

Efficient one-pot alkylation of imines using nanosilver iodide in aqueous media

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An efficient ecofriendly method for the alkylation reaction of various imines is described by a simple one-pot reaction of aldehydes, amines and alkyl iodides in the presence of AgI nanoparticles in aqueous media. Silver iodide nanoparticles mediated an enhanced rate and facility of reaction and showed high influence in the green synthesis of some amine derivatives. Moreover, this nanoparticle increased the yields of products and decreased the reaction times in all cases. The heterogeneous mediator was fully characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and FT-IR experimental techniques.

Key Words: Imine, alkylation, nanoparticles, amine, aqueous media, heterogeneous mediator, one-pot reaction

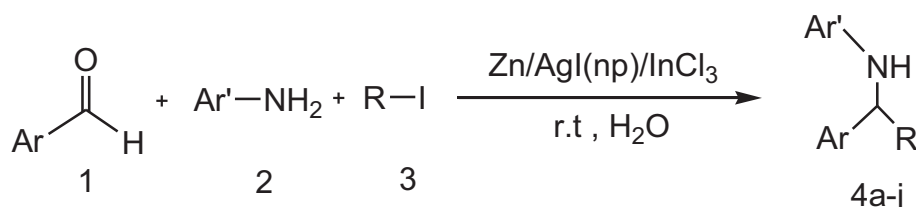
Introduction

The transformation of imine to amine is an important reaction in current organic chemistry. Amines are important building blocks for pharmaceutical and chemical production.¹⁻⁴ In recent years, there has been great interest in the development of organic reactions in aqueous media.^{5,6} The use of water as solvent in organic reactions has many advantages from both economic and environmental aspects.⁷ Preparation of alkylated amines from imines was reported by several methods. In one method aldehydes and amines were reacted in the presence

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of L-proline as organocatalyst.⁸ The other method is synthesis of secondary amine derivatives under condensation of diethyl phosphonate, amine, and aldehyde with lanthanide triflate catalysis.⁹ Chiral propargylamines also can be prepared by 1-pot 3-component reaction between an alkyne, an aldehyde, and a secondary amine at room temperature in the presence of CuBr and (R)-quinap as catalyst.¹⁰ Recently, Barbier-type alkylation reactions have been extensively studied with aldehydes, ketones, imines, acetals, and nitriles.^{11,12} The Barbier-Grignard reaction using metallic mediates and alkyl halides in water is one of the most useful and convenient methods for performing alkylation reactions. Most of the metal-mediated alkylation reactions of imines were reported using indium, silver, or zinc as mediates.^{13,14} Recently, it was reported that the combination Zn/AgI/InCl₃ was an efficient system for alkylation reaction of imines using unactivated alkyl iodides in water.¹⁵ Thus far, there has been no report of the Grignard-Barbier-type alkylation of imines using nanoparticles as mediate in aqueous media. The higher efficiency of nanoparticles as mediate in organic reactions under mild conditions, in comparison with of traditional solid state catalysts, has been demonstrated.¹⁶ Nowadays application of nanostructures is an important versatile method for the preparation of organic compounds. Recently, nanoparticles are attracting great attention since they display homogeneous-like activities due to their large surface areas relative to their bulk forms.^{17–20} It has been demonstrated to be efficient on nanoscale materials for various useful chemical transformations for the synthesis of diverse organic compounds, such as preparations of propargylamines,^{21,22} triazole derivatives,²³ quinoxalines compounds,²⁴ C-N cross coupling reactions,²⁵ alkyne-azide cycloadditions,²⁶ β -acetamido ketones/esters,²⁷ and synthesis of diaryl sulphides.²⁸

Herein, we wish to report a novel and efficient aqueous Barbier-Grignard-type alkylation of imines with alkyl iodides in a zinc-nanosilver-indium chloride system. A series of experiments were carried out in an effort to develop an improved procedure for the synthesis of secondary amine by 3-component coupling between aldehydes, amines, and alkyl iodides in aqueous media (Scheme).



Scheme. Alkylation of imines using nanosilver iodide in aqueous media.

Experimental

Chemicals were purchased from Merck in high purity. All of the materials were of commercial reagent grade. Flash-column chromatography was performed using Merck silica gel 60 with freshly distilled solvents. The NMR spectra (¹H, ¹³C) were recorded on a Bruker 400 Ultrashield spectrometer using TMS as an internal standard. The FT-IR spectrum was recorded on a Magna-IR, spectrometer 550 Nicolet in KBr pellets in the range of 400–4000 cm⁻¹. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Powder X-ray diffraction (XRD) was carried out on a Philips diffractometer of X'pert Company with monochromatized Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Microscopic morphology of the products was visualized by SEM (LEO 1455VP).

Preparation of silver iodide nanoparticle

A solution of 0.415 g of KI (25×10^{-4} mol) in 25 mL of distilled water was added dropwise to AgNO₃ solution (0.425 g, 25×10^{-4} mol in 25 mL of distilled water) under ultrasound power in the presence of 0.2 g of SDS as surfactant. The yellow as-synthesized precipitate was separated by centrifugation and washed with distilled water and ethanol to remove impurities several times and then dried

Typical procedure for zinc-silver iodide and zinc-(silver iodide nanoparticle) alkylation of imines (4a-j)

A mixture of water (10 mL), aldehyde (0.5 mmol), amine (0.6 mmol), and InCl₃ was stirred well in a round-bottomed flask for 10 min at room temperature. Then zinc (3 mmol), AgI (2 mmol), or AgI nanoparticle (0.5 mmol) and alkyl iodide (2.5 mmol) were added sequentially to the reaction system. The reaction mixture was stirred at room temperature at the times indicated in the Table. After completion of the reaction, the mixture was extracted using ether, dried over anhydrous sodium sulfate, and filtered, and the solvent was evaporated in vacuum to give the crude product. The product was separated using silica-gel column chromatography using hexane:ethyl acetate (8:1) as eluent. The identity and purity of the product were confirmed by ¹H and ¹³C-NMR spectroscopy.

N-Phenyl-(1-(p-bromophenyl)-1-cyclohexylmethyl)amine (4a)

IR (KBr, cm⁻¹): 3423 (NH), 3050, 2923, 2851, 1600, 744, 691 (CH). ¹H-NMR (400 MHz, CDCl₃) δ: d = 1.29-1.49 (m, 6H), 1.53-2.18 (m, 5H), 4.09 (d, J = 6.04 Hz, 1H), 4.12 (br s, 1H), 6.45-6.47 (d, J = 7.83 Hz, 2H), 6.61-6.65 (t, J = 7.31 Hz, 1H), 7.05-7.09 (t, 2H), 7.17-7.19 (d, 2H), 7.41-7.43 ppm (d, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: d = 147.42 (C), 141.78 (C), 131.33 (2CH), 129.11 (2CH), 120.44 (C), 128.99 (2CH), 117.25 (CH), 113.18 (2CH), 62.92 (CH), 44.81 (CH), 30.11 (CH₂), 29.35 (CH₂), 26.36 (CH₂), 26.36 (CH₂), 26.36 ppm (CH₂). UV (CHCl₃): λ_{max} (nm) = 360, 270.

N-Phenyl-(1-(p-chlorophenyl)-1-cyclohexylmethyl)amine (4b)

IR (KBr, cm⁻¹): 3424 (NH), 3050, 3020, 2852, 2926, 1600, 748, 692 (CH). ¹H-NMR (400 MHz, CDCl₃) δ: 1.26-1.53 (m 6H), 1.57-1.94 (m 5H), 4.13 (d, J = 6/03Hz 1H) 4.09 (br s, 1H), 6.42-6.51 (d, J = 7.80 Hz, 2H), 6.61-6.65 (t, J = 7.32 Hz, 1H), 7.59-7.09 (t, 2 H), 7.22-7.24 (d, 2H), 7.27-7.28 ppm (d, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: d = 147.43 (C), 141.21 (C), 132.31 (C), 129.98 (2CH), 128.57 (2CH), 128.38 (2CH), 117.21 (CH), 113.17 (2CH), 62.58 (CH), 44.84 (CH), 30.10 (CH₂), 29.35 (CH₂), 26.35 (CH₂), 26.35 (CH₂), 26.35 ppm (CH₂). UV (CHCl₃): λ_{max} (nm) = 365, 275.

N-Phenyl-(2-methyl-1-phenylpropyl)amine (4c)

IR (KBr, cm⁻¹): 3416 (NH), 3049, 3016, 2852, 2924, 1602, 747, 691 (CH). ¹H-NMR (400 MHz, CDCl₃) δ: d = 1.21-1.34 (m, 1 H), 1.38-1.48 (m, 5H), 1.53-1.74 (m, 4H), 1.87-2 (m, 1H), 2.31 (s, 3H), 4.08 (s, 1H), 4.09 (s, 1H), 6.50 (d, J = 7.61 Hz, 2H), 6.59 (t, J = 7.30 Hz, 1H), 7.02-7.09 (m, 2H), 7.11-7.27 ppm (m, 5H). ¹³C-NMR (100 MHz, CDCl₃) δ: d = 147.42 (C), 139.78 (C), 136.33 (C), 129.11 (2CH), 128.99 (2CH), 127.44 (2CH),

117.25 (CH), 113.18 (2CH), 62.92 (CH), 44.81 (CH), 30.11 (CH₂), 29.35 (CH₂), 26.36 (CH₂), 26.36 (CH₂), 26.36 (CH₂), 21.16 ppm (CH₃). UV (CHCl₃): λ_{\max} (nm) = 363, 272.

N-Phenyl-(1-phenyl-1-cyclohexylmethyl)amine (4d)

IR (KBr, cm⁻¹): 3415 (NH), 3054, 3023, 2853, 2923, 1601, 750, 698 (CH). ¹H-NMR (400 MHz, CDCl₃) δ : d = 1.11-1.21 (m, 5H), 1.46-1.56 (m, 1 H), 1.65-1.75 (m, 4H), 1.88-1.91 (m, 1H), 4.11 (d, J = 6.31 Hz, 1H), 4.13 (br s, 1H), 6.51 (d, J = 7.71 Hz, 2H), 6.60 (t, J = 7.46 Hz, 1H), 7.04-7.08 (m, 2H), 7.21-7.23 (m, 1H), 7.27-7.30 ppm (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ : d = 147.34 (C), 141.21 (C), 129.11 (2CH), 128.28 (2CH), 127.17 (2CH), 126.48 (CH), 116.21 (CH), 113.17 (2CH), 62.85 (CH), 44.84 (CH), 30.10 (CH₂), 29.35 (CH₂), 26.35 (CH₂), 26.35 (CH₂), 26.35 ppm (CH₂). UV (CHCl₃): λ_{\max} (nm) = 340, 275.

N-Phenyl-(2-methyl-1-phenylpropyl)amine (4e)

IR (KBr, cm⁻¹): 3418 (NH), 3051, 3020.66, 2852, 2924, 1601, 755, 698 (CH). ¹H-NMR (400 MHz, CDCl₃) δ : d = 0.92-0.98 (d, J = 6.80 Hz, 3H), 1-1.01 (d, J = 6.77 Hz, 3H), 1.16-1.37 (m, 1H), 4.13 (s, 1H), 4.15 (s, 1H), 6.51 (d, J = 7.61 Hz, 2H), 6.63 (t, J = 7.31 Hz, 1H), 7.06-7.10 (m, 2H), 7.22-7.32 ppm (m, 5H). ¹³C-NMR (100 MHz, CDCl₃) δ : d = 147.23 (C), 141.13 (C), 129.31 (2CH), 128.98 (2CH), 128.57 (CH), 128.38 (CH), 126.21 (CH), 117.22 (CH), 113.31 (2CH), 63.85 (CH), 34.84 (CH), 19.70 (CH₃), 18.55 ppm (CH₃). UV (CHCl₃): λ_{\max} (nm) = 365, 270.

N-(p-Chlorophenyl)-(1-phenyl-1-cyclohexylmethyl)amine (4f)

IR (KBr, cm⁻¹): 3410 (NH), 3050, 3020, 285.96, 2924, 1663, 703 (CH). ¹H-NMR (400 MHz, CDCl₃) δ : d = 1.13-1.34 (m, 5 H), 1.51-1.54 (m, 1H), 1.64-1.77 (m, 4H), 1.87-2.18 (m, 1H), 4.09 (d, J = 6.16 Hz, 1H), 4.14 (br s, 1H), 6.41 (d, J = 8.79 Hz, 2H), 6.99 (d, J = 8.79 Hz, 2H), 7.22-7.32 ppm (m, 5H). ¹³C-NMR (100 MHz, CDCl₃) δ : d = 146.29 (C), 142.10 (C), 128.84 (2CH), 128.82 (2CH), 127.17 (2CH), 126.91 (CH), 121.47 (C), 114.25 (2CH), 63.55 (CH), 44.81 (CH), 30.20 (CH₂), 29.50 (CH₂), 26.40 (CH₂), 26.35 (CH₂), 26.31 ppm (CH₂). UV (CHCl₃): λ_{\max} (nm) = 347, 275.

N-(m-Chlorophenyl)-(1-phenyl-1-cyclohexylmethyl)amine (4g)

IR (KBr, cm⁻¹): 3419 (NH), 3061, 3026, 2852, 2926, 1597, 759, 639 (CH). ¹H-NMR (400 MHz, CDCl₃) δ : 0.89-1.09 (m, 5 H), 1.17-1.26 (m, 1H), 1.56-1.66 (m, 4H), 1.75-1.86 (m, 1H), 2.13 (s, 3H), 4.08-4.23 (m, 2 H), 6.36 (d, J = 7.90 Hz, 1H), 6.48 (s, 1H), 6.56 (d, J = 7.30 Hz, 1H), 6.95 (t, J = 7.70 Hz, 1H), 7.26-7.41 ppm (m, 5H). ¹³C-NMR (100 MHz, CDCl₃) δ : 148.85 (C), 146.7 (C), 141.98 (C) 130.01 (CH), 128.30 (CH), 127.11 (2CH), 127.10 (CH), 126.96 (CH), 116.82 (CH), 112.93 (CH), 111.30 (CH), 63.26 (CH), 44.77 (CH), 30.20 (CH₂), 29.44 (CH₂), 26.83 (CH₂), 26.36 (CH₂), 26.36 ppm (CH₂). UV (CHCl₃): λ_{\max} (nm) = 365, 270. Anal. Calcd. for C₁₉H₂₂ClN: C 76.11, H 7.40, N 4.67. Found C 76.08, H 7.45, N 4.63.

N-(p-bromophenyl)-(1-phenyl-1-cyclohexylmethyl)amine (4h)

IR (KBr, cm^{-1}): 3422 (NH), 3051, 3025, 2852, 2925, 1593, 755, 701 (CH). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : d = 1.42-1.47 (m, 5 H), 1.50-1.57 (m, 1H), 1.64-1.75 (m, 4H), 1.85-1.98 (m, 1H), 4.05 (d, $J = 6.07$ Hz, 1H), 4.19 (br s, 1H), 6.36 (d, $J = 8.4$ Hz, 2H), 7.13 (d, $J = 8.8$ Hz, 2H), 7.22-7.35 ppm (m, 5H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : d = 146.66 (C), 142.15 (C), 128.90 (2CH), 128.28 (2CH), 127.15 (2CH), 126.93 (CH), 121.50 (C), 114.25 (2CH), 63.43 (CH), 44.78 (CH), 30.16 (CH_2), 29.45 (CH_2), 26.36 (CH_2), 26.32 (CH_2), 26.32 ppm (CH_2). UV (CHCl_3): λ_{max} (nm) = 335, 255. Anal. Calcd. for $\text{C}_{19}\text{H}_{22}\text{BrN}$: C 66.28, H 6.44, N 4.07. Found C 66.32, H 6.46, N 4.01.

N-(m-Chlorophenyl)-(2-methyl-1-phenylpropyl)amine (4i)

IR (KBr, cm^{-1}): 3421 (NH), 3052, 3027, 2926, 2960, 1597, 748, 697 (CH). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 1.67 (d, $J = 6.78$ Hz, 3H), 1.32 (d, $J = 6.72$ Hz, 3H), 1.01-2.05 (m, 1 H), 4.07 (d, $J = 6.16$ Hz, 1 H), 4.14 (br s, 1H), 6.43 (d, $J = 8.79$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 2H), 7.33-7.50 ppm (m, 5H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : d = 146.21 (C), 142.01 (C), 129.25 (2CH), 128.86 (2CH), 128.28 (2CH), 127.12 (CH), 121.42 (C), 114.29 (2CH), 63.91 (CH), 34.83 (CH), 19.66 (CH_3), 18.63 ppm (CH_3). UV (CHCl_3): λ_{max} (nm) = 350, 255. Anal. Calcd. for $\text{C}_{16}\text{H}_{18}\text{ClN}$: C 73.98, H 6.98, N 5.39. Found C 73.94, H 6.97, N 5.43.

N-Benzyl-(1-(p-methylphenyl)-1-cyclohexylmethyl)amine (4j)

IR (KBr, cm^{-1}): 3409 (NH), 3051, 3025, 2853, 2923, 1602, 750, 693 (CH). $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : d = 1.34-1.13 (m, 5 H), 1.39-1.70 (m, 6H), 1.96-1.98 (m, 1H), 2.37 (s, 3 H), 3.33 (d, $J = 7.12$ Hz, 1 H), 3.46 (d, $J = 13.23$ Hz, 1 H), 3.66 (d, $J = 13.5$ Hz, 1 H), 7.13-7.54 ppm (m, 9H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : d = 141.13 (C), 139.91 (C), 136.31 (C), 128.98 (2CH), 128.57 (2CH), 128.38 (2CH), 128.3 (2CH), 126.21 (CH), 67.58 (CH), 51.74 (CH_2), 44.84 (CH), 30.10 (CH_2), 29.55 (CH_2), 26.35 (CH_2), 26.35 (CH_2), 26.35 (CH_2), 21.10 ppm (CH_3). UV (CHCl_3): λ_{max} (nm) = 360, 257.

Results and discussion

Among the different metals investigated, indium, zinc, and silver were observed to be effective metals for the alkylation reactions of imines to the corresponding amines in aqueous media.¹⁵ We carried out the one-pot Barbier-Grignard-type alkylation reaction of simple imines by using $\text{Zn}/\text{AgI}(\text{np})/\text{InCl}_3$ in water. The scope and versatility of the present reaction were investigated by using various aldehydes, amines, and alkyl iodides. It was found that both primary aliphatic and aromatic amines were able to react smoothly to afford the corresponding amines in good yields. This reaction is an efficient method for alkylation of imines so that yield is up to 90%, as shown in the Table. Utilization of AgI nanoparticles increased the yield of the reaction and also decreased the time of reaction impressively. The usage of nanoparticles as mediates has a very remarkable effect on the reaction and so we can achieve even 97% yield in 9 h (entry b, Table). Nanoparticles are well dispersed in solvent and so the reactant reaches the active site by diffusion. The comparison between time of reaction in the presence of AgI nanoparticles and bulk AgI is shown in the Table.

Table. Zinc-silver iodide mediated alkylation reaction of imines in water.^c

Entry	Ar	Ar'	R	Time[h]/Yield[%] ^a	Yield [%] ^b in 24 h
a	p-BrC ₆ H ₄	C ₆ H ₅	C ₆ H ₁₁	10/95	83 ¹⁵
b	p-ClC ₆ H ₄	C ₆ H ₅	C ₆ H ₁₁	9/97	85 ¹⁵
c	p-CH ₃ C ₆ H ₄	C ₆ H ₅	C ₆ H ₁₁	10/93	82 ¹⁵
d	C ₆ H ₅	C ₆ H ₅	C ₆ H ₁₁	12/90	76 ¹⁵
e	C ₆ H ₅	C ₆ H ₅	C ₃ H ₇	16/60	43 ¹⁵
f	C ₆ H ₅	p-ClC ₆ H ₄	C ₆ H ₁₁	11/75 ^d	65 ^{d, 15}
g	C ₆ H ₅	m-ClC ₆ H ₄	C ₆ H ₁₁	13/92 ^d	78 ^d
h	C ₆ H ₅	p-BrC ₆ H ₄	C ₆ H ₁₁	14/75	60
i	C ₆ H ₅	m-ClC ₆ H ₄	C ₃ H ₇	16/62	48
j	p-CH ₃ C ₆ H ₄	CH ₂ (C ₆ H ₅)	C ₆ H ₁₁	17/72 ^{d,e}	53 ^{d,e, 15}

^a In presence of AgI nanoparticles. ^b In presence of bulk AgI. ^c Unless otherwise noted, the reaction was carried out at room temperature for 24 h. ^d By using MeOH/H₂O 1:1. ^e By using 2 equiv. of amine.

In order to investigate the morphology and particle size of AgI nanoparticles, a SEM image of AgI nanoparticles was recorded and is presented in Figure 1. These results show that spherical AgI nanoparticles were obtained from AgNO₃ and KI with particle size 45-50 nm under ultrasound power.

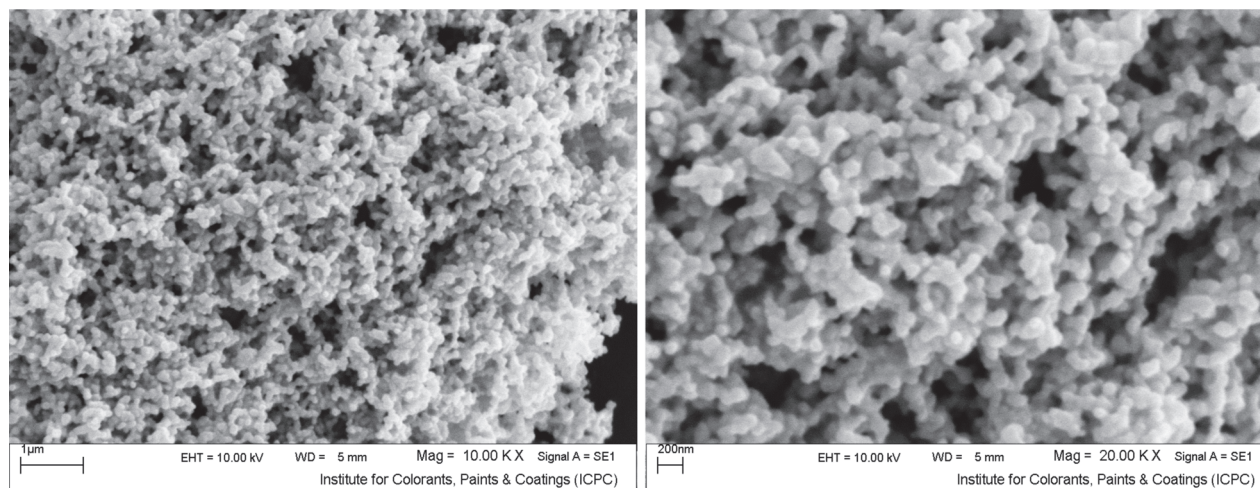
**Figure 1.** SEM images of AgI nanoparticles.

Figure 2 shows the FT-IR spectrum of AgI nanoparticles. The broad peaks at 3436 and 1628 cm⁻¹ can be attributed to the ν (OH) stretching and bending vibrations, respectively. Thus, these peaks indicate the presence of physisorbed water linked to nanoparticles.

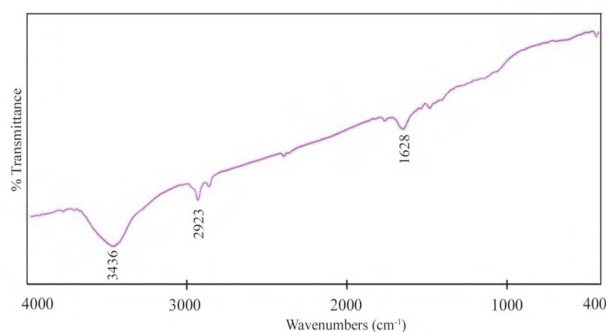


Figure 2. FT-IR spectrum of AgI nanoparticles.

As shown in Figure 2, a peak corresponding to CH₂ stretching vibration of SDS (sodium dodecyl sulfonate) at 2923 cm⁻¹ can be seen. The appearance of this peak suggests that a trace amount of SDS was coated on the surface of AgI nanoparticles.

Figure 3 shows the XRD pattern of AgI nanoparticles. All reflection peaks in Figure 1 can be readily indexed to the pure cubic phase of AgI with F-43m space group (JCDPS No. 78-0641). The crystallite size diameter (D) of the AgI nanoparticles was calculated by the Debye-Scherrer equation ($D = K\lambda/\beta\cos\theta$), where β FWHM (full-width at half-maximum or half-width) is in radians and θ is the position of the maximum of diffraction peak, K is the so-called shape factor, which usually takes a value of about 0.9, and k is the X-ray wavelength (1.5406 Å for Cu K α). Crystallite size of AgI was found to be 48 nm.

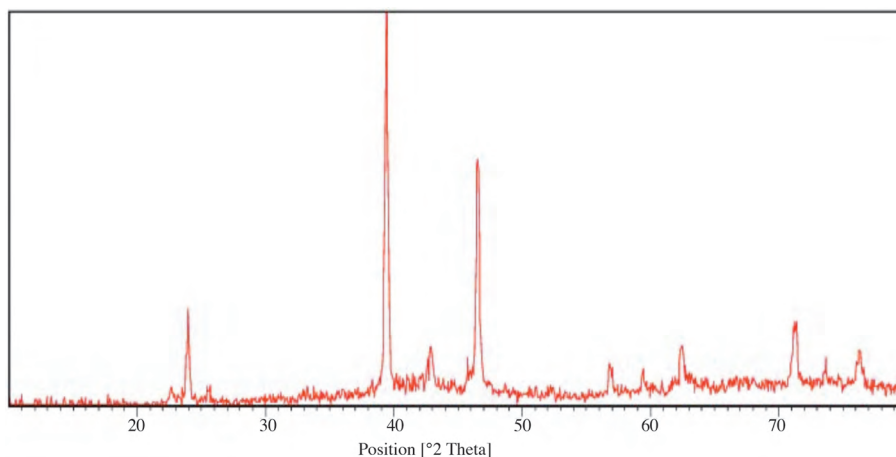


Figure 3. The XRD pattern of AgI nanoparticles.

Conclusions

An efficient, facile, and economical method for the alkylation of imines has been developed using AgI-nanoparticles as the mediator in aqueous media. The products were obtained in excellent yields and the reaction times were significantly reduced in comparison to using bulk silver iodide. The present protocol represents a simple method for C-N bond formation in order to prepare some amines derivatives in the presence of novel nanoscale materials.

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