



Original article

Graphite oxide-catalyzed acetylation of alcohols and phenols

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ABSTRACT

Graphite oxide (GO) was used as a catalyst for the reactions of alcohols and phenols with acetic anhydride. The acetates of primary and secondary alcohols were prepared in good to excellent yields in short reaction time under mild conditions. Electron deficient phenols could be converted to the corresponding acetates steadily. As an efficient catalyst, GO is easily available, cheap, moderately toxic and weakly acidic.

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1. Introduction

As high production-volume (HPV) chemicals in industry, esters have been used extensively for the production of paints, inks, adhesives, polyesters, drugs, agrochemicals, flavoring agents and fragrances [1]. Esters are generally prepared by the acylation of alcohols with acyl halides, anhydrides, carboxylic acids, esters, etc. In addition, the reactions of carboxylic acids with diazomethane, alkyl halides, other electrophiles such as *tert*-butyl acetoacetate, dimethyl sulfate and methyl trichloroacetate are also common esterification methods [1,2]. Among these methods, acylation with anhydrides is facile and widely used in organic synthesis and manufacturing of pharmaceuticals [1]. Various catalysts, such as poly(*N*-vinylimidazole), *p*-toluenesulfonyl chloride, V(HSO₄)₃ and immobilized cobalt(II), have been employed for acylation with anhydrides [3–6].

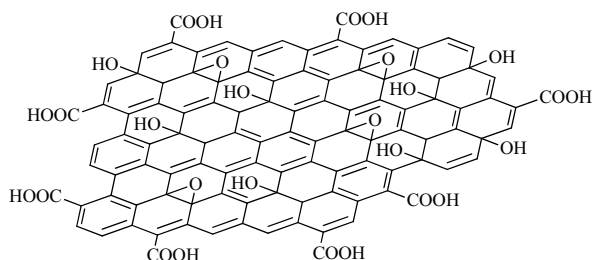
Graphite oxide (GO) has attracted much attention recently because its exfoliated single layered structure (graphene oxide) has been intensively exploited in nanomaterials as a precursor of graphene (or reduced graphene oxide) [7]. GO is generally prepared by treating graphite with strongly oxidative reagents, such as KMnO₄ and KClO₃ [8,9]. It is an amorphous, nonstoichiometric, hygroscopic, moderately toxic and weakly acidic solid. The

precise structure of GO is ambiguous up to now. It is generally thought that the continuous aromatic lattice of graphite is interrupted by various oxygen-containing functional groups, such as hydroxyls, carbonyls, epoxides and carboxyls, and all these groups are introduced to the surface or the edge of the basal plane of graphene oxide under the harsh oxidative conditions. One of the proposed models for the structure of graphene oxide is shown in Scheme 1 [9].

Recently, GO has emerged as efficient catalysts in various organic transformations [10,11]. As a carbocatalyst for redox reactions, it catalyzed the oxidation of alcohols by air [12], the selective oxidation of thiols to disulfides and sulfides to sulfoxides [13], the one-pot base-free synthesis of amides from aromatic aldehydes and secondary amines [14]. As an acid catalyst, GO could catalyze the room temperature ring opening of epoxides with alcohols [15], the one-pot conversion of carbohydrates into 5-ethoxymethylfurfural [16], the production of bio-additives from glycerol esterification [17], aza-Michael addition of amines to activated alkenes [18], the condensation of 4-hydroxycoumarin and aryl glyoxals in the synthesis of new dicoumarols [19]. Moreover, Loh *et al.* explored a GO-catalyzed carbon-carbon or/and carbon-heteroatom bond formation strategy to functionalize primary amines in tandem to produce a series of valuable products [20]. We also disclosed that GO could serve as a catalyst for esterification and transesterification [21], tetrahydropyranylation/depyranylation of alcohols and phenols [22], and the deprotection of Boc-protected alcohols and phenols [23]. GO could act as a weak solid acid to protonate the carbonyls in carboxylic acids or esters

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Scheme 1. Simplified structure model of graphene oxide.

and facilitate the nucleophilic substitution with alcohols. As a continuation of our research work, we herein wish to report that acetic anhydride can be activated by GO and react with alcohols and phenols to yield the corresponding acetates efficiently.

2. Experimental

Reagents and apparatus: Graphite powder (synthetic, 99.99%) was purchased from Tainjin Huabei Reagent Co., of China. KMnO_4 , NaNO_3 , 98% H_2SO_4 , 36%–38% HCl and 30% H_2O_2 were received as guaranteed reagents and used without further purification. All the other reagents were received as analytical reagents and used without further purification. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were performed on a Bruker Avance III (400 MHz) spectrometer using CDCl_3 as a solvent and TMS as an internal standard, chemical shifts were given in ppm. FT-IR spectroscopy was performed using a Bruker ALPHA spectrophotometer. Powder XRD was performed on a BDX-3300 X-ray diffractometer at 40 kV and 20 mA with 2θ ranging from 10° to 40° using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm). XPS spectrum was recorded using an XPS-PHI5000VersaProbe and AES-PHI670xi Scanning Auger Nanoprobe instrument with a monochromated $\text{Al K}\alpha$ radiation ($h\nu = 1486.6$ eV).

Preparation of GO: A 250 mL three-necked round-bottom flask equipped with a mechanical stirrer was charged with graphite powder (3.0 g), NaNO_3 (1.5 g) in an ice bath. Concentrated H_2SO_4 (69 mL) was added slowly into the mixture. Then KMnO_4 (9.0 g) was added in portions under stirring to prevent the temperature from exceeding 20°C . The reaction mixture was stirred at 35°C for 7 h. After being cooled to room temperature, additional KMnO_4 (9.0 g) was added slowly in portions into the mixture, then the reaction mixture was stirred at 35°C for 12 h. After the flask was cooled to room temperature, the resulted suspension was poured into 420 mL of ice-cold deionized water and 3 mL of 30% H_2O_2 was added. Then the mixture was filtered and the isolated solid was washed with 200 mL of 30% HCl , 200 mL of deionized water and filtered in succession five times. Then washing with water and filtering was repeated five times until the pH value of the filtrate was 6–7. The solid was dried in a desiccator in the presence of P_2O_5 under vacuum until its weight was constant to afford GO as a dark brown powder.

General procedure for GO-catalyzed acetylation of alcohols and phenols: To a solution of alcohols or phenols (3 mmol) and Ac_2O (4.5 mmol; 9 mmol for dihydroxybenzenes) in CH_3CN or CH_2Cl_2 (2 mL) in a round-bottom flask was added GO (5 wt% of alcohols or phenols). The mixture was stirred at 20°C and the progress of the reaction was monitored by thin layer chromatography (TLC) analysis. After the completion of the reaction, the catalyst was filtered and washed with ethyl acetate (20 mL \times 2). The filtrate was combined and washed with 15 mL of saturated sodium carbonate. The organic phase was dried over Na_2SO_4 and evaporated in vacuo to obtain the desired products.

3. Results and discussion

GO was prepared by the improved Hummers method with a combination of KMnO_4 , NaNO_3 and H_2SO_4 [24]. As-prepared GO was characterized by IR, XRD and XPS. IR spectra showed the peaks of the oxygen-containing functional groups (Fig. S1 in Supporting information, 3400 cm^{-1} for O–H, 1739 cm^{-1} for C=O, 1227 cm^{-1} for epoxy C–O, 1056 cm^{-1} for C–O). XRD pattern revealed a broad peak centered at 11.46, which is characteristic for GO (Fig. S2 in Supporting information). XPS analysis indicated that a large amount of oxygen-containing functional groups were incorporated during the harsh oxidation process (Fig. S3 in Supporting information).

We then examined the reaction of alcohols with acetic anhydride in the presence of GO. First, we tried several solvents for the acetylation of 2-phenylethanol and found that acetonitrile or dichloromethane was best; which could produce the corresponding ester in a yield of 94% (Table 1). Thus acetonitrile or dichloromethane was used as the solvent for all reactions. As shown in Table 2, the reaction of 2-phenylethanol with acetic anhydride was accelerated by GO remarkably. The reaction was completed in 5 min (entry 1, Table 2), while the product was hardly detected by ^1H NMR in the reaction without GO (entry 8, Table 1). Other primary alcohols, such as benzyl alcohol and 1-dodecanol, were also converted to their acetates in excellent yields under similar conditions (entries 2 and 3, Table 2). In the case of cinnamic alcohol, **2d** was obtained in a yield of 67%. Some undesired side reactions occurred. We attempted to identify the by-products, but they were difficult to isolate by column chromatography (entry 4, Table 2). When the hydroxy groups in the substrates are more sterically hindered, such as cyclohexanol, 4-methylcyclohexanol and 2-octanol, the reaction was relatively slow. It needed longer reaction time (50 min, 80 min and 18 min) to convert these alcohols completely, but good yields of 77%, 87% and 82% still could be achieved, respectively (entries 5, 6 and 7, Table 2). In the case of tertiary alcohol 1-ethynyl-1-cyclohexanol, the reaction seemed more difficult and 1-ethynyl-1-cyclohexanol was acetylated in a yield of 40% in 1440 min (entry 8, Table 2). Phenol was efficiently transformed to its acetate in short reaction time (entry 9, Table 2). As for substituted phenols with electron donating or electron withdrawing groups, such as catechol, hydroquinone, *p*-acetylphenol, and *p*-nitrophenol (entries 10 to 13, Table 2), the corresponding acetates were prepared in excellent yields. Even a sterically hindered phenol could be converted to its acetate in a yield of 77% in 70 min (entry 14, Table 2). When GO was used as the catalyst, it needed 4.5 mmol of acetic anhydride to react with 3 mmol of alcohols or phenols. While other catalysts, such as *p*-toluenesulfonyl chloride [4] and heterogeneous cobalt(II) Salen [6],

Table 1
Optimization of the reaction conditions^a

Entry	Catalyst	Temperature ($^\circ\text{C}$)	Solvent	Time	Yield (%)
1	GO	20	H_2O	1 h	0 ^b
2	GO	20	EtOAc	1.5 h	0 ^b
3	GO	20	DMF	3.5 h	0 ^b
4	GO	20	THF	3.5 h	89
5	GO	20	CH_3CN	5 min	94
6	GO	20	CH_2Cl_2	5 min	94
7	GO	20	Cyclohexane	3 h	92
8	–	20	CH_3CN	5 min	0 ^b

^a Reaction conditions: 2-phenylethanol **1a** (3 mmol), Ac_2O (4.5 mmol), GO (5 wt% of **1a**).

^b Not react according to NMR.

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