



Ultrasound assisted direct oxidative esterification of aldehydes and alcohols using graphite oxide and Oxone



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ABSTRACT

A sonochemical procedure for direct oxidative esterification of aldehydes and alcohols using graphite oxide and Oxone in an alcoholic solvent is described. Mild reaction conditions, short reaction times, cost-effectiveness, and facile isolation of the products make the present system as a practical method.

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1. Introduction

Ester groups are among the most important and abundant functional groups in chemistry and are used in medicine, biology, chemistry, industry, fine chemicals, natural products, and polymers [1,2]. The traditional esterification method is accessed by a two-step procedure that involves the stoichiometric activation of a carboxylic acid as an anhydride, acyl halide or activated ester followed by subsequent nucleophilic substitution with alcohols. For example, HfCl₄, ZrCl₄, ZrOCl₂ and HfOCl₂ were applied for the direct ester condensation using equimolar amounts of carboxylic acids and alcohols [3,4].

Aldehydes are bulk scale raw chemicals in industry and esterification of readily available aldehydes with alcohols is an attractive alternative. Indeed, it is often required direct conversion of aldehydes or alcohols into esters during various stages in the synthesis of different natural products [1,2]. Several reagents and catalysts have been reported for the direct oxidative esterification of aldehydes [5–16]. For example, iodine and sodium nitrite [5], bis(pyridine)iodonium tetrafluoroborate [6], *N*-bromosuccinimide-pyridine [7], methyltrioxorhenium–H₂O₂ [8], Cu(ClO₄)₂–InBr₃–TBHP [9], CuF₂–TBHP [10], and styrene–divinyl benzene copolymer supported palladium catalyst [11] have been investigated for this

chemical transformation. Recently, Delany et al. demonstrated the oxidative esterification of aldehydes with alcohols catalyzed by *N*-heterocyclic carbenes in the presence of 110 mol% of DBU after 12–92 h [12].

Furthermore, the direct transformation of alcohols to esters constitutes a more sustainable alternative, which does not make use of the corresponding acid derivatives. Indeed, different conditions and methods have been investigated for the synthesis of esters from alcohols that are based on precious metals such as palladium [17], gold [18], ruthenium [19], and iridium [20] or catalyst based on bio-relevant metals such as cobalt [21], copper [22], and the use of heterogeneous catalysts such as gold [23], Co₃O₄ [24], and Au/PCPs [25]. However, some of these protocols suffer from numerous drawbacks such as the use of large amounts of toxic reagents, high temperature, long reaction times, inert atmosphere, co-catalyst, etc., which renders these methods expensive and environmentally unsafe. The various catalysts and experimental conditions used are summarized in Table 1. Thus, further efforts are necessary for the direct synthesis of esters from aldehydes and alcohols.

Graphite oxide (GO) [26], a readily available and inexpensive material, has been utilized as a heterogeneous catalyst for various organic transformations [27–29]. Recently, we have demonstrated that graphite oxide can be applied for the synthesis of aldehydes or ketones via the oxidation of various alcohols using ultrasonic irradiation [30].

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Table 1
Various catalysts and conditions for esterification of aldehydes and alcohols.

Substrate	Catalyst and conditions	Time (h)	Yield (%)	Refs.
Aromatic aldehydes	I ₂ (1 mmol), NaNO ₂ (1 mmol), 70 °C	14–36	7–97	[5]
Aliphatic and aromatic aldehydes	Cu(ClO ₄) ₂ (5 mol%)-InBr ₃ (5 mol%)-TBHP (1.1 mmol), 100 °C	16	42–91	[9]
Aromatic aldehydes	CuF ₂ (0.05 mmol)-TBHP (6 mmol), DMSO/H ₂ O, 120 °C	12	44–85	[10]
Aromatic aldehydes	NHC (15 mol%), DBU (110 mol%), THF, 25 °C	0.5–92	15–94	[12]
Aliphatic and aromatic aldehydes	Oxone (1 mmol), 50 °C	18	9–98	[14]
Aliphatic and aromatic aldehydes	Pd(OAc) ₂ (2.5 mol%), XPhos (5 mol%), K ₂ CO ₃ (0.2 mmol), CH ₃ OH/acetone, N ₂ , 50 °C	2–24	17–86	[16]
Aliphatic and aromatic aldehydes	Ru(PPh ₃) ₃ (CO)H ₂ (5 mol%), Xantphos (5 mol%), CH ₃ OH/Toluene, reflux	4	76–100	[19]
Benzyl alcohols	KI (0.2 mmol), TBHP (3 mmol), CH ₃ OH, 60 °C	24	45–71	[13]
Benzyl alcohols	Pd(OAc) ₂ (5 mol%), Na ₂ CO ₃ (2 mmol), PMHS (0.1 mmol), CH ₃ OH, 40 °C	24	58–95	[17]
Aliphatic and aromatic alcohols	PI–Au (1 mol%), K ₂ CO ₃ (0.5 mmol), O ₂ (1 atm.), CH ₃ OH/H ₂ O, 25 °C	24	10–92	[18]
Aliphatic and aromatic alcohols	Ru(PPh ₃) ₃ (CO)H ₂ (5 mol%), Xantphos (5 mol%), CH ₃ OH/Toluene, reflux	24–48	70–76	[19]
Aliphatic and aromatic alcohols	[Cp*IrCl ₂] ₂ (2 mol%), MAE (6 mol%), Cs ₂ CO ₃ (10 mol%), acetone, 25 °C	24	23–92	[20]
Benzyl alcohols	CuI (20 mol%), DTBP (4 mmol), 1,3-diketimine (nacac) ligand, DMF, 90 °C	4	71–91	[22]



Scheme 1. Sonochemical direct oxidative esterification of aldehydes and benzyl alcohols using GO/Oxone in alcoholic solvent.

The effect of ultrasound in chemical reactions is known [31,32]. Moreover, the application and efficiency of ultrasound in oxidation of alcohols have been reported [33–36]. For example, Mills and co-workers showed that the initial rate of oxidation of alcohols to their corresponding ketones with NaBrO₃, mediated by RuO₄ in an aqueous CCl₄, was greater with ultrasonic irradiation than with stirring alone [33]. The oxidation of alcohols into respective aldehydes and ketones by Ni(NO₃)₂·6H₂O/I₂/water system under ultrasonic irradiation has been demonstrated [34].

Several groups have utilized Oxone (potassium hydrogen monoperoxysulfate) as an effective oxidant for numerous organic transformations [37,38]. Parida and co-workers have reported the oxidation of primary and secondary alcohols into their corresponding oxidized products using 2–6 equivalents of Oxone [37]. Esterification of heterocyclic aldehydes has been investigated by Mineno and co-workers using Oxone in the presence of In(OTf)₃ [38]. More recently, we have reported the use of Oxone/iron(II)sulfate/GO as a highly efficient system for the oxidation of alcohols to the corresponding carboxylic acid or ketone compounds under ultrasonic irradiation in water [39]. We have demonstrated that GO most likely participates in the oxidation process through the generation of sulfate and hydroxyl radicals or as an oxidant itself. In continuation of our efforts on the use of graphite oxide as an effective oxidant [29,30,39], we report herein a new and simple method for direct oxidative esterification of various aromatic aldehydes and alcohols using GO/Oxone in an alcoholic solvent under ultrasonic irradiation (Scheme 1).

2. Experimental section

2.1. Typical procedure for the oxidative esterification of aldehydes

To a solution of aldehyde (1 mmol) in 4 mL of methanol was added Oxone (1 mmol) and GO (0.2 g). The resulting mixture was sonicated with an Elmasonic P ultrasonic cleaning unit (ultrasonic bath) with a frequency of 37 kHz and 100% output power at 60 °C for the time indicated in Table 3. The mixture was filtered through a sintered funnel and extracted with ethyl acetate (EtOAc). The organic layer was dried over Na₂SO₄, filtered and evaporated under reduced pressure. Purification was achieved by column chromatography using *n*-hexane/EtOAc: 100/3 as eluent. The spectroscopic data of the obtained acids were compared with authentic samples [5,15,40,41].

2.2. Typical procedure for the oxidative esterification of benzyl alcohols

To a solution of alcohol (1 mmol) in 2 mL of toluene was added GO (0.3 g). 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 80 °C for the time indicated in Table 4. Then Oxone (1 mmol) and 2 mL of an alcoholic solvent was added in the reaction medium and the resulting mixture was irradiated for the time indicated in Table 4. The mixture was filtered through a sintered funnel and evaporated under reduced pressure, and extracted with ethyl acetate. The organic layer was dried over Na₂SO₄, filtered and evaporated under reduced pressure. Purification was achieved by column chromatography using *n*-hexane/EtOAc: 100/3 as eluent. The spectroscopic data of the obtained esters were compared with authentic samples [5,40,42,43]. Spectroscopic data for methyl 3,4-dichlorobenzoate (entry 9, Table 4): Pale yellow, M.P. 44.7 °C; IR (KBr) ν = 3089, 3022, 2958, 1729, 1589, 1435, 1378, 1301, 1110, 757 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ = 3.94 (s, 3H, CH₃), 7.53 (d, *J* = 8.3 Hz, 1H, CH Arom), 7.87 (dd, *J* = 8.3, 1.9 Hz, 1H, CH Arom), 8.13 (d, *J* = 1.9 Hz, 1H, CH Arom); ¹³C NMR (75 MHz, CDCl₃) δ = 52.54, 128.63, 129.94, 130.52, 131.53, 132.92, 137.56, 165.21; MS (EI) (70 eV), *m/z* (%): 208 (5) [M+4]⁺, 206 (31) [M+2]⁺, 204 (50) [M]⁺, 177 (10), 175 (62), 173 (100), 145 (30), 109 (20), 74 (18).

3. Results and discussion

Initially, we screened the oxidative esterification of 4-nitrobenzaldehyde (1 mmol) in the presence of GO/Oxone in methanol under different conditions. The results are summarized in Table 2. First, the oxidative esterification of 4-nitrobenzaldehyde (1 mmol) in the presence of Oxone (2 mmol) without GO at reflux of methanol afforded the corresponding ester in 80% yield after 7.5 h (entry 1, Table 2). When the oxidation of 4-nitrobenzaldehyde was performed in the presence of 0.2 g of GO and Oxone (2 mmol) in methanol, the corresponding ester methyl 4-nitrobenzoate was obtained in 70% yield after 90 min using an ultrasonic homogenizer (Bandelin Sonopuls HD 3100) with probe model MS 73 at 100% power (entry 2, Table 2). The oxidative esterification of 4-nitrobenzaldehyde in the presence of 0.2 g of GO and Oxone (1 mmol) in reflux of methanol gave methyl 4-nitrobenzoate in 70% yield after 4 h (entry 3, Table 2). Finally, this reaction was carried out in the presence of 0.2 g of GO and 1 mmol of Oxone in an Elmasonic P ultrasonic cleaning unit (ultrasonic bath) with a frequency of 37 kHz and 100% output power at 60 °C. A rise in the yield and a decrease in the reaction time were observed; methyl 4-nitrobenzoate was isolated in 95% yield only after 15 min (entry 4, Table 2). The comparison of entries 3 and 4 clearly indicates that

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