid [bmim][BF_4], which was also used in this article.

Ionic liquids have been the subject of considerable current interest as environmentally benign reaction media in organic synthesis because of their unique properties of nonvolatility, nonflammability, recyclability, and ability to dissolve a wide range of materials.[14]

We discovered that diethylamine ($pK_b = 2.89$) can promote the reaction of p-cyanbenzaldehyde and 2′-hydroxyacetophenone to produce 1,3,5-triaryl-1,5-pentanedione. Do other weak bases also have this kind of ability? Morpholine, a reagent that had never been used as a catalyst, was sought out for the contrasting experiment.

We first established that using morpholine, a cheap and facile weak base ($pK_b = 5.51$), as the catalyst involving sequential aldol and Michael addition reactions of aromatic aldehydes with 2′-hydroxyacetophenone in one pot, and the ionic liquid 1-n-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]), a colorless, flavorless, nonvolatile liquid,[15] was used as the solvent with 58–80% yield. Overall, this versatile new approach can be applied to the synthesis of a range of pyridines in general bearing aryl groups on the 2, 4, and 6 positions. The significance of our finding also relates to reducing the use of organic solvents, potentially toxic and

hazardous materials, as well as its simplicity, mild conditions, and lower costs. Moreover, the findings are further evidence that it is possible to synthesize activated natural products and analogous natural products.

The signal crystal structure of product **3a** (Figure 1 and Scheme 1) was established on the basis of spectroscopic data and confirmed by X-ray diffraction studies. (The crystallographic data are given in the Experimental section.)

We used seven other amines as the catalysts in the reaction of p-cyanbenzaldehyde and 2′-hydroxyacetophenone, and the yields were lower than the reaction catalyzed by morpholine (Table 1). We chose morpholine as the catalyst throughout. Why didn't the Mannish reaction take place in this reaction? We speculated that the reason was that the ionic liquid weakened the nucleophilicity of the amines. That proves that ionic liquid has good selectivity and superiority, as it is used as the reaction medium. The effect of different ionic liquids on the yields was investigated in the reaction of p-cyanbenzaldehyde and 2′-hydroxyacetophenone (Table 2).

Table 1 indicates that there was no direct relationship between yields and the pK_b of amines. Even weaker bases such as aniline can catalyze this reaction. We used morpholine as the catalyst throughout. Table 2 indicates that with increasing basicity of the anion (increasing pKa of the corresponding

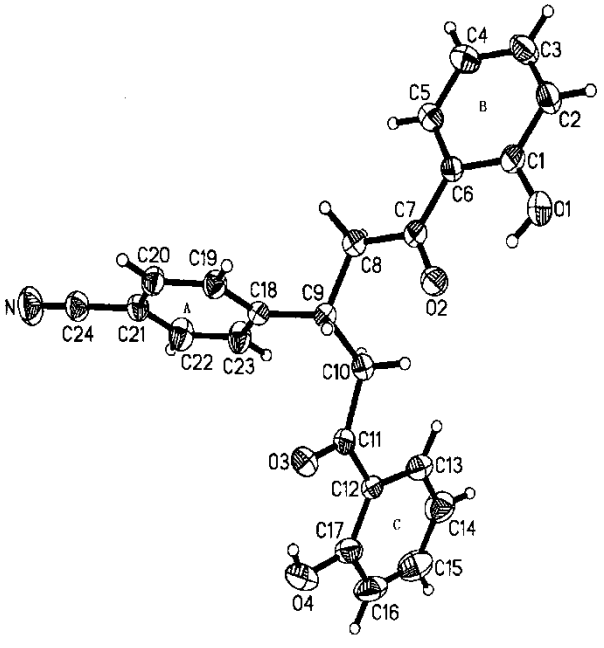
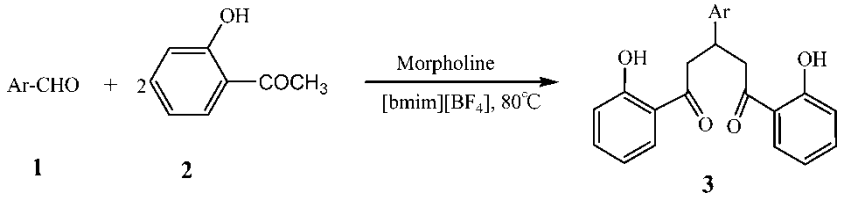


Figure 1. X-ray crystal structure of **3a**.



Scheme 1.

acid), there is a progressive increase in the yield, so we chose [bmim][BF_4] throughout. The yields of the products are shown in Table 3.

The results shown in Table 3 indicate that the steric hindrance of the adjacent group of aromatic aldehydes influenced the yields more than the other ones, and the electronic effect of the substitutes almost has no influence on the yields.

EXPERIMENTAL

Melting points were measured with a Fisher-Johns melting-point apparatus without correction. IR spectra were recorded on a Nicolet Nexus 670 spectrometer in KBr. The proton nuclear magnetic resonance (^{1}H NMR) spectra were measured on a Bruker AM-400 spectrometer with Me_4Si (TMS) as the internal reference and $CDCl_3$ as solvent. X-Ray diffraction was measured on a Siemens P4 diffractometer with graphite monochromated MoK\α radiation.

Silica gel (200–400 mesh), from Qingdao Ocean Chemical Co. Ltd. (China), was used for column and thin-layer chromatography. The other reagents were all analytical pure.

The ionic liquid [bmim][BF_4] was synthesized according to the literature.[16]

Table 1. Effect of amines on the yields of the corresponding reactions

Amines	pK_b (25 °C)	Yield (%)
Aniline	9.40	59.0
p-Methyl-aniline	8.92	63.0
Morpholine	5.51	78.6
Ammonium acetate	4.70	48.7
Cholamine	4.50	53.9
Methylamine	3.38	60.4
Cyclopentamine	3.35	52.6
Diethylamine	2.89	51.3

Table 2. Effect of ionic liquid on the yield of **3a**

IL	pK_a^a	Isolated yield (%)
[bmim[b]][Br]	−9	44.0
[bmim][BF_4]	0.5	78.6
[bmim][ClO_4]	−11	9.1
[bp[c]] [Br]	−9	23.6
[bp][BF_4]	0.5	33.6
[bp][ClO_4]	−11	8.1

[a]The pKa value of the parent acid of the anions.
[b][bmim] = 1-n-butyl-3-methylimidazolium.
[c][bp] = 1-n-butylpyridinium.

General Procedure

A dry 50-mL flask was charged with aromatic aldehydes (**1**) (2 mmol), 2′-hydroxyacetophenone (**2**) (4 mmol), morpholine (1 mmol), and [bmim][BF_4] (2 mL). The mixture was stirred at 80°C for 8–20 h. Then the system was poured into the water, and the precipitate was washed with water 2–3 times and purified by recrystallization from absolute EtOH and DMF to give (**3**).

Data

3a: IR (KBr, ν, cm^{-1}): 3320, 3025, 2950, 1680, 1600, 1265, 2223 (C≡N); H^1 NMR ($CDCl_3$, δ, ppm): 11.63 (s, 2H, –OH), 7.87–7.89 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.71–7.73 (d, 2H, $J = 8$ Hz, Ar-H), 7.56–7.58 (d, 2H, $J = 8.4$ Hz, Ar-H), 7.48–7.52 (m, 2H, Ar-H), 6.93-6.96 (m, 4H, Ar-H), 3.95–4.03 (m, 1H, –CH), 3.54–3.60 [m, 4H, $-CH(CH_2)_2$].

Table 3. Physical properties and yields of the products (IL: [bmim][BF_4])

Entry	Ar	Molecular formula	Mp (°C)	Yield (%)	Time (h)
3a	4-CNC_6H_4	$C_{24}H_{19}NO_4$	162.7–163.2	78.6	8.5
3b	4-ClC_6H_4	$C_{23}H_{19}O_4Cl$	205.2–205.9	80.3	18.0
3c	4-BrC_6H_4	$C_{23}H_{19}O_4Br$	110.5–111.7	79.5	17.5
3d	4-$CH_3C_6H_4$	$C_{24}H_{22}O_4$	205.9–207.0	68.7	19.0
3e	4-$NO_2C_6H_4$	$C_{23}H_{19}NO_6$	195.0–199.4	75.6	9.5
3f	4-$OCH_3C_6H_4$	$C_{24}H_{22}O_5$	114.5–118.6	70.4	20.0
3g	3-$NO_2C_6H_4$	$C_{23}H_{19}NO_6$	135.1–138.2	60.4	13.5
3h	2-ClC_6H_4	$C_{23}H_{19}O_4Cl$	143.4–146.5	65.8	17.0
3i	2-BrC_6H_4	$C_{23}H_{19}O_4Br$	158.4–160.4	57.6	18.5
3j	2-$OCH_3C_6H_4$	$C_{24}H_{22}O_5$	162.9–163.4	58.9	20.0

3b: IR (KBr, ν, cm^{-1}): 3323, 3046, 2975, 1685, 1612, 1260, 1092 (C_{Ar}-Cl); H^1 NMR ($CDCl_3$, δ, ppm): 11.46 (s, 2H, –OH), 8.12–8.14 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.86–7.78 (dd, 2H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.66–7.68 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.49–7.52 (m, 2H, Ar-H), 6.93–6.97 (m, 4H, Ar-H), 4.00–4.10 [m, 1H, $-CH(CH_2)_2$], 3.62–3.64 [m, 4H, $-CH(CH_2)_2$].

3c: IR (KBr, ν, cm^{-1}): 3300, 3025, 2970, 1663, 1597, 1253, 1073 (C_{Ar}-Br); H^1 NMR ($CDCl_3$, δ, ppm): 11.52 (s, 2H, –OH), 8.10–8.12 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.85–7.87 (dd, 2H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.64–7.66 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.48–7.51 (m, 2H, Ar-H), 6.91–6.95 (m, 4H, Ar-H), 3.90–4.00 [m, 1H, $-CH(CH_2)_2$], 3.62–3.64 [m, 4H, $-CH(CH_2)_2$].

3d: IR (KBr, ν, cm^{-1}): 3296, 3030, 2980, 1665, 1590, 1254, 1600 (C_{Ar}-C_{al}); H^1 NMR ($CDCl_3$, δ, ppm): 12.35 (s, 2H, –OH), 7.92–7.94 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.85–7.87 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.62–7.64 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.46–7.49 (m, 2H, Ar-H), 6.89–6.93 (m, 4H, Ar-H), 4.00–4.10 [m, 1H, $-CH(CH_2)_2$], 3.38–3.40 [m, 4H, $-CH(CH_2)_2$], 2.51 (s, 3H, $-CH_3$).

3e: IR (KBr, ν, cm^{-1}): 3325, 3035, 2963, 1680, 1584, 1255, 1341 (C_{Ar}-NO_2); H^1 NMR ($CDCl_3$, δ, ppm): 11.63 (s, 2H, –OH), 8.11–8.13 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.87–7.90 (dd, 2H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.65–7.67 (d, 2H, $J = 8.8$ Hz, Ar-H), 7.48–7.50 (m, 2H, Ar-H), 6.93–6.96 (m, 4H, Ar-H), 4.00–4.11 m, 1H, $-CH(CH_2)_2$, 3.62–3.65 [m, 4H, $-CH(CH_2)_2$].

3f: IR (KBr, ν, cm^{-1}): 3315, 3022, 2960, 1696, 1575, 1258, 1055 (C_{Ar}-OCH_3); H^1 NMR ($CDCl_3$, δ, ppm): 12.01 (s, 2H, –OH), 7.84–7.86 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.76–7.78 (dd, 2H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.62–7.64 (d, 2H, $J = 8.0$ Hz, Ar-H), 7.44–7.47 (m, 2H, Ar-H), 6.87–6.91 (m, 4H, Ar-H), 3.92–4.03 [m, 1H, $-CH(CH_2)_2$], 3.56–3.58 [m, 4H, $-CH(CH_2)_2$], 3.34 (s, 3H, $-OCH_3$).

3g: IR (KBr, ν, cm^{-1}): 3310, 3018, 2978, 1678, 1577, 1263, 1351 (C_{Ar}-NO_2); H^1 NMR ($CDCl_3$, δ, ppm): 12.12 (s, 2H, –OH), 7.85–7.87 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.41–7.51 (m, 2H, Ar-H), 7.39–7.42 (dd, 1H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.33–7.35 (dd, 1H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.21–7.24 (dd, 2H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.18–7.20 (dd, 1H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, Ar-H), 6.70–6.98 (d, 3H, $J = 8.4$ Hz, Ar-H), 6.90–6.94 (t, 1H, Ar-H), 4.56–4.59 (m, 1H, $-CH(CH_2)_2$), 3.50–3.56 (m, 4H, $-CH(CH_2)_2$).

3h: IR (KBr, ν, cm^{-1}): 3306, 3037, 2969, 1673, 1600, 1248, 1036 (C_{Ar}-Cl); H^1 NMR ($CDCl_3$, δ, ppm): 11.67 (s, 2H, –OH), 7.90–7.93 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz; Ar-H), 7.54–7.56 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.48–7.53 (m, 2H, Ar-H), 7.37–7.39 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.24–7.28 (m, 2H, Ar-H), 7.18–7.21 (dd,

2H, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, Ar-H), 6.92–6.96 (m, 4H, Ar-H), 4.35–4.45 [m, 1H, $-CH(CH_2)_2$), 3.53–3.55 (m, 4H, $-CH(CH_2)_2$].

3i: IR (KBr, ν, cm^{-1}): 3295, 3024, 2958, 1683, 1592, 1267, 1038 (C_{Ar}-Br); H^1 NMR ($CDCl_3$, δ, ppm): 12.11 (s, 2H, –OH), 7.85–7.87 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.59–7.61 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.47–7.51 (m, 2H, Ar-H), 7.30–7.33 (m, 2H, Ar-H), 7.09–7.13 (m, 2H, Ar-H), 6.97–7.00 (dd, 2H, $^3J = 8.4$ Hz, $^4J = 1.2$ Hz, Ar-H), 6.90–6.94 (m, 2H, Ar-H), 4.56–4.60 (m, 1H, $-CH(CH_2)_2$), 3.46–3.59 [m, 4H, $-CH(CH_2)_2$].

3j: IR (KBr, ν, cm^{-1}): 3315, 3033, 2960, 1680, 1584, 1270, 1063 (C_{Ar}-OCH_3); H^1 NMR ($CDCl_3$, δ, ppm): 11.97 (s, 2H, –OH), 7.85–7.87 (dd, 2H, $^3J = 8.4$ Hz, $^4J = 1.6$ Hz, Ar-H), 7.38–7.46 (m, 3H, Ar-H), 7.28–7.30 (dd, 1H, $^3J = 8.0$ Hz, $^4J = 1.2$ Hz, Ar-H), 7.21–7.25 (m, 1H, Ar-H), 6.95–7.00 (m, 1H, Ar-H), 6.86–6.90 (m, 4H, Ar-H), 3.89–3.96 [m, 1H, $-CH(CH_2)_2$], 3.48–3.52 [m, 4H, $-CH(CH_2)_2$], 3.54 (s, 3H, $-OCH_3$).

Crystallographic Data of 3a

Empirical formula: $C_{24}H_{19}NO_4$; formula weight: 385.40; shape/color: dimetric/brown; temperature: 292 (2) K; wavelength: 0.71073 Å; crystal system, space group: monoclinic, *P2(1)/c*; unit cell dimensions: $a = 9.114$ (2) Å; $\alpha = 90.00^\circ$, $b = 21.023$ (4) Å, $\beta = 106.98^\circ$ (2), $c = 10.628$ (2) Å, $\gamma = 90.00^\circ$; volume: 1947.4 (7) $Å^3$; *Z*, calculated density: 4, 1.314 g/cm^3; absorption coefficient: 0.090 mm^{-1}; *F* (000): 808; crystal size: 0.50 × 0.38 × 0.16 mm; θ range for data collection: 1.94 to 25.50°; limiting indices: $0 \le h \le 11$, $0 \le k \le 25$, $-12 \le l \le 12$; reflections collected/unique: 4125/1500 [R (int) = 0.0273]; absorption correction: none; refinement method: full-matrix least-squares on F^2; data/restraints/parameters: 3620/2/271; goodness of fit on F^2: 0.839; final R indices [$I > 2\sigma$ (*I*)]: $R_1 = 0.0399$, $wR_2 = 0.0512$; final R indices [$I > 2\sigma$ (*I*)]: $R_1 = 0.1221$, $wR_2 = 0.0591$; largest diff. peak and hole: 0.123 and −0.129 e. $Å^{-3}$.

CONCLUSION

In summary, we have demonstrated the application of a multicomponent reaction for the synthesis of a series of 1,3,5-triaryl-1,5-pentanedione derivatives in good yields, which have developed a facile synthesis of 2,4,6-triphenylpyridine derivatives. We first used the amines in this sequential aldol and Michael reactions in ionic liquid as a mild condition.

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