Research Journal of Applied Sciences 6 (7-12): 464-466, 2011
ISSN: 1815-932X

Synthesis of Amidoalkyl Naphthols from Reaction of β-Naphthol, Acetamide and Aromatic Aldehydes in the Presence of Potassium Hydrogen Sulfate

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Abstract: The multicomponent condensation reaction of β-naphthol, aromatic aldehydes and acetamide in the presence of potassium hydrogen sulfate was carried out under solvent-free condition to afford amidoalkyl naphthols in 83-96% yields.

Key words: Amidoalkyl naphthol, acetamide, benzaldehyde, Potassium hydrogen sulfate, Saudi Arabia

INTRODUCTION

The multicomponent reactions are responsible for this higher efficiency (Bienayme *et al*., 2000) not only because of intrinsic aspects of the reaction such as superior atom economy (Trost, 1991), atom utilization and selectivity as well as lower level of by-products but also because of extrinsic aspects of the processing reaction such as simpler procedures and equipment (Trost, 2002; Mitchell *et al*., 2001), lower costs, time and energy as well as more environmentally friendly criteria. It is noteworthy that 1-carbamato-alkyl-2-naphthols can be converted to important biologically active 1-aminomethyl-2-naphthol derivatives by carbamate hydrolysis. The hypotensive and bradycardiac effects of these compounds have been evaluated (Trost, 2002).

Amidoalkyl naphthols can be prepared by multicomponent condensation of aldehydes, β-naphthols and acetonitrile or different amides in the presence of Lewis or Brosted acids such as iodine (Jahnisch *et al*., 2004), $FeCl_3$•SiO_2s, $K_5CoW_{12}O_{40}$•$3H_2O$ (Das *et al*., 2007), $HClO_4$-SiO_2 (Das *et al*., 2007), Brosted acids ionic liquid (Shaterian and Yarahmadi, 2008; Nagarapu *et al*., 2007), P_2O_5 (Mahdavinia *et al*., 2008), cyanuric chloride (Polshettiwar and Varma, 2009; Nandi *et al*., 2009), montmorillonite K10 (Polshettiwar and Varma, 2009), sulfamic acid (Nandi *et al*., 2009), Thiamine hydrochloride (Mahdavinia and Bigdeli, 2009; Kantevari *et al*., 2007; Patil *et al*., 2007), $Sr(OTf)_2$ (Kantevari *et al*., 2007), silica sulfuric acid (Patil *et al*., 2007). Yb $(Otf)_3$ (Lei *et al*., 2009) and Ce $(SO_4)_2$ (Srihari *et al*., 2007; Kumar *et al*., 2009; Nagwade and Shinde, 2007). However, some of the reported protocols suffer from certain drawbacks such as prolonged reaction time, use of carcinogenic solvent, unsatisfactory yield, high temperature (120-125°C) and use of toxic, highly acidic, nexpensive catalysts and 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 amidoalkyl naphthols have gained considerable attention. Potassium hydrogen sulfate is a cheap and efficient catalyst for the condensation reactions (Selvam and Perumal, 2006; Huang *et al*., 2005). In the present study, a simple and green procedure for the synthesis of amidoalkyl naphthols by the condensation of aldehydes with β-naphthol, acetamide or urea in the presence of potassium hydrogen sulfate ($KHSO_4$) at 100°C under solvent-free conditions is shown in Fig. 1.

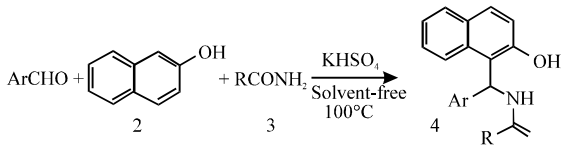

Fig. 1: A simple green procedure

MATERIALS AND METHODS

General procedure: To a solution of the paricular aldehyde (1 mmol), β-naphthol (1 mmol), acetamide (1.1 mmol), potassium hydrogen sulfate (0.15 mmol) was added then the reaction mixture was stirred at 100°C and maintained for the appropriate time (Table 1). After completion of the reaction (monitored by thin layer chromatography), the reaction mixture was diluted with water and the resulting solid product was collected by filtration and was recrystallized from aqueous ethanol.

N-[(4-Fluorophenyl) (2-hydroxynaphthalen-1-yl) methyl] acetamide 4e, ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 10.16 (s, 1 H), 8.08 (d, J = 8.2 Hz, 1 H), 7.88 (d, J = 12.2 Hz, 1 H), 7.65-7.81 (m, 2 H), 7.05-7.38 (m, 8 H), 2.02 (s, 3 H); ESI-MS, m/z: 308 (M-H, 100%); Anal. Calcd for

Table 1: Synthesis of amidoalkyl naphthols with potassium hydrogen sulfate as catalyst under solvent-free condition

Product[a]	Ar	R	Time (h)	Yield[b] (%)	Mp (°C) found	Mp (°C) reported
4a	C_6H_5	CH_3	1.0	90	232-233	229-230[13]
4b	4-MeC_6H_5	CH_3	1.0	91	223-224	224-225[10]
4c	4-ClC_6H_5	CH_3	0.5	95	233-234	237-238[10]
4d	4-$MeOC_6H_5$	CH_3	1.0	94	172-174	163-164[10]
4e	4-FC_6H_5	CH_3	0.5	95	205-207	203-205[13]
4f	4-$NO_2C_6H_5$	CH_3	0.5	96	239-240	237-238[10]
4g	3-$NO_2C_6H_5$	CH_3	0.5	93	238-240	236-247[13]
4h	4-BrC_6H_5	CH_3	0.5	92	230-231	229-231[9]
4i	2-ClC_6H_5	CH_3	0.5	93	194-195	194-196[13]
4j	3-$MeOC_6H_5$	CH_3	1.0	88	192-194	202-204[11]
4k	2-Furyl	CH_3	1.5	83	218-220	220 dec[13]
4l	C_6H_5	NH_2	1.0	90	173-174	172-174[13]
4m	4-ClC_6H_5	NH_2	0.5	94	170-171	168-169[13]
4n	4-$NO_2C_6H_5$	NH_2	0.5	96	181-183	-
4o	3-$NO_2C_6H_5$	NH_2	1.0	95	186-188	184-186[13]
4p	4-BrC_6H_5	NH_2	1.0	92	173-175	170-172[13]
4q	2-Furyl	NH_2	1.5	85	162-163	-

[a]All known compounds were characterized by comparing their spectral data with those reported; [b]Isolated yields

$C_{19}H_{16}FNO_2$: C, 73.77; H, 5.21; N, 4.53; F, 6.14. Found: C, 73.72; H, 5.25; N, 4.52; F, 6.14. [(Furan-2-yl) (2-hydroxynaphthalen-1-yl) methyl] urea 4q: ^{1}H-NMR (400 MHz, $CDCl_3$, δ ppm): 10.20 (s, 1 H), 7.08-7.67 (m, 7 H), 6.73 (s, 2 H), 6.35 (br. s, 1 H), 6.22 (m, 1 H), 6.09 (m, 1 H), 5.73 (br. s, 1 H). ESI-MS, m/z: 281 (M-H, 100%). Found (%): C, 67.89; H, 5.06; N, 9.85. Calc. for $C_{16}H_{14}N_2O_3$ (%): C, 67.92; H, 5.02; N, 9.89.

RESULTS AND DISCUSSION

Benzaldehyde was selected as a representative aldehyde along with β-naphthol, acetamide and potassium hydrogen sulfate which were reacted under solvent-free conditions at 100°C inorder to optimize the reaction conditions. The condensation of mixture of benzaldehyde 1a (1 mmol) with β-naphthol 2 (1 mmol) and acetamide 3 (1.1 mmol) in the presence of potassium hydrogen sulfate (0.15 mmol) was carried out at 100°C for 1 h under solvent free conditions. The reaction proceeded smoothly and gave the corresponding amidoalkyl naphthol 4a as the sole product in 90% isolated yield (Table 1). Water was added to the reaction mixture and simply filtering the mixture to obtain the crude product which was purified by crystallization from 30% aqueous ethanol as white solid.

In order to demonstrate the generality of the process, some examples illustrating the present method for the synthesis of amidoalkyl naphthols 4 was studied (Table 1). The reaction of β-naphthol 2 with various aromatic aldehydes bearing electron withdrawing groups (such as nitro, halo), electron releasing groups (such as methyl or methoxy groups) and acetamide was carried out in the presence of potassium hydrogen sulfate as a catalyst. In all cases, clean and complete conversion leading to the corresponding amidoalkyl naphthols (4a-4k) as observed in shorter reaction times (0.5-1.5 h).

Aromatic aldehydes with electron-withdrawing groups reacted faster than aromatic aldehydes with electron-donating groups as would be expected. Similar results were obtained under the same conditions when urea was used in place of acetamide to give the respective compounds (4l-4q).

CONCLUSION

In this study, a novel and highly efficient methodology for the synthesis of amidoalkyl naphthols by condensation reaction of aldehydes, β-naphtol and acetamide or urea in the presence of catalytic amounts of potassium hydrogen sulfate under solvent-free conditions is reported. This method offers significant advantages such as high conversions, easy handling and shorter reaction times which collectively makes it a useful and attractive process for the rapid synthesis of substituted amidoalkyl naphthols.

ACKNOWLEDGEMENTS

The researcher would like to express his thanks and appreciation to Dr. Abualgasium Abuker Abdelrosul who revised the manuscript before sending it for publication and his valuable discussion with the researcher.

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