Silver nanoparticles: An efficient and versatile reagent for the synthesis of 1-amidoalkyl-2-naphtols

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Abstract

Silver nanoparticles has been prepared and shown to efficiently catalyse the one-pot, three-component reaction of 2-naphtol, aldehydes, and acetamide at reflux, to afford the corresponding 1-amidoalkyl-2-naphtols high yield. The present method has several advantages such as high yields, easy purification, mild reaction conditions, easy work-up, survival of different functional groups and short reaction times.

Keywords

Silver nanoparticles, 2-naphtol, aldehydes, acetamide, 1-amidoalkyl-2-naphtols, one-pot reaction

1. Introduction

Multicomponent reaction (MCR_S) are very important and efficient methods in organic synthesis to access complex structures from three or more reactions. Compounds bearing 1,3-amino-oxygenated functional groups are usually found in various biologically important natural products and potent drugs, including nucleoside antibiotics and HIV protease inhibitors.[1] 1-Amidoalkyl-2-naphtol derivatives which exhibit important cardiovascular, bradycardiac,[2] and hypertensive[3] activity. Previously some catalysis have been utilized for synthesis of 1-amidoalkyl-2-naphtols.[4-24]

Catalytic activities of nanoparticles differ from the chemical properties of the bulk materials. For instance,[8] showed that the bleaching of the organic dyes by application of potassium peroxodisulphate in aqueous solution at room temperature is enhanced strongly by the application of silver containing nanoparticles.[8] Furthermore, silver nanoparticles (AgNPs) was found to catalyze the chemiluminescence from luminol–hydrogen peroxide system with catalytic activity better than Au and Pt colloid.[9] Moreover, used silver nanoparticles supported halloysite nanotubes (Ag/HNTs), with Ag content of about 11% to catalyze the reduction of 4-nitrophenol with $NaBH_4$ in alkaline aqueous solutions.[25]

In this article we investigated the new method for synthesis of 1-amidoalkyl-2-naphtols derivatives in the presence of AgNPs at reflux.

2.Experimental

2.1. Material and instrumentation

Melting points were determined with an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer. ^1H and ^{13}C NMR spectra were recorded on Bruker

DRX-400 Avance spectrometer for solutions in d_6-DMSO using TMS as an internal standard. The morphologies of the products were observed using TEM of Philips CM10 and SEM of a Holland Philips XL30 microscope with an accelerating voltage of 20 kV. The chemicals for this work were purchased from Fluka (Buchs, Switzerland) and were used without further purification.

2.2. Synthesis of silver nanocrystals

Silver nitrate (1 mol) and dodecanoic acid DDA (0.3 mol) were dissolved into *n*-butylamine (2 mol)/toluene (300 mL) completely, which resulted in a molar concentration [Ag] above 2 M. After addition of equimolar reductant, the solution became dark brown and then was refluxed for 1 h. After completion of the reaction, products were precipitated by addition of an acetone/methanol mixture. The precipitates were collected through a glass funnel filter and then washed several times with methanol and acetone.

2.3. General procedure for preparation of compounds 3a-l

A mixture of 2-naphthol (1 mmol,), aldehyde (1 mmol), acetamide (1.2 mmol) and catalyst (0.03 g) Ag NPs was grounded in a mortar for 2 minute and then refluxed in ethyl acetate for 30 min. The progress of the reaction was monitored by TLC. The product is insoluble in hot ethyle acetate. After completion of the reaction the mixture was dissolved in C_2H_5OH, filtered and washed with diethyl ether (5 ml) for isolation of catalyst. The solvent was evaporated under reduced pressure and the product was obtained.

2.4. Selected data :

2.4.1. N-[(2-hydroxy-3-methoxyphenyl)(2-hydroxynaphthalen-1-yl)methyl] acetamide (3j):

Yellow powder, m.p. 157-159^{o}C, IR (KBr) (ν_{max} cm^{-1}): 3347, 3321, 1635. Analyses: Calcd. for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15%. Found: C, 71.4; H, 5.5; N, 4.3. MS (m/z, %): 337 (6). ^{1}H NMR (400 MHz, d_6-DMSO): δ 2.02 (3H, s, CH_3), 3.73 (3H, s, OCH_3), 5.11(1 H, broad s, OH), 6.16 (1H, d, $^{3}J_{HH}$ = 8 Hz, NCH), 7.04-7.74 (9H, m, aromatic), 8.00 (1 H, d, $^{3}J_{HH}$ = 8 Hz, NH), 9.53 (1 H, broad s, OH)ppm. ^{13}C NMR (100.6 MHz, d_6-DMSO): δ 21.4 (CH_3), 37.2 (CH), 55.2 (OCH_3), 112.1, 115.3, 118.7, 119.6, 121.0, 122.0, 123.9, 126.3, 128.3, 129.2, 129.4, 130.1, 133.0, 143.0, 151.8, 152.1 and 173.0 ppm.

2.4.2. Methyl 4-[acetylamino(2-hydroxynaphtalen-1-yl)methyl]benzoate (3k):

Pale brown powder, m.p. 220-222^{o}C, IR (KBr) (ν_{max} cm^{-1}): 3343, 3310, 1743, 1641. Analyses: Calcd. for $C_{21}H_{19}NO_4$: C, 72.19; H, 5.48; N, 4.01%. Found: C, 72.0; H, 5.3; N, 4.2. MS (m/z, %): 349 (3). ^{1}H NMR (400 MHz, d_6-DMSO): δ 2.10 (3H, s, CH_3), 3.79 (3H, s, OCH_3), 6.24 (1H, d, $^{3}J_{HH}$ = 8 Hz, NCH), 6.73-7.86 (10H, m, aromatic), 8.13 (1 H, d, $^{3}J_{HH}$ = 8 Hz, NH), 9.55 (1 H, broad s, OH)ppm. ^{13}C NMR (100.6 MHz, d_6-DMSO): δ 23.3 (CH_3), 48.6 (CH), 51.4 (OCH_3), 115.4, 117.5, 118.8, 119.3, 122.1, 122.5, 123.2, 126.3, 128.1, 128.8, 130.4, 133.3, 147.2, 153.4, 167.9 and 171.3 ppm.

2.4.3. N-[(2-hydroxynaphthalen-1-yl)(4-methylaminophenyl)methyl]acetate (3l).

Brown powder, m.p. 121-123^{o}C, IR (KBr) (ν_{max} cm^{-1}): 3350, 3345, 1681. Analyses: Calcd. for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74%. Found: C, 75.1; H, 6.4; N, 8.9. MS (m/z, %): 320 (5). ^{1}H NMR (400 MHz, d_6-DMSO): δ 2.17 (3H, s, CH_3), 2.69 (3H, s, NCH_3), 3.90 (1H, broad s,

NH), 6.23 (1H, d, $^{3}J_{HH}$ = 8 Hz, NCH), 6.85-7.64 (10H, m, aromatic), 8.16 (1 H, d, $^{3}J_{HH}$ = 8 Hz, NH), 9.67 (1 H, broad s, OH)ppm. ^{13}C NMR (100.6 MHz, d_6-DMSO): δ 23.5 (CH_3), 29.6 (NCH_3), 48.5 (CH), 114.2, 115.3, 118.8, 121.9, 123.3, 126.8, 128.7, 128.9, 129.6, 133.5, 145.2, 131.3, 134.0, 153.2, and 172.1 ppm.

3. Result and Discussions

Herein, we attempted to synthesize organicsoluble silver nanoparticles in the organic phase using silver nitrate as a precursor by adsorption method as versatile reagent for the synthesis of 1-amidoalkyl-2-naphtols by the three-component condensation of 2-naphthol **1**, aldehyde **2**, and acetamide (Scheme 1).

Initially, the fully organic phase system contains silver nitrate as a silver precursor, *n*-butylamine ($CH_3(CH_2)_3NH_2$) as a medium for dissolving the silver salt, dodecanoic acid ($CH_3(CH_2)_{10}CO_2H$) [DDA] as a capping molecule, toluene as a medium, and $NaBH_4$ as a reducing reagent were used for silver NPs synthesis as received without further purification. The dodecanoic acid is held as a silver salt and the mechanistic role of silver ions that are stabilizing the enolates of the 1,3-dicarbonyl compound that would be required for the reaction. A scheme for direct synthesis of silver nanoparticles from silver nitrate in the organic phase is illustrated in scheme 2. Formation of silver nanoparticles was observed with UV spectroscope, which showed surface plasmon peaks in the range between 380 and 450 nm in scheme 3.

The product was characterised by SEM in Scheme 4. The sem image shows that particle size is between 70-100nm. The nanoparticles were typically dispersed in toluene for further characterization using fieldemission transmission electron microscopy (TEM). TEM samples

were prepared by placing a drop of the colloidal dispersion in toluene on an amorphous carbon-coated grid in scheme 5. The tem image shows nanoporous that their size is 5nm. The molecular structure of the capping molecule on the as synthesized nanoparticles was investigated through ^{1}H NMR in scheme 6. It shows that there were no protons in polar groups such as amino or carboxylic acid, but only in hydrocarbon (C–H).

To optimize the reaction conditions, the reaction of 2-naphthol, 4-nitrobenzaldehyde and acetamide was used as a model reaction.

In order to establish the better catalytic activity of silver NPs, we have compared the reaction using other catalysts at reflux and for 30 min. The results are listed in Table 1. The problems in the reported protocols such as prolonged reaction time and poor yields prompted us to develop a new rapid method affording excellent yield using a solid phase acidic green catalyst for the synthesis of 1-amidoalkyl-2-naphtols.

To determine the optimum quantity of Ag NPs, the reaction of 2-naphthol, 4-nitrobenzaldehyde and acetamide was carried out at reflux using different quantities of Ag NPs (Table 2). Ag NPs of 0.03 g gave an excellent yield in 30 min (Table 2, entry 2).

The above reaction was also examined in various solvents (Table 3). The results indicated that different solvents affected the efficiency of the reaction. Most of these solvents required a longer time and gave moderate yields, and the best results were obtained when ethyl acetate was used as solvent (Table 3, entry 4).

To optimise the temperature in the mentioned reaction, we have carried out a model study with a 2-naphthol, 4-nitrobenzaldehyde and acetamide using 0.03 g of catalyst at various temperatures

(Table 4). Table 3 clearly demonstrates that reflux is an effective temperature in terms of reaction time and yield.

To study the scope of the reaction, a series of aldehydes, 2-naphthol and acetamide catalysed by Ag NPs as catalyst were examined. The results are shown in Table 5. In all cases, aldehydes substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave products in good yields.

The compounds **3a-i** were characterised by ^{1}H, ^{13}C-NMR and IR spectroscopy and elemental analyses.[26-31]

Compounds **3j-l** were new and their structures were deduced by elemental and spectral analysis. The mass spectrum of compound **3j** showed the molecular ion peak at 337. The ^{1}H NMR spectrum of **3j** exhibits two sharp lines at δ = 2.02 and 3.73 ppm for the protons of methyl groups. The methine proton (δ= 6.16) and NH proton couple each other and a doublet is observed for NH proton at 8.00 ppm which disappears after addition of some D_2O to the d_6-DMSO solution of **3j**. There are observed multiplets between 7.04 and 7.74 ppm which are related to aromatic protons. The ^{13}C NMR spectrum of compound **3j** shows 20 distinct signals in consistent with the proposed structure. The IR spectrum of compound **3j** also supported the suggested structure and showed absorption bonds at 3347, 3321 and 1635 cm^{-1}.

4. Conclusions

In conclusion, we have developed using Ag NPs as an inexpensive, non- volatile, non- explosive, easy to handle, non-corrosive and environmentally benign catalyst for the synthesis of

biologically active 1-amidoalkyl-2-naphtols from 2-naphthol, acetamide and various aldehyde compounds.

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Table 1 Evaluation of the activity of different catalysts for the synthesis of 1-amidoalkyl-2-naphtols

[a]Isolated yield.

Entry	Catalyst	Time /min)	Yield[a] /%
1	-	30	20
2	$Ce(SO_4)_2$	30 30	30
3	I_2	10 30	35
4	K. 10 clay	30 30	46
5	$K_5CoW_{12}O_{40}.3H_2O$	30	57
6	$FeCl_3.SiO_2$	30	60
7	$HClO_4$-SiO_2	30	80
8	$NaHSO_4.H_2O$	30	72
9	$Al(H_2PO_4)_3$	30	75
10	*p*-TSA	30	58
11	Sulfamic acid		65
12	Silica sulfuric acid		70
13	Silver NPs		98

Table 2 Optimisation amount of Ag NPs for the synthesis of 1-amidoalkyl-2-naphtols

[a]Isolated yield.

Entry	Catalyst	Time (min)	Yield[a](%)
1	0.04	30	96
2	0.03	30	98
3	0.02	30	80
4	0.01	30	60

Table 3 Effect of the solvent on the synthesis of 1-amidoalkyl-2-naphtols by Ag NPs

Entry	Solvent	Time /min	Yield[a]/%
1	$CHCl_3$	30	30
2	EtOH	30	45
3	Solvent-free	30	40
4	EtOAc	30	98

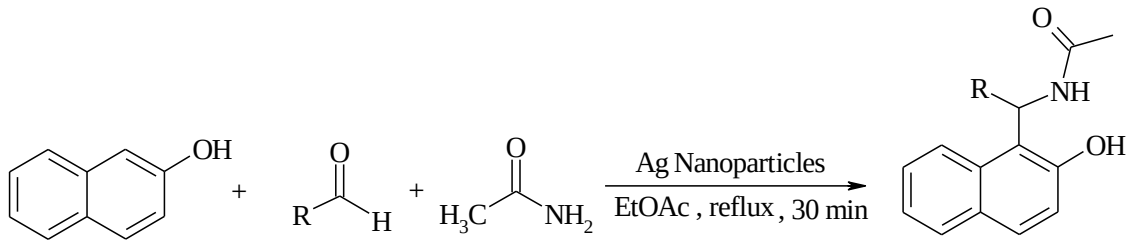
[a]Isolated yield.

Table 4 Optimisation of temperature using Ag NPs as catalyst

Entry	Temperature /°C	Time /min	Yield[a] /%
1	25	30	20
2	60	30	30
3	Reflux	30	98

[a]Isolated yield.

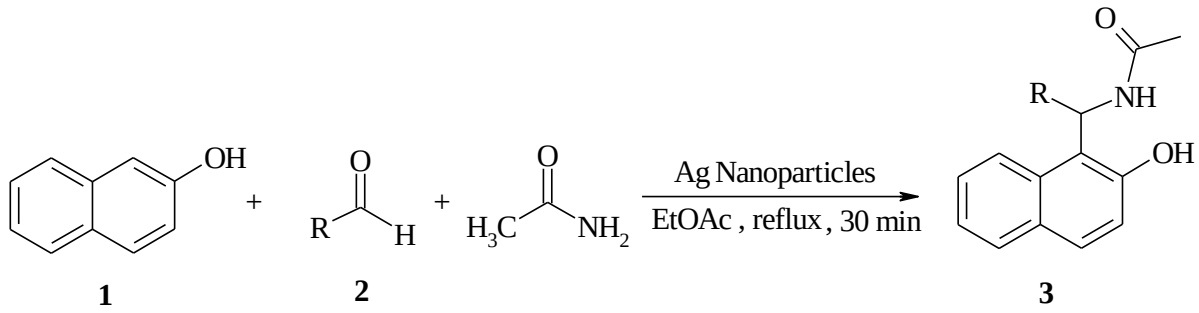
Table 5 Reaction between 2-naphthol, aldehydes and acetamide catalyzed by Ag nanoparticles (0.03 g) at reflux



1 **2** **3**

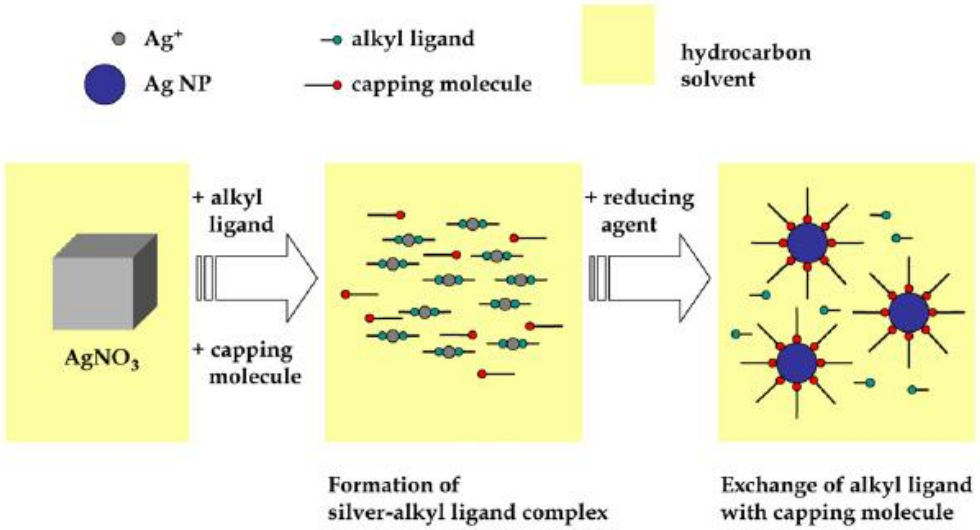
3	R	%Yield *	m.p.(°C) found	m.p.(°C) reported [Ref.]
a	2-NO_2 C_6H_4	98	260-262	263-265[26]
b	3-NO_2 C_6H_4	97	254-256	252-256[27]
c	4-NO_2 C_6H_4	98	243-245	242-243[28]
d	3-Cl C_6H_4	94	238-240	237-238[27]
e	4-ClC_6H_4	96	228-230	226-228[27]
f	2-OHC_6H_4	90	214-216	215-217[28]
g	3-CH_3O C_6H_4	92	208-210	206-208[29]
h	4-OH-3-CH_3O C_6H_3	85	213-214	212[30]
i	Me	80	211-213	212[31]
j	2-OH-3-CH_3O C_6H_3	90	157-159	-
k	4-CO_2CH_3 C_6H_4	90	220-222	-
l	4-$NHCH_3$ C_6H_4	85	121-123	-

*Yields refer to the pure isolated prodoucts

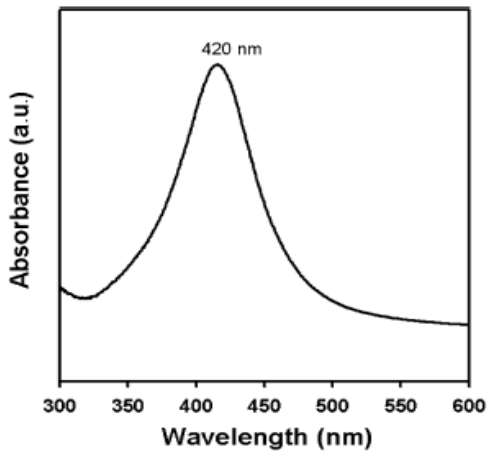


1 **2** **3**

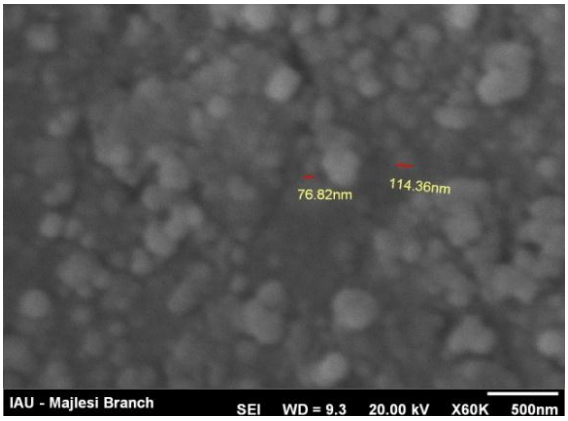
Scheme 1: Synthesis of 1-amidoalkyl-2-naphtols in the presence of silver NPs as catalyst



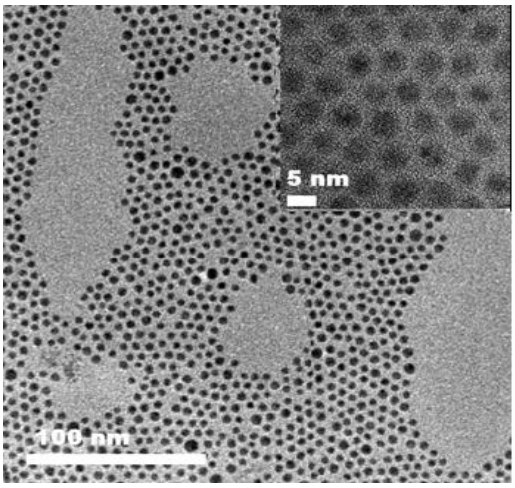
Scheme 2: Experimental schemes for direct synthesis of silver nanoparticles in fully organic phase through in situ ligand exchange



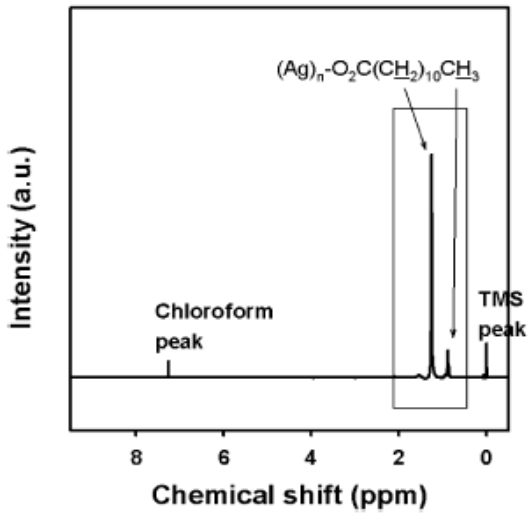
Scheme 3: UV–visible spectrum for silver nanoparticles dissolved into toluene



Scheme 4: The SEM images of silver nanoparticles



Scheme 5: The TEM images of silver nanoparticles



Scheme 6: The ^{1}H-NMR spectrum of silver nanoparticles dissolved into deuteratedchloroform