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Polyaniline sulphate salt catalyzed synthesis of amidoalkyl naphthols under solvent free conditions

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ABSTRACT

An alternative synthesis of amidoalkyl naphthols, employing a three-component condensation reaction of β-naphthol, aromatic aldehyde, amides or urea in the presence of polyaniline sulphate salt under solvent free conditions has been described. The present procedure offers advantages such as shorter reaction time, simple workup, excellent yields, recovery and reusability of catalyst

Keywords: Polyaniline sulphate salt, One-pot reaction, amidoalkyl naphthol; *β*-naphthol, Solvent free and condensation.

INTRODUCTION

One-pot multicomponent reactions (MCRs) by virtue of their convergence, productivity, facile execution and high yield have attracted considerable attention in recent years[1]. There has been tremendous development in three or four component reaction specially the Bignelli[2], Passerni[3], Ugi[4], and Mannich[5] reactions, which have further led to renaissance of MCRs. Nevertheless, great efforts have been and still are being made to find and develop new MCRs.

In recent years, the development of more economical and environmental friendly conversion processes is gaining interest in the chemical community. In this context, a recent report[6] and related publications[7] on one-pot three-component synthesis of amidoalkyl naphthols by the condensation of aldehydes, amides or urea with *β*-naphthol in the presence of acid p-TSA through the tandem process of ortho-quinone methide (O-QMs)[8] has attracted out attention. Although the use of substoichiometric amount of p-TSA satisfies the reaction, the method suffers from the drawbacks of green chemistry such as prolongedreaction times, recovery and reusability of catalyst. The demand for environmentally benign procedure with reusable catalyst necessitated us to develop an alternate method for the synthesis of amidoalkyl naphthols. In continuation of our work on the use of heterogeneous solid acid catalysts[9], we describe in this report, a alternative method for the preparation of amidoalkyl naphthols, employing a three-component one-pot condensation reaction of *β*-naphthol, aldehydes, amides or urea in the presence of polyaniline sulphate salt under solvent free conditions.

MATERIALS AND METHODS

All the commercial reagents and solvents were used without further purification unless otherwise stated. Melting points were recorded on a Buchi 535 melting point apparatus and are uncorrected. All the reactions were monitored

by thin layer chromatography performed on precoated silica gel $60F_{254}$ plates (Merck). Compounds were visualized with UV light at 254 nm and 365 nm, I_2 and heating plates after dipping in 2% phosphomolybdic acid in 15% aq. H_2SO_4 soln. IR spectra were recorded on a Perkin-Elmer 683 or a 1310 FT-IR spectrometers with KBr pellets. NMR spectra were recorded on a Varian Unity-400 MHz and BRUKER AMX 300 spectrometers using TMS as an internal standard. Mass spectra were recorded on a VG. Micromass 7070H and a Finnigan Mat 1020B mass spectrometers operating at 70eV.

General Procedure for the preparation of amidoalkyl naphthols by conventional heating: To a mixture of the aromatic aldehydes **1** (1 mmol), *β*-naphthol **2** (1 mmol), amide **3** the catalyst polyaniline sulphate salt (5 mg) was added and the reaction mixture was stirred at 125 °C for the appropriate time as mentioned in Table 1. On the completion of reaction as indicated by TLC, the reaction mixture was diluted with 10 mL dichloroethane and filtered to separate catalyst, catalyst was washed with dichloroethane (2x10 mL) and the combined organic extracts were washed with water (2x10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the residue obtained was recrystallized from ethyl alcohol to provide corresponding amidoalkyl naphthols **4a-n** as solids in 80-90% yields. All the products were characterized by comparison of their physical constants and spectral data with those reported in literature.

Spectral data for representative examples:

***N*- ((2-Hydroxynaphthalen-1-yl) (phenyl) methyl) acetamide 4a:** M.p. 242–243 °C. IR (KBr) 3394, 3245, 3060, 1636, 1580, 1515, 1436, 1371, 1272, 1207, 1160, 1060, 1026, 985, 930, 876, 806, 740 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 9.86 (brs, 1H), 9.64 (s, 1H), 8.20 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 7.6 Hz, 1H), 7.10–7.24 (m, 9H), 2.00 (s, 3H). ESIMS (*m/z*) 292 $(M + H)^+$.

***N*-((4-Bromophenyl) (2-hydroxynaphthalen-1-yl) methyl) acetamide 4b:** M.p. 230-231°C. IR (KBr) 3460, 3352, 2969, 1647, 1590, 1576, 1500, 1462, 1371, 1346, 1270, 1025, 826 cm^{-1}. ^1H NMR (200 MHz, DMSO-d_6): δ 9.85 (brs, 1H), 9.64 (s, 1H), 8.23 (d, *J* = 8.8 Hz, 1H), 7.92 (d, *J* = 11.4 Hz, 1H), 7.80–7.66 (m, 2H), 7.42-7.05 (m, 8H) 2.05 (s, 3H). ESIMS (*m/z*) 371 $(M+2)^+$.

***N*-((4-Chlorophenyl) (2-hydroxynaphthalen-1-yl) methyl) acetamide 4d:** M.p. 228– 230 °C. IR (KBr) 3460, 3355, 2964, 1645, 1595, 1575, 1430, 1345, 1290, 1145, 1060, 825 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 9.85 (brs, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.64– 7.66 (m, 2H), 7.08–7.45 (m, 8H), 2.06 (s, 3H). ESIMS (*m/z*) 327 $(M+H)^+$.

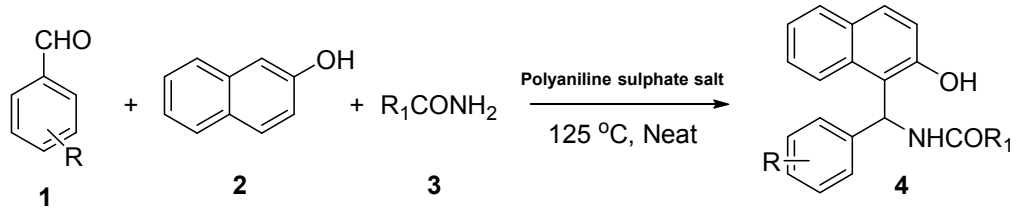
***N*-((2-Hydroxynaphthalen-1-yl) (3-methoxy phenyl)methyl)acetamide 4f:** M.p. 202–204 °C. IR (KBr): 3445, 3215, 1646, 1570, 1513, 1420, 1355, 1253, 926, 818 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6): δ 9.70 (s, 1H), 8.15-7.90 (d, *J* = 7.50 Hz, 2H), 7.75-7.62 (m, 2H), 7.45-7.04 (m, 7H), 6.80 (s, 1H), 3.66 (s, 3H), 2.00 (s, 3H). ESIMS (*m/z*) 322 $(M+H)^+$.

***N*-((4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl) benzamide 4h:** ^1H NMR (300 MHz, DMSO-d_6): δ 7.76 (d, *J*=8.66 Hz, 2H), 7.04(d, *J* = 8.85 Hz, 5H), 6.75-6.55 (m, 9H), 6.05 (d, *J* = 7.30, 1H), 5.75 (s, 1H). ESIMS (*m/z*) 388 $(M+H)^+$.

***N*-(((2-Hydroxynaphthalen-1-yl) (*p*-tolyl)methyl)benzamide 4i:** ^1H NMR (300 MHz, MSO-d_6): δ 7.76 (d, *J*=8.66, 2H), 7.04 (d, *J* = 8.85 Hz, 5H), 6.77-6.52 (m, 9H), 6.02 (d, *J* = 7.33, 2H), 5.76 (s, 1H), 2.30 (s, 3H). ESIMS (*m/z*) 368$(M+H)^+$.

RESULTS AND DISCUSSION

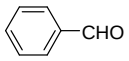
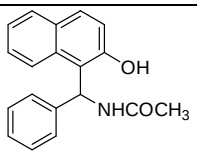
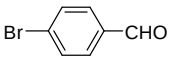
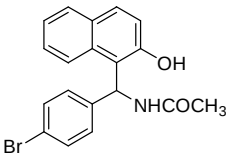
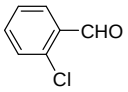
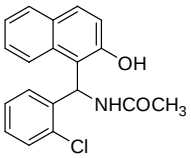
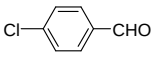
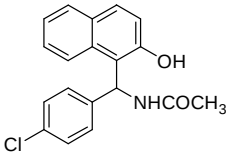
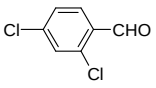
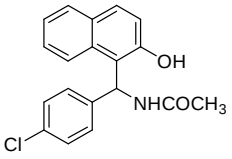
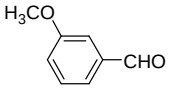
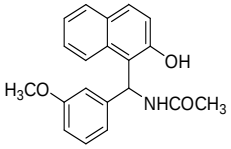
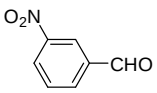
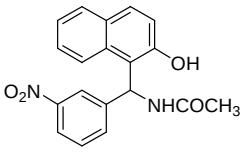
The condensation of mixture of benzaldehyde **1a** (1 mmol) with *β*-naphthol **2** (1 mmol) and acetamide **3a** (1.1 mmol) in the presence of polyaniline sulphate (5 mg) was carried out at 125 ^oC for 6-8 h under solvent-free conditions (Scheme 1). The reaction proceeded smoothly and gave the corresponding amidoalkyl naphthol **4a** as the sole product in 80% isolated yield. Methanol was added to the reaction mixture and simply filtering the mixture and evaporating the solvent from the filtrate gave the crude product, which was purified by crystallization in ethanol: water (1:3) to obtain **4a** as white solid.

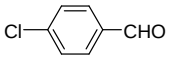
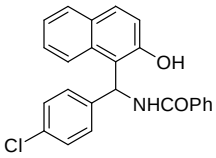
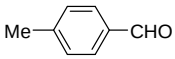
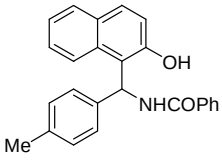
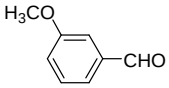
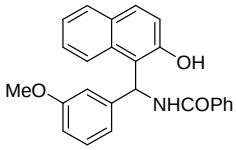
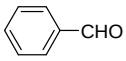
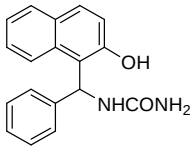
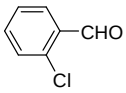
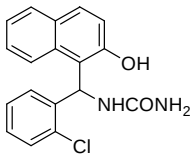
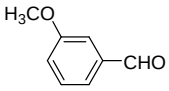
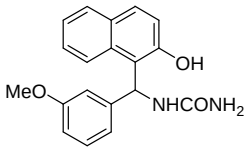
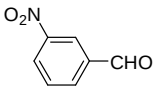
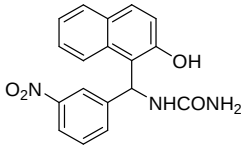


Scheme 1: Polyaniline Sulphate Salt Catalyzed Synthesis of Amidoalkyl Naphthols under Solvent Free Conditions

In order to evaluate the generality of the process, several examples illustrating the present method for the synthesis of amidoalkyl napthols 4 was studied (Table 1). The reaction of *β*-naphthol 2 with various aromatic aldehydes bearing electron withdrawing groups, electron releasing groups and acetamide / benzamide or urea was carried out in the presence of polyaniline sulphate salt as a catalyst. In all these reactions, clean and the complete conversion leading to the corresponding amidoalkyl naphthols as observed in shorter reaction times. The yields obtained were good to excellent without formation of any side products.

TABLE-1 Polyaniline sulphate salt catalyzed synthesis of amidoalkyl naphthols

Entry	Aldehyde	Urea/amide	Product 4	Time (h)	Yield (%)
a		H_3CCONH_2		6	90
b		H_3CCONH_2		6	84
c		H_3CCONH_2		6	90
d		H_3CCONH_2		6	90
e		H_3CCONH_2		6	90
f		H_3CCONH_2		7	85
g		H_3CCONH_2		7	82

h		$PhCONH_2$		6	90
i		$PhCONH_2$		6	85
j		$PhCONH_2$		6	82
k		H_2NCONH_2		8	82
l		H_2NCONH_2		8	81
m		H_2NCONH_2		8	80
n		H_2NCONH_2		8	80

CONCLUSION

In conclusion, we have developed an alternative simple and efficient method for the synthesis of amidoalkyl naphthols by one-pot three-component coupling of *β*-naphthol, various aromatic aldehydes and urea or amides using polyaniline sulphate salt as a heterogeneous solid acid catalyst.

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