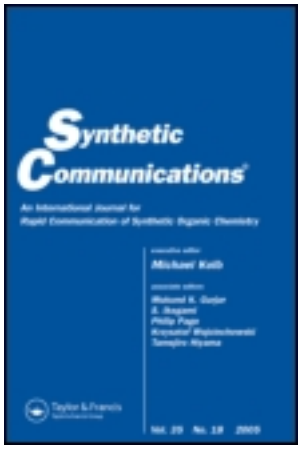

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Brønsted Acidic Ionic Liquid as an Efficient and Reusable Catalyst for One-Pot, Three-Component Synthesis of Pyrimidinone Derivatives via Biginelli-Type Reaction Under Solvent-Free Conditions

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BRØNSTED ACIDIC IONIC LIQUID AS AN EFFICIENT AND REUSABLE CATALYST FOR ONE-POT, THREE-COMPONENT SYNTHESIS OF PYRIMIDINONE DERIVATIVES VIA BIGINELLI-TYPE REACTION UNDER SOLVENT-FREE CONDITIONS

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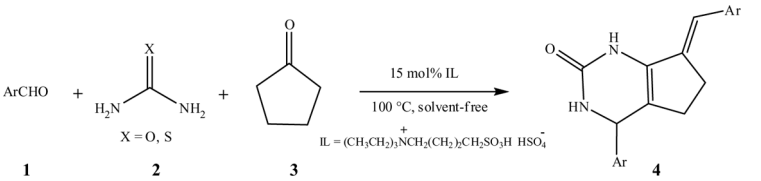
GRAPHICAL ABSTRACT



Abstract *A mild and efficient method has been developed for the preparation of pyrimidinone derivatives from the reaction of aromatic aldehydes with cyclopentanone and urea or thiourea in the presence of* N-*(4-sulfonic acid) butyl triethyl ammonium hydrogen sulfate ([TEBSA][HSO$_4$]) as the Brønsted acidic ionic liquid and effective catalyst under thermal and solvent-free conditions. Good yields, short reaction times, straightforward workup, reusability of the catalyst, and green conditions are the most obvious advantages of this procedure.*

Keywords Biginelli-type reaction; Brønsted acidic ionic liquid; one-pot; pyrimidinone; solvent-free

INTRODUCTION

One-pot multicomponent reactions have attracted significant attention in organic and medicinal chemistry. In these reactions, highly diverse and complex compounds are produced from easily available precursors in a single step by formation of multiple new bonds in one pot. Thus, multicomponent reactions are known as important and environmentally benign processes in synthetic chemistry because

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they decrease the number of steps and reduce energy consumption and waste production.[1–4]

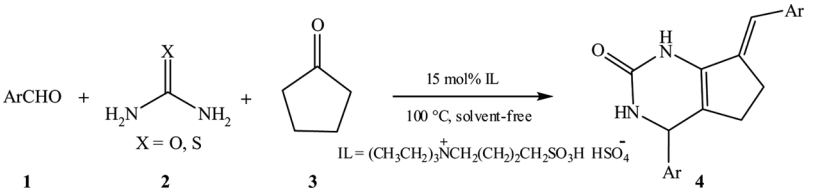
Pyrimidinone and its derivatives constitute an important class of natural and synthetic products that possess significant biological and pharmaceutical properties.[5,6] In particular, functionalized pyrimidinones such as fused pyrimidinones with an arylidene part are essential heterocyclic motifs in antitumor agents.[7] These compounds as important key intermediates are employed for preparation of many biologically active products.[8–10] Because of the potential of arylidene heterobicyclic pyrimidinones, numerous methods including the reaction of α,α'-bis (arylidene)cycloalkanones with urea or thiourea catalyzed by strong bases such as sodium ethoxide[7] or strong acids such as HCl have been developed for their synthesis.[11] In recent years, a Biginelli-type reaction involving one-pot, three-component condensation of aromatic aldehydes, cyclopentanone, and urea or thiourea was also reported as an efficient method for the synthesis of these compounds using TMSCl as reagent in dimethylformamide (DMF)/CH_3CN as solvent.[12] Also, ytterbium chloride has effectively catalyzed this reaction under solvent-free conditions.[13] However, these procedures suffered from long reaction times and used excess reagent and mixed solvents. Regarding the importance of arylidene heterobicyclic pyrimidinones and the great need for environmentally benign chemical productions, the development of suitable green synthetic methods for these compounds has attracted considerable interest.

Recently, ionic liquids as useful green solvents or catalysts have been applied in many reactions[14,15] because of their specific properties such as undetectable vapor pressure, resistance to combustion, wide liquid range, reusability, and high thermal stability.[16,17] In particular, Brønsted acidic ionic liquids, containing useful characteristics of solid acids and mineral liquid acids, are designed to replace traditional mineral liquid acids such as sulfuric acid and hydrochloric acid in chemical procedures.[18,19] *N*-(4-Sulfonic acid) butyl triethyl ammonium hydrogen sulfate ([TEBSA][HSO_4]) has been synthesized and used as an efficient catalyst for nitration of aromatic compounds,[20] esterification of various alcohols by different acids,[21] and selective alkylation of m-cresol with *tert*-butanol.[22] Also, we applied this Brønsted acidic ionic liquid as an efficient and reusable catalyst for synthesis of amidoalkyl naphthol derivatives.[23] In continuation of our investigations for developing new synthetic methodologies,[24,25] herein we report a new, convenient, mild, and efficient procedure for one-pot, three-component synthesis of pyrimidinone derivatives from various aryl aldehydes, cyclopentanone, and urea or thiourea in the presence of [TEBSA][HSO_4] as an effective and recoverable catalyst under solvent-free conditions (Scheme 1). To the best of our knowledge, this is the first report using a Brønsted acidic ionic liquid for synthesis of these pyrimidinone derivatives.

EXPERIMENTAL

General Remarks

All reagents were purchased from Merck and Aldrich and were used without further purification. All yields refer to isolated products after purification. Products were characterized by spectroscopy data [infrared (IR), ^{1}H NMR, and ^{13}C NMR



Scheme 1. One-pot, three-component reaction of aryl aldehydes, cyclopentanone, and urea/thiourea.

spectra] and melting point. ^{1}H NMR (400 and 500 MHz) and ^{13}C NMR (100 and 125 MHz) spectra were run in dimethylsulfoxide (DMSO-d_6) solvent relative to tetramethylsilane (TMS). IR spectra were recorded on a Shimadzu 435 IR spectrophotometer and performed using KBr pellets. All melting points were taken on a Gallenkamp melting-point apparatus and are uncorrected.

General Procedure for the Preparation of Pyrimidinone Derivatives

A mixture of aldehyde (1 mmol), cyclopentanone (1 mmol, 0.084 g), urea (1.2 mmol, 0.072 g) or thiourea (1.2 mmol, 0.091 g), and [TEBSA][HSO_4] (synthesized according to our previous work[23] (0.15 mmol, 0.050 g) was stirred at 100 °C in oil bath. The completion of the reaction was monitored with thin-layer chromatography (TLC; ethyl acetate/cyclohexane, 1/1). After the completion of the reaction, water (10 mL) was added, and the product was filtered. Then, it was recrystallized from ethyl alcohol. The products were characterized by spectral data (IR, ^{1}H NMR, and ^{13}C NMR) and comparison of their physical data with the literature data. The spectral data of some synthesized compounds are given.

Compound 4a. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.94–2.05 (m, 1H), 2.31–2.41 (m, 1H), 2.78–2.90 (m, 2H), 5.15 (s, 1H), 6.62 (s, 1H), 7.14–7.40 (m, 11H), 8.76 (s, 1H); IR (KBr) cm^{-1}: 3410, 3215, 3118, 2922, 2848, 1672, 1467, 1444, 1353, 1071, 754.

Compound 4b. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.92–2.01 (m, 1H), 2.37–2.45 (m, 1H), 2.65–2.80 (m, 2H), 5.62 (s, 1H), 6.76 (s, 1H), 7.17–7.54 (m, 9H), 9.08 (s, 1H); IR (KBr) cm^{-1}: 3421, 3229, 3115, 2925, 2851, 1677, 1616, 1492, 1459, 1439, 1037, 867, 813, 754.

Compound 4h. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.95–2.05 (m, 1H), 2.38–2.45 (m, 1H), 2.76–2.94 (m, 2H), 3.83 (s, 6H), 5.29 (s, 1H), 6.72 (s, 1H), 7.33 (s, 1H), 7.43 (d, $J = 7.6$ Hz, 4H), 7.91 (d, $J = 7.6$ Hz, 2H), 7.98 (d, J = 7.2 Hz, 2H), 8.91 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 28.76, 29.11, 52.43, 52.56, 57.66, 116.60, 120.15, 127.11, 127.29, 128.36, 129.31, 129.89, 130.09, 136.76, 142.52, 142.90, 148.72, 153.61, 166.45; IR (KBr) cm^{-1}: 3382, 3219, 3119, 2950, 2850, 1688, 1599, 1435, 1282, 1108, 898, 770. Anal. calcd. for $C_{24}H_{22}N_2O_5$: C, 68.89; H, 5.30; N, 6.69%; Found: C, 68.80; H, 5.44; N, 6.70%.

Compound 4i. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.95–2.02 (m, 1H), 2.33–2.40 (m, 1H), 2.71–2.85 (m, 2H), 5.17 (s, 1H), 6.62 (s, 1H), 7.13–7.22 (m, 5H),

7.27–7.38 (m, 4H), 8.77 (s, 1H);^{13}C NMR (125 MHz, DMSO-d_6) δ 29.00, 57.48, 116.11, 116.15, 116.28, 116.32, 116.51, 119.07, 129.32, 129.38, 130.48, 130.54, 135.10, 136.79, 139.64, 140.41, 153.95, 160.31, 163.30; IR (KBr) cm^{-1}: 3415, 3220, 3123, 2987, 2918, 1681, 1603, 1507, 1455, 1352, 1229, 1157, 1076, 886, 825, 755.

Compound 4l. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.65–2.02 (m, 1H), 2.32–2.38 (m, 1H), 2.68–2.83 (m, 2H), 3.73 (s, 3H), 3.74 (s, 3H), 5.07 (s, 1H), 6.55 (s, 1H), 6.75–6.87 (m, 4H), 7.08 (s, 1H), 7.17 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 8.65 (s, 1H); IR (KBr) cm^{-1}: 3374, 3214, 3114, 2957, 2932, 2835, 1682, 1604, 1511, 1449, 1349, 1276, 1247, 1176, 1029, 890, 821, 755.

Compound 4m. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.94–2.02 (m, 1H), 2.27 (s, 6H), 2.31–2.39 (m, 1H), 2.73–2.82 (m, 2H), 5.08 (s, 1H), 6.57 (s, 1H), 7.11–7.25 (m, 9H), 8.70 (s, 1H); IR (KBr) cm^{-1}: 3445, 3217, 3119, 2917, 2847, 1687, 1512, 1458, 1348, 1081, 889, 808, 750.

Compound 4o. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 1.98–2.08 (m, 1H), 2.28–2.35 (m, 1H), 2.85–3.05 (m, 2H), 5.36 (s, 1H), 6.83 (s, 1H), 7.33 (s, 1H), 7.41–7.55 (m, 6H), 7.77–7.97 (m, 8H), 8.89 (s, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 29.25, 29.46, 58.60, 117.68, 119.64, 125.77, 125.82, 126.50, 126.87, 127.10, 127.23, 127.63, 128.26, 128.45, 128.71, 129.33, 132.33, 133.41, 133.73, 134.11, 136.25, 137.11, 140.72, 141.62, 154.10; IR (KBr) cm^{-1}: 3433, 3207, 3107, 2923, 2849, 1671, 1615, 1507, 1457, 1360, 1123, 901, 813, 745. Anal. calcd. for $C_{28}H_{22}N_2O$: C, 83.56; H, 5.51; N, 6.96%; Found: C, 83.29; H, 5.68; N, 6.71%.

Compound 4q. ^{1}H NMR (DMSO-d_6, 500 MHz) δ 1.95–2.02 (m, 1H), 2.34–2.42 (m, 1H), 2.71–2.87 (m, 2H), 5.18 (s, 1H), 6.62 (s, 1H), 7.23 (s, 1H), 7.27–7.34 (m, 4H), 7.41 (d, $J = 8.7$ Hz, 2H), 7.45 (d, $J = 12.0$ Hz, 2H), 8.80 (s, 1H); IR (KBr) cm^{-1}: 3409, 3223, 3122, 2919, 2850, 1673, 1489, 1453, 1406, 1352, 1272, 1090, 1013, 887, 827, 815, 755.

Compound 4r. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.06–2.14 (m, 1H), 2.54–2.61 (m, 1H), 2.82–2.99 (m, 2H), 5.49 (s, 1H), 7.09 (s, 1H), 7.51–7.60 (m, 4H), 8.19 (d, $J = 8.4$ Hz, 2H), 8.29 (d, $J = 7.6$ Hz, 2H), 9.19 (s, 1H), 10.31 (s, 1H); IR (KBr) cm^{-1}: 3387, 3202, 2923, 2848, 1667, 1587, 1518, 1475, 1340, 1181, 1110, 858, 750.

Compound 4s. ^{1}H NMR (DMSO-d_6, 400 MHz) δ 2.01–2.11 (m, 1H), 2.33–2.42 (m, 1H), 2.62–2.73 (m, 2H), 3.79 (s, 6H), 5.48 (s, 1H), 6.87–7.04 (m, 5H), 7.12–7.21 (m, 2H), 7.25–7.33 (m, 2H), 8.67 (s, 1H), 10.18 (s, 1H); IR (KBr) cm^{-1}: 3423, 3163, 2962, 2900, 2834, 1666, 1594, 1552, 1488, 1461, 1243, 1194, 1178, 1028, 873, 760.

RESULTS AND DISCUSSION

To obtain the best reaction conditions, the reaction of benzaldehyde (1 mmol, 0.106 g), cyclopentanone (1 mmol, 0.084 g), and urea (1.2 mmol, 0.072 g), was examined in the presence of 10 mol% of [TEBSA][HSO_4] (0.1 mmol, 0.033 g) as catalyst in refluxing acetonitrile. When the reaction mixture was refluxed for 3 h, undesired products were observed. In view of the current interest in environmentally benign

catalytic processes, a procedure performed under solvent-free conditions would be more appreciated, and therefore we decided to carry out this reaction under solvent-free conditions at 100 °C and found the reaction to be completed after 10 min. Also, this reaction was checked under different temperatures including room temperature and 80, 100, and 120 °C. The greatest yield in the shortest reaction time was obtained under solvent-free conditions at 100 °C. The optimized amount of the catalyst was determined using different molar amounts of [TEBSA][HSO_4] such as 0.05, 0.10, 0.15, 0.30, 0.50, and 1 mmol under solvent-free conditions at 100 °C. It was observed that 15 mol% of [TEBSA][HSO_4] was the best of amount of the catalyst at 100 °C. In addition, excess amounts of cyclopentanone and urea were necessary to give the best yields. Accordingly, the best yield in the shortest reaction time was obtained using the molar ratio of 1:1:1.2:0.15 of benzaldehyde, cyclopentanone, urea, and acidic ionic liquid respectively.

Using these optimized conditions, various pyrimidinone derivatives were prepared by the reaction of various aryl aldehydes with urea or thiourea and cyclopentanone under solvent-free conditions at 100 °C (Table 1, entries 1–20). As demonstrated in Table 1, aromatic aldehydes were reacted with cyclopentanone and urea or thiourea to produce the corresponding arylidene heterobicyclic pyrimidinones in good to excellent yields in short reaction times. The aromatic aldehydes with electron-withdrawing substituents (Table 1, entries 5–9) were converted to the related pyrimidinone derivatives in shorter reaction times than aromatic aldehydes

Table 1. The one-pot three-component reaction of aryl aldehydes, cyclopentanone and urea/thiourea in the presence of ionic liquid at 100 °C under solvent-free conditions[a]

Entry	Aldehyde (Ar)	X	Product	Time (min)	Yield (%)[b]	Mp[Ref.]
1	C_6H_5	O	4a	5	86	207–210[12]
2	2-ClC_6H_4	O	4b	10	88	219–222[12]
3	4-ClC_6H_4	O	4c	10	91	208–211[12]
4	4-BrC_6H_4	O	4d	10	83	217–220[13]
5	3-$O_2NC_6H_4$	O	4e	5	88	227–230[12]
6	4-$O_2NC_6H_4$	O	4f	5	82	217–220[12]
7	4-NCC_6H_4	O	4g	5	91	225–228[13]
8	4-$CH_3OCOC_6H_4$	O	4h	5	81	218–222
9	4-FC_6H_4	O	4i	5	90	214–217[12]
10	2-$MeOC_6H_4$	O	4j	10	82	227–230[13]
11	3-$MeOC_6H_4$	O	4k	10	91	180–183[13]
12	4-$MeOC_6H_4$	O	4l	10	90	212–215[12]
13	4-MeC_6H_4	O	4m	10	75	210–213[12]
14	1-Naphthyl	O	4n	25	73	218–221[13]
15	2-Naphthyl	O	4o	15	80	207–211
16	C_6H_5	S	4p	10	88	225–227[12]
17	4-ClC_6H_4	S	4q	10	91	208–211[12]
18	4-$O_2NC_6H_4$	S	4r	15	78	202–206[12]
19	2-$MeOC_6H_4$	S	4s	5	76	223–226[12]
20	4-MeC_6H_4	S	4t	10	84	208–211[13]

[a]Aldehyde/cyclopentanone/urea or thiourea/IL = 1:1:1.2:0.15.

[b]Yields refer to isolated pure products and all synthesized pyrimidinone derivatives were characterized by spectral data (IR, ^1H and ^{13}C NMR), melting points and comparison with authentic samples.

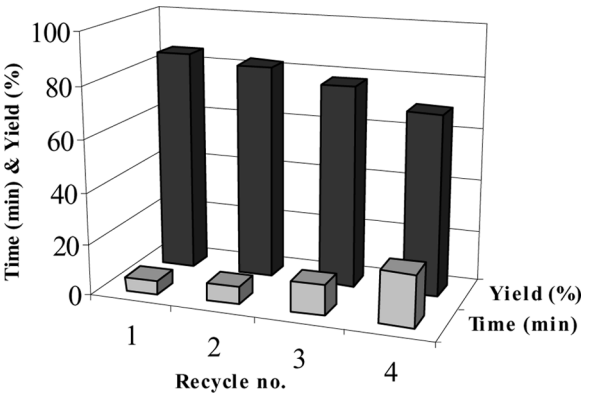
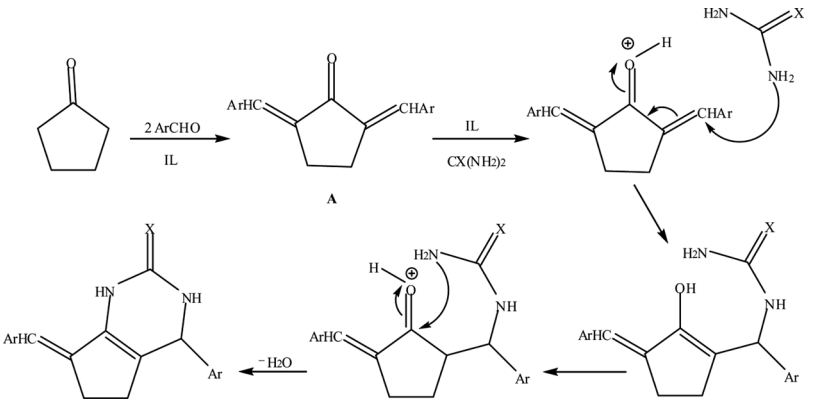


Figure 1. Recycling of the Brønsted acidic ionic liquid catalyst.

with electron-donating substituents (Table 1, entries 10–13). It should be mentioned that *ortho*-substituted benzaldehydes were converted to the corresponding arylidene heterobicyclic pyrimidinones with good yields (Table 1, entries 2 and 10). When the thiourea was used, the yields of the related products were high (Table 1, entries 16–20). It is noteworthy that the reaction times are very short and workup of products is very convenient. All of the products were isolated by adding water to the reaction mixture, and the solid compounds were filtered off as pure products. Furthermore, this procedure is environmentally benign because it uses halogen-free and recyclable acidic ionic liquid under solvent-free conditions without any organic solvent.

To investigate the reusability of the [TEBSA][HSO_4] catalyst, after each run, the catalyst was extracted from the reaction mixture according to the previously reported method[23] and reused for the reaction of benzaldehyde with cyclopentanone and urea under solvent-free conditions at 100 °C (Fig. 1). The catalyst could be employed four times, although the efficiency of the catalyst was gradually



Scheme 2. Mechanism of one-pot, three-component reaction of aryl aldehydes, cyclopentanone, and urea/thiourea.

decreased. This demonstrates that the acidic ionic liquid ([TEBSA][HSO_4]) can be used as an effective and reusable catalyst for the synthesis of pyrimidinone derivatives.

As shown in Scheme 2, the reaction of cyclopentanone with aromatic aldehydes in the presence of an acid catalyst is known to provide α,α′-bis (arylidene) cyclopentanone (**A**).[13] Then compound **A** has reacted with urea or thiourea to produce pyrimidinone derivatives (Scheme 2).

CONCLUSION

In conclusion, we have demonstrated that an acidic ionic liquid, *N*-(4-sulfonic acid) butyl triethyl ammonium hydrogen sulfate ([TEBSA][HSO_4]), can be used as a highly efficient and recyclable catalyst for the one-pot synthesis of pyrimidinone derivatives by coupling various aromatic aldehydes with cyclopentanone and urea or thiourea under solvent-free conditions. Use of the relatively nontoxic (halogen-free) and reusable acidic ionic liquid as an effective green catalyst, high catalytic efficiency, good yields, short reaction times, and straightforward workup under green conditions are advantages of this protocol.

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