Short communication

Ultrasound-assisted direct oxidative amidation of benzyl alcohols catalyzed by graphite oxide

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ABSTRACT

Ultrasound irradiation was successfully applied for the direct oxidative amidation of benzyl alcohols with amines into the corresponding amides using graphite oxide (GO) as an oxidative and reusable solid acid catalyst in acetonitrile as solvent at 50 °C under air atmosphere. The direct oxidative amidation of benzyl alcohols takes place under mild conditions yielding the corresponding amides in good to high yields (69–95%) and short reaction times under metal-free conditions.

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1. Introduction

The amide linkage is a key functional group in organic and biological chemistry [1–2]. Beyond traditional methods for the preparation of amides [3–4], several alternative strategies have been reported [5–6]. Various procedures have been investigated for the preparation of amide compounds, including rearrangement of aldoximes [7], transamidation of amides with amines [8], aminocarbonylation of aryl halides [9], hydration of nitriles [10] and Ugi reaction [11]. Recently, catalytic procedures using transition metal catalysts were developed for the synthesis of amides directly from alcohols and amines, as highly atom economical and environmentally benign methods [12–15]. Homogeneous [13, 15] and heterogeneous [16–18] catalysts were developed for dehydrogenative [19, 20] or oxidative amidation [13, 21–23]. In this context, ruthenium complexes and especially NHC-compounds have been applied for the dehydrogenative amidation of alcohols, aldehydes, and esters in the presence of an excess of a strong base (10–40 mol% of NaH or KO-t-Bu) [16]. For example, dehydrogenative coupling reaction between alcohols and amines using 1 mol% of [Ru(py-NHC)(CO)$_2$Br$_2$] catalyst in presence of 5 mol% of NaH at 110 °C in toluene gave the corresponding amides in 45–92% yield after 24 h [24]. Recently, a tandem process for the oxidative amidation of benzyl alcohols with amine hydrochloride salts using Fe(NO$_3$)$_3$ (5 mol%) as catalyst, air and aqueous tert-butyl hydroperoxide (TBHP) (1.1 eq.) as oxidants in acetonitrile at 60 °C for 16 h has been successfully applied for the synthesis of a wide range of benzamides in 45–81% yield [15]. A new domino reaction has been proposed for the preparation of benzamides (40–89%) from direct oxidative amidation of benzyl alcohols in the presence of a cheap copper oxide (2 mol%), CaCO$_3$ (1 eq.), and TBHP (5.5 eq.) as an oxidant in acetonitrile at 80 °C for 4 h [13]. Superparamagnetic Fe$_3$O$_4$@EDTA-Cu(II) nanoparticles were also applied as a catalyst for the tandem transformation of benzyl alcohols and amine hydrochloride salts into the corresponding amides using TBHP (4 eq.) as an oxidant in acetonitrile at 80 °C for 4 h [18]. In another report, the synthesis of amides was described from the reaction of alcohols and amines through a tandem oxidation process that uses molecular oxygen as a terminal oxidant and carbon-black-stabilized polymer-incarcerated gold (PICB-Au) or gold/cobalt (PICB-Au/Co) nanoparticles as a heterogeneous catalyst in the presence of NaOH for 12 h [25].

Application of microwaves for the synthesis of amides was reported in several reports [26, 27]. The effect of ultrasound in chemical reactions is also known and well documented in the literature [28]. However, up to date, there are only a few examples on the amidation reaction using ultrasonic irradiation [29, 30]. To the best of our knowledge, there is still no report on using ultrasonic irradiation on the direct oxidative amidation of benzyl alcohols.

Graphite oxide (GO) has been investigated as a useful heterogeneous catalyst for certain organic transformations [31–35]. For example, GO was used as a highly efficient reagent for the preparation of aldehydes *via* the oxidation of various alcohols under ultrasonic irradiation [33]. The potential of Oxone/iron(II)sulfate/GO system for the efficient oxidation of alcohols into the corresponding carboxylic acids or ketones under ultrasonic irradiation in water was also demonstrated [34]. More recently, the sonochemical method was applied for the direct oxidative formation of esters from the reaction between aldehydes and alcohols using GO and Oxone in an alcoholic solvent [35]. We have shown the efficiency of reduced graphene oxide (rGO-SO$_3$H) as a reusable and solid acid catalyst for amidation of carboxylic acids with amines using ultrasonic irradiation [36]. In continuation of our efforts on the use of GO for organic transformations, we report herein a simple ultrasonic procedure for the direct oxidative amidation of benzyl alcohols with amines into the corresponding amides in the presence of GO as an oxidative and reusable solid acid catalyst in acetonitrile as solvent at 50 °C (Scheme 1).

2. Experimental section

Ultrasonic irradiation was accomplished with an Elmasonic P ultrasonic cleaning unit (bath ultrasonic) with a frequency of 37 kHz and 100% output power. IR spectra were recorded from KBr disks using a Bruker Vector 22 FT-IR spectrometer. GC–MS analysis was performed on a FISON GC 8000 series TRIO 1000 gas chromatograph equipped with a capillary column CP Sil.5 CB, 60 m × 0.25 mm i.d. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 500, 300, 125 and 75 MHz spectrometers using tetramethylsilane as internal standard. Melting point was determined in evacuated capillaries with a Buchi B-545 apparatus. Elemental analysis was performed on a ThermoFinigan Flash EA 1112 series elemental analyser.

2.1. Synthesis of GO

GO was synthesized according to a previously reported procedure and was characterized using powder XRD, UV–Vis spectroscopy, and FT-IR spectroscopy to establish its authenticity [33].

2.2. Typical procedure for the direct oxidative amidation of benzyl alcohols with amines under ultrasonication

0.15 g of GO was added to a mixture of benzyl alcohol (1 mmol) and amine (1 mmol) in 4 mL of acetonitrile. The resulting mixture was sonicated in an Elmasonic P ultrasonic cleaning unit (ultrasonic bath) with a frequency of 37 kHz and 100% output power at 50 °C under air atmosphere for the time indicated in Table 2. The resulting mixture was filtered for catalyst separation then water was added and the mixture was extracted with ethyl acetate. The organic layer was dried over Na$_2$SO$_4$, filtered and evaporated under reduced pressure. Purification was achieved by column chromatography with silica gel as support using *n*-hexane. The spectroscopic data of the obtained amides were compared with authentic samples.
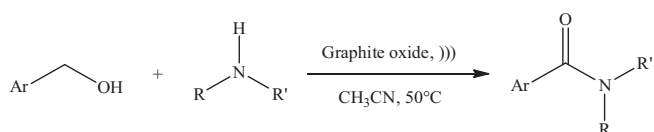
Scheme 1. Direct sonochemical oxidative amidation of benzyl alcohols with amines into the corresponding amides using GO catalyst.

4-(tert-Butyl)-N-(2,5-dimethylphenyl)benzamide (entry 16, Table 2)

Pink oil, TLC R_f = 0.50 (ethyl acetate/*n*-hexane, 1:5); IR (KBr) v = 3433, 1641, 1552, 1099, 802 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ = 1.49 (s, 9H, CH$_3$), 2.24 (s, 3H, CH$_3$), 2.40 (s, 3H, CH$_3$), 6.61 (s, 1H, CH Arom), 6.70 (d, J = 7.5 Hz, 1H, CH Arom), 7.08 (d, J = 7.5 Hz, 1H, CH Arom), 7.41 (d, J = 8.5 Hz, 2H, CH Arom), 7.52 (d, J = 8.5 Hz, 2H, CH Arom), 9.35 (s, 1H, NH); ^{13}C NMR (125 MHz, CDCl$_3$) δ = 17.38, 21.60, 31.94, 35.04, 116.56, 120.10, 120.18, 125.89, 127.42, 130.86, 137.05, 138.66, 144.72, 150.94; MS (EI) (70 eV), m/z (%): 177 (30) [MH-(2,5-dimethylphenyl)]$^+$, 162 (27), 147 (100) [M-H-4-(*tert*-butyl)-phenyl]$^+$, 134 (52), 120 (92), 105 (12), 91 (70), 77 (25), 56 (55).

4-Hydroxy-3-methoxy-N,N-diphenylbenzamide (entry 19, Table 2)

Yellow oil, TLC R_f = 0.57 (ethyl acetate/*n*-hexane, 1:2); IR (KBr) v = 3509, 1597, 1264, 806, 560 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ = 3.95 (s, 3H, CH$_3$), 6.98 (m, 7H, CH Arom), 7.14 (m, 3H, CH Arom), 7.33 (m, 3H, CH Arom), 9.35 (s, 1H, OH); ^{13}C NMR (125 MHz, CDCl$_3$) δ = 56.35, 110.40, 114.72, 115.73, 118.27, 120.68, 121.44, 129.78, 133.40, 143.59, 145.72, 147.11; MS (EI) (70 eV), m/z (%): 305 (100) [MH-CH$_3$]$^+$, 290 (20) [MH$_2$-OCH$_3$]$^+$, 244 (7), 196 (7) [M-4-hydroxy-3-methoxyphenyl]$^+$, 180 (50), 165 (10) [M-diphenyl]$^+$, 151 (10) [M-*N,N*-diphenyl]$^+$, 123 (10), 115 (10), 97 (10), 77 (20).

4-Hydroxy-N-(4-hydroxyphenyl)-3-methoxybenzamide (entry 20, Table 2)

Pink solid, TLC R_f = 0.10 (ethyl acetate/*n*-hexane, 1:2); Mp. = 102 °C; IR (KBr) v = 3434, 1621, 1509, 1236, 1096, 967, 592 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.74 (s, 3H, CH$_3$), 4.98 (s, 1H, OH), 6.46 (m, 5H, CH Arom), 6.69 (d, J = 7.9 Hz, 1H, CH Arom), 6.87 (s, 1H, CH Arom), 8.32 (s, 1H, OH), 8.75 (s, 1H, NH); ^{13}C NMR (75 MHz, DMSO-d_6) δ = 55.51, 111.04, 115.05, 115.29, 115.57, 119.11, 133.49, 140.65, 145.29, 147.36, 148.27; MS (EI) (70 eV), m/z (%): 166 (8) [M-4-hydroxyphenyl]$^+$, 151 (8), 138 (8) [MH$_2$-(4-hydroxy-3-methoxyphenyl)]$^+$, 97 (23), 83 (84), 77 (10), 70 (34), 67 (85), 55 (100), 41 (94); Anal. calcd. for C$_{14}$H$_{13}$NO$_4$: C, 64.86; H, 5.05; N, 5.40%. Found: C, 64.01; H, 5.18; N, 5.22%.

3. Results and discussion

The synthesis of *N*-benzylbenzamide was chosen as the model reaction to optimize the reaction conditions. The results of the direct oxidative amidation of benzyl alcohol (1 mmol) with benzyl amine (1 mmol) under various conditions are summarized in Table 1. The reaction of benzyl alcohol with benzyl amine in absence of catalyst at room temperature gave only the starting materials after 48 h (entry 1, Table 1). When the amidation of benzyl alcohol with benzyl amine was carried out in presence of 0.15 g of GO in acetonitrile, the corresponding amide was isolated in low yield (12%) after 48 h at room temperature (entry 2, Table 1). Increasing the reaction temperature (reflux conditions) did not impact significantly the reaction yield (entry 3, Table 1). Next, we examined the effect of ultrasound irradiation on this chemical transformation. Direct sonication of a mixture of benzyl alcohol, benzylamine and GO (0.15 g) in an Elmasonic P ultrasonic cleaning unit (ultrasonic bath) with a frequency of 37 kHz and 100% output at room temperature under air atmosphere afforded *N*-benzylbenzamide in 64% yield after 120 min (entry 4, Table 2). It should be noted that, under these experimental conditions, the formation of benzaldehyde from oxidation of benzyl alcohol after 15 min was observed by GC and thin-layer chromatography (TLC) analyses. Increasing the temperature to 50 °C led to a significant increase of the reaction yield to 87% after 90 min (entry 5, Table 1). The solvent seems to play a major role on the reaction yield.