

Bronsted acidic ionic liquid as an efficient and reusable catalyst for one-pot synthesis of 1-amidoalkyl 2-naphthols under solvent-free conditions

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ABSTRACT

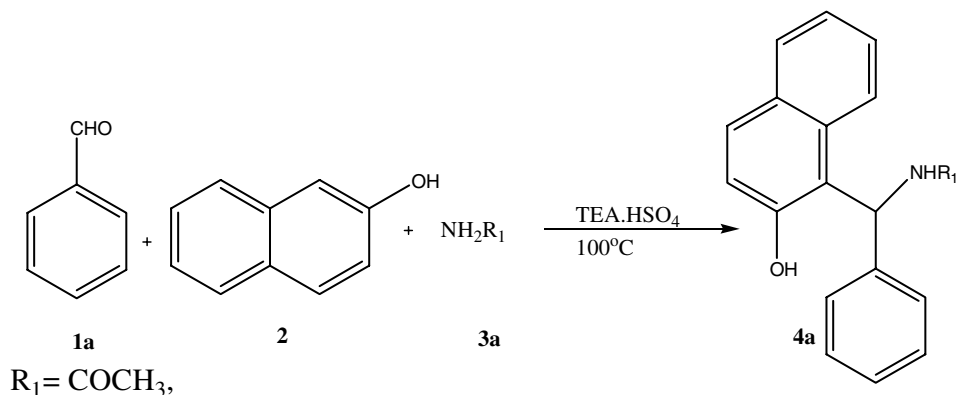
A mild and efficient method has been developed for the preparation of amidoalkyl naphthols from condensation of aldehydes with amides or urea and 2-naphthol in the presence of a catalytic amount of Brønsted acidic ionic liquid ($[\text{TEA}][\text{HSO}_4]$) under thermal solvent-free conditions. High yields, short reaction time, easy work-up and reusability of the catalyst are advantages of this procedure.

Keywords: Bronsted acidic ionic liquid, 2-naphthol, Multicomponent reaction, urea.

INTRODUCTION

Multicomponent reactions (MCRs) are very important and attractive subjects in organic synthesis due to formation of carbon-carbon and carbon-hetero atom bonds in one pot.¹⁻⁴ Simple procedures, high bond forming efficiency, time and energy saving and low expenditures are advantages of these reactions.⁵ Therefore, researchers have made great efforts to find and develop new MCRs.

Compounds containing 1,3-amino-oxygenated functional groups are frequently found in biologically active natural products and potent drugs such as nucleoside antibiotics and HIV protease inhibitors⁶⁻⁹ Furthermore, 1-amidoalkyl 2-naphthols can be converted to useful and important biological building blocks and to 1-amino methyl 2-naphthols by an amide hydrolysis reaction, since compounds exhibit depressor and bradycardia effects in humans.^{10,11} 1-Amidoalkyl 2-naphthols can be prepared by multicomponent condensation of aldehydes, 2-naphthols and acetonitrile or different



amides in the presence of Lewis or Brønsted acids such as p-TSA,¹² montmorillonite K10,¹³ Ce(SO₄)₂,¹⁴ Iodine,¹⁵ Fe(HSO₄)₃,¹⁶ Sr(OTf)₂,¹⁷ K₅CoW₁₂O₄₀·3H₂O,¹⁸ sulfamic acid,^{19,20} molybdophosphoric acid,²¹ cation-exchange resins²² and silica sulfuric acid.²³ However some of the reported methods suffer from disadvantages such as prolonged reaction time, low yield of products, toxic and corrosive reagents and the use of additional microwave or ultrasonic irradiation. Therefore, the discovery of clean procedures and the use of green and eco-friendly catalysts with high catalytic activity and short reaction times for the production of 1-amidoalkyl-2-naphthols have gained considerable attention.

RESULTS AND DISCUSSION

Here we report a new, convenient, mild and efficient procedure for one-pot three component synthesis of amidoalkyl naphthol derivatives from various aryl aldehydes, 2-naphthol and urea in the presence of TEA.HSO₄ as an effective and recoverable catalyst under solvent-free conditions.

Initially to optimize the amount of ionic liquid, the reaction of 2-naphthol (1mmol), benzaldehyde (1mmol) and urea (1.2 mmol) was performed under solvent free conditions at 100°C in the presence of different quantities of TEA.HSO₄ (Table 1). The yields of product 4a using high amounts of [TEA][HSO₄] were low and the reaction time was long (entries 1-3). No improvement in the

reaction rate was observed by decreasing the amount of ionic liquid from 0.17 to 0.01 mmol but the yield of 4a in the presence of 0.05 mmol of [TEA][HSO₄] was higher than others. Therefore 5 mol% of ionic liquid was chosen as optional quantity of [TEA][HSO₄]. And the same thing is happened with temperature of the reaction. We optimize the temperature for the reaction and we saw that at the 100°C the maximum yield was obtained (Table 2)

The reaction of β-naphthol 2 with aromatic aldehydes bearing electron withdrawing groups (halide), electron releasing groups (methoxy groups) and urea was carried out in the presence of [TEA][HSO₄] as a catalyst. In all these reactions, clean and the complete conversion leading to the corresponding amidoalkyl naphthols as observed in shorter reaction times (0.5–2 h). The yields obtained were good to excellent without formation of any side products such as di-benzoxanthenes, which are normally observed under the influence of strong acids. The reaction of aromatic aldehydes having electron withdrawing groups reacted very well compared with aromatics aldehydes substituted with electron releasing groups.

General procedure

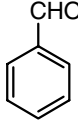
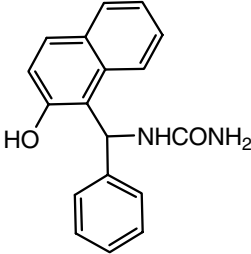
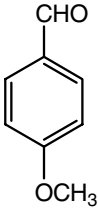
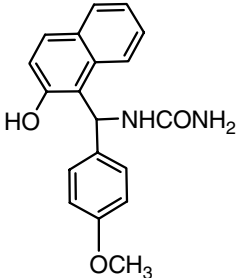
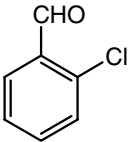
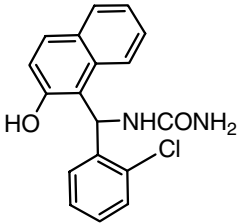
A mixture of β-naphthol 2 (1 mmol), aldehyde (1 mmol), urea (1.2 mmol) and [TEA][HSO₄] (0.05 mmol) was rapidly stirred and heated at 100°C in an oil bath. After completion of the reaction as monitored by the TLC, the reaction was cooled to room temperature, methanol (20 ml) was added and insoluble material was filtered to

Table 1: The effect of different amount of [TEA][HSO₄] on the reaction of 2-naphthol, urea and benzaldehyde

S. No.	[TEA][HSO ₄] (mmol)	Time (min)	Yield of 4a (%)
1	3	35	0
2	1	30	65
3	0.5	20	70
4	0.17	10	80
5	0.09	10	82
6	0.05	10	88
7	0.01	10	68

Table 2: The effect of temperature of reaction of 2-naphthol, urea and benzaldehyde

S. No.	Temperature (°C)	Time (min)	Yield of 4a (%)
1	rt	120	10
2	60	90	30
3	70	60	70
4	80	45	75
5	90	30	82
6	100	10	88

Entry	Aldehyde	Amide/amino acid	product	Reaction time (min)	yield	m.p.
1		NH ₂ CONH ₂		14	89	172
2		NH ₂ CONH ₂		15	80	123
3		NH ₂ CONH ₂		10	90	145

separate the catalyst. The filtrate was concentrated under vacuum and the crude residue was purified by crystallization in ethanol: water (1: 3) to afford the pure amidoalkyl naphthol. All the products obtained were fully characterized by spectroscopic method such as IR, HNMR ¹³C NMR and mass spectroscopy and have been identified by the comparison of the spectral data with those reported.

1.

2.

3. ¹H NMR (200 MHz, DMSO-*d*₆): δ 9.68 (1H, brs), 8.12–7.98 (2H, m), 7.78–7.59 (2H, m), 7.30 (1H, m), 7.28–7.06 (7H, m), 2.02 (3H, s); FABMS: *m/z* 329, 327 [*M*+H]⁺.

CONCLUSION

We have developed a very simple and efficient method for the high-yielding synthesis of amidoalkyl naphthols by one-pot three-component coupling of β-naphthol, various aromatic aldehydes and urea or amides and amino acids using 5 mol% [TEA][HSO₄]. The advantage of this method, in which a relatively non-toxic (halogen-free) and reusable ionic liquid (which is cheap and easily available) as an effective catalyst, are high catalytic efficiency, short reaction time, high yield, a straightforward work-up and environmental benignancy.

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