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Graphite oxide: an efficient reagent for oxidation of alcohols under sonication

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ABSTRACT

Graphite oxide (GO) was used as an effective oxidizing agent for the synthesis of aldehydes and ketones from various alcohols under ultrasonic irradiation. Under optimized conditions, quantitative yields of the products were obtained. Compared to other reagents used for the same chemical transformation, GO displays several advantages, including low cost, ease of synthesis, and high stability to ambient conditions.

Modified graphite, in particular graphite oxide (GO), which is prepared by exhaustive oxidation of graphite has been explored as a heterogeneous catalyst for various organic transformations.[1,2] Vijay Kumar et al. reported the Friedel–Crafts addition of indoles to α,β-unsaturated ketones and nitrostyrenes using graphite oxide as the catalyst.[2a] Recently, graphene oxide (the exfoliated counterpart of GO) was applied for the oxidation of alcohols and alkenes, and the hydration of various alkynes into their respective aldehydes and ketones in moderate to high yields. The reactions proceeded under relatively mild conditions and simple filtration was shown to be a convenient and effective method for catalyst recovery.[2b,c] However, long reaction times (24 h) were needed for this transformation. GO was also exploited as an effective reagent for the oxidation of alkenes to their respective diones. The temperatures used in this reaction were 100–120 °C for a period of 24 h.[2d] In another report, various alkynes or alcohols were hydrated or oxidized in situ to their corresponding methyl ketones or aldehydes, respectively, which underwent a subsequent Claisen–Schmidt condensation at 80 or 100 °C after 24 h.[2e]

The use of ultrasound in chemistry offers a method for chemical activation, which has broad applications and uses equipment which is relatively inexpensive. The observed effects of ultrasound during organic reactions are due to cavitation, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid. Cavitation induces very high local temperatures and pressures inside the bubbles (cavities), leading to turbulent flow of the liquid and enhanced mass transfer. Ultrasound has been utilized to accelerate a number of synthetically useful organic reactions.[3] In addition to the field of organic chemistry, sonochemistry has also been used in the preparation of micro and nanomaterials.[4]

In a previous report, we demonstrated that graphite oxide (GO) could be used as a mild and efficient oxidizing agent for the aromatization of Hantzsch 1,4-dihydropyridine derivatives.[5] Herein, we report the use of GO, a readily available and inexpensive material, as a highly efficient reagent for the synthesis of aldehydes or ketones from various alcohols under ultrasonic irradiation (Scheme 1).

GO is an economical reagent as it can be prepared easily from readily available graphite flakes by oxidation with $KMnO_4$/H_2SO_4.[6] The GO utilized in this work was synthesized according to a modified Hummers method.[7,8] The prepared GO was characterized using powder XRD, UV/Vis spectroscopy, and FT-IR spectroscopy to establish its authenticity. [2a,9]

Although, the use of graphene oxide for oxidation of alcohols was previously described,[2b] a long reaction time of 24 h was needed for this transformation. For example, benzyl alcohol was converted into benzaldehyde using GO after 24 h at 100 °C under solvent-free conditions.[2b] In this work, we have examined the beneficial effects of ultrasonic irradiation on this chemical transformation.

$$\text{Alcohol} \xrightarrow{\text{GO,)))}} \text{Aldehyde or Ketone}$$

Scheme 1. Oxidation of various alcohols to aldehydes or ketones using GO under ultrasonic irradiation.

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In a typical experimental procedure, a solution of benzyl alcohol (1 mmol) and GO in different solvents was subjected to ultrasonic (bath or ultrasonic probe) irradiation. Various experimental conditions were screened to obtain the maximum yield of product. The results are summarized in Table 1.

When the oxidation was performed in pure water in the presence of 200 wt% of GO, the reaction did not proceed at all and only the starting material was recovered after 45 min. However, when acetonitrile was used as the solvent, the reaction proceeded quantitatively within 240 min (Table 1, entries 1 and 2). It should be noted that in chloroform, benzaldehyde was obtained in 55% yield along with dibenzyl ether (44%) as a by-product (Table 1, entry 3). High yields of dibenzyl ether were obtained in chloroform and hexane when the reaction was conducted under ultrasonic probe or bath irradiation (Table 1, entries 3, 7, and 10). It is worth noting that in the absence of GO, no oxidation or coupling took place in chloroform (Table 1, entry 4). The results in Table 1 indicated that 200 wt% of GO was sufficient to afford a 58% yield of benzaldehyde when the reaction was carried out in toluene under ultrasonic probe irradiation (Table 1, entry 5). Increasing the amount of GO to 300 wt% led to an increase in the amounts of unidentified products (Table 1, entry 6). The highest yields were obtained using 200 wt% of GO in acetonitrile within 240 min under ultrasonic probe irradiation (Table 1, entry 2). Quantitative yields were obtained under ultrasonic bath irradiation and the reaction time decreased by half (120 min) in chloroform and toluene, respectively (Table 1, entries 11 and 13).

In a similar fashion, various alcohols reacted smoothly with GO (200 wt%) in toluene under ultrasonic bath irradiation at 80 °C to give the corresponding aldehydes. The results are summarized in Table 2. Under these experimental conditions, the reactions of benzyl alcohol, 4-chlorobenzyl alcohol, 3,4-dichlorobenzyl alcohol, 2,4-dichlorobenzyl alcohol, 4-nitrobenzyl alcohol, 3-nitrobenzyl alcohol, 2-fluorobenzyl alcohol, and cinnamyl alcohol gave the corresponding aldehydes in 45–98% yields (Table 2, entries 1–9). Oxidation of substrates containing electron-donating groups such as 4-methoxybenzyl alcohol and 4-*tert*-butylbenzyl alcohol resulted in formation of the corresponding aldehyde derivatives in low yields (Table 2, entries 10 and 11). Similarly, oxidation of heterocyclic alcohols such as thiophene-2-methanol and 3-pyridinylmethanol afforded the expected aldehydes in low yields (Table 2, entries 12 and 13). In contrast, oxidation of the aliphatic alcohol cyclohexanol using this method afforded cyclohexanone in 98% yield under ultrasonic bath irradiation (Table 2, entry 14).

Oxidation of the secondary benzylic alcohol, benzhydrol gave only a 35% yield of benzophenone after 1 h under solvent-free conditions (Table 2, entry 15). It should be noted that a coupling reaction occurred when using GO (200 wt%) in hexane under ultrasonic probe irradiation to give bis(diphenylmethyl)ether [$(Ph_2CH)_2O$][10,11a] in 95% yield after only 10 min (entry 16, Table 2). We also investigated the oxidation of 1-indanol using 200 wt% GO in toluene at 80 °C under ultrasonic bath irradiation. Under these experimental conditions, 1*H*-indene was formed in 71% yield by dehydration (Table 2, entry 17), whereas 2-(2,3-dihydro-1*H*-inden-3-yl)-1*H*-indene[11] was obtained in 55% yield using 300 wt% of GO in toluene under ultrasonic probe irradiation (Table 2, entry 18). The formation of the 2-(2,3-dihydro-1*H*-inden-3-yl)-1*H*-indene dimer resulted most likely from consecutive dehydration followed by a coupling reaction. A similar dehydration process was observed for 2-(4-biphenylyl)-2-propanol to give 4-(prop-1-en-2-yl)-1,1′-biphenyl[12] in 95% yield (Table 2, entry 19).

We also examined the reusability of the oxidizing agent for the oxidation of 4-nitrobenzyl alcohol. After completion of the reaction, the solvent was evaporated and methylene chloride was added. GO is insoluble in methylene chloride and could be removed by simple filtration. The resulting GO was dried and re-used for three consecutive oxidation reactions of 4-nitrobenzyl alcohol. The results in Table 3 showed a loss in the activity of the recycled GO after each reaction. 4-Nitrobenzaldehyde was obtained in 78%, 51%, and 24% yields in the second, third, and fourth runs, respectively (Table 3).

The role of ultrasonication in oxidation processes is not very clear. Although the technique was commonly used to exfoliate GO into graphene oxide, it is not excluded that ultrasonication participates in the oxidation process by generating locally high temperatures.[14] XRD, FT-IR spectroscopy, and UV/Vis absorption characterization of GO before and after the reaction with alcohols clearly suggested the reduction of GO (see Supplementary data). Indeed, the characteristic GO peak at $2\theta = \sim 11^\circ$ in the XRD pattern shifted to $2\theta = \sim 24\text{–}25^\circ$ after the 7th run. Moreover, FT-IR spectroscopy revealed the disappearance of the stretching modes due to the carbonyl functions and the appearance of peaks due to aromatic $C{=}C$ stretching of the carbon network. Finally, the shift of the UV/Vis absorption band from 231 nm for the starting GO to 266 nm after reaction with alcohols indicated the reduction of GO. These results are in accordance with those reported for the reduction of graphene oxide to graphene using different procedures.[15]

The dependence of the reaction on the solvent type might also originate from the reduction of GO. While GO can be easily dispersed in various solvents including water, reduced GO precipitates in water and can be only dispersed in organic solvents such as DMF and CH_3CN.[15a]

Table 1
Effect of the solvent, and ultrasonic probe or bath irradiation on the oxidation of benzyl alcohol in the presence of GO

Entry	Conditions	GO (wt%)	Time (min)	Yield[a] (%)		
				Benzaldehyde	Dibenzyl ether	Benzyl alcohol
1	H_2O, ultrasonic probe	200	45	0	0	100
2	MeCN, ultrasonic probe	200	240	100	—	—
3	$CHCl_3$, ultrasonic probe	200	45	55	44	1
4	$CHCl_3$, ultrasonic probe	—	45	—	—	100
5	Toluene, ultrasonic probe	200	45	58	—	1 (41% Unknown products) [b]
6	Toluene, ultrasonic probe	300	30	41	7	— (52% Unknown products)[b]
7	Hexane, ultrasonic probe	200	30	46	54	—
8	Hexane, ultrasonic probe	100	30	14	9	77
9	Solvent-free, 80 °C, ultrasonic bath	50	120	12	3	85
10	Hexane, 80 °C, ultrasonic bath	50	120	32	54	14
11	$CHCl_3$, 80 °C, ultrasonic bath	200	120	94	6	—
12	Toluene, 80 °C, ultrasonic bath	300	120	90	1	9
13	Toluene, 80 °C, ultrasonic bath	200	120	98	—	—

[a] Determined by GC.
[b] We observed several unidentified products using GC analysis.

Table 2
Oxidation of alcohols using GO

Entry	Substrate	Product[13]	Conditions[a]	Time (h)	Yield[b] (%)
1	Benzyl alcohol	Benzaldehyde	A	2	98
2	Benzyl alcohol	Benzaldehyde + dibenzyl ether	B	2	32 + 54
3	4-Chlorobenzyl alcohol	4-Chlorobenzaldehyde	A	2	94
4	3,4-Dichlorobenzyl alcohol	3,4-Dichlorobenzaldehyde	A	2	92
5	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	A	3	60
6	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	A	1.5	92
7	3-Nitrobenzyl alcohol	3-Nitrobenzaldehyde	A	2	92
8	2-Fluorobenzyl alcohol	2-Fluorobenzaldehyde	C	1	45
9	Cinnamyl alcohol	Cinnamaldehyde	A	2	70
10	4-Methoxybenzyl alcohol	4-Methoxybenzaldehyde	A	0.50	24
11	4-*tert*-Butylbenzyl alcohol	4-*tert*-Butylbenzaldehyde	A	1.5	13
12	Thiophene-2-methanol	Thiophene-2-carbaldehyde	A	1.5	10
13	3-Pyridinylmethanol	Nicotinaldehyde	A	2	Trace
14	Cyclohexanol	Cyclohexanone	A	2	98
15	Benzhydrol	Benzophenone	D	1	35
16	Benzhydrol	Bis(diphenylmethyl) ether[10]	E	0.16	95
17	1-Indanol	1*H*-indene[11]	A	1.5	71
18	1-Indanol	2-(2,3-Dihydro-1*H*-inden-3-yl)-1*H*-indene[11]	F	0.25	55
19	2-(4-Biphenylyl)-2-propanol	4-(Prop-1-en-2-yl)-1,1′-biphenyl[12]	G	0.5	95

[a] Conditions: (A) 200 wt% GO, toluene, 80 °C, ultrasonic bath; (B) 50 wt% GO, hexane, 50 °C, ultrasonic bath; (C) 300 wt% GO, toluene, 80 °C, ultrasonic bath; (D) 200 wt% GO, solvent-free conditions, 80 °C, ultrasonic bath; (E) 200 wt% GO, hexane, ultrasonic probe; (F) 300 wt% GO, toluene, ultrasonic probe; (G) 200 wt% GO, toluene, ultrasonic probe.

[b] Determined by GC-MS.

Table 3
Reusability of GO for the oxidation of 4-nitrobenzyl alcohol[a]

Entry	Run	Yield[b] (%)
1	First	92
2	Second	78
3	Third	51
4	Fourth	24

[a] Conditions: 200 wt% GO, toluene, 80 °C, 1.5 h, ultrasonic bath.

[b] Determined by GC.

In conclusion, we have investigated the oxidation of aromatic, heterocyclic, and aliphatic alcohols using graphite oxide under ultrasonic irradiation. This protocol is advantageous as the reactions take place under mild conditions in short reaction times. The yields were good to high for benzyl alcohol derivatives with electron-withdrawing groups and moderate for those with electron-donating groups. The yields were low for heterocyclic alcohols, but high yields were obtained for aliphatic alcohols. In addition, GO is a cost effective material and can be easily recovered from the reaction mixture by a simple filtration. Further investigations using GO for other chemical transformations are currently in progress.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.07.016.

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8. Synthesis of graphite oxide using the modified Hummers' method:[7] graphite (8 g) was added to a mixture of 98% H_2SO_4 (14 mL), $K_2S_2O_8$ (4 g), and P_2O_5 (4 g) with stirring. The solution was kept at 80 °C for 6 h. The resulting preoxidized product was washed with H_2O and dried. CAUTION: The preoxidized product (8 g) was added to 98% H_2SO_4 (180 mL), followed by the slow addition of $KMnO_4$ (24 g) with the temperature kept at <20 °C in order to avoid overheating and explosion. The temperature was increased to 35 °C and maintained for 2 h. Next, H_2O (400 mL) was added over 15 min. Further H_2O (1.1 L) was added to dilute the solution, and 30% H_2O_2 (20 mL) was injected into the solution to quench the excess $KMnO_4$. A brown solution was obtained, which was washed with 1:10 (37%) HCl: H_2O solution (2 L) in order to remove metal ions and finally washed with H_2O (2 L). Dried graphite oxide was obtained by centrifugation followed by dehydration on a rotary evaporator under vacuum. The prepared GO was characterized using powder XRD, UV/Vis spectroscopy, and FT-IR spectroscopy to establish its authenticity (see the Supplementary data).
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13. Ultrasonic irradiation was performed in an Elmasonic P ultrasonic cleaning unit (ultrasonic bath) with a frequency of 80 kHz and an output power of 80%, or using an ultrasonic homogenizer (Bandelin Sonopuls HD 3100) with probe model MS 73 and 100% power.
Typical procedure for the oxidation of alcohols: To a solution of alcohol (0.1 g) in 2 mL of solvent was added the appropriate amount of GO (as indicated in Table 2). The resulting mixture was irradiated in an ultrasonic bath or with an ultrasonic probe (methods A to G) for the time indicated in Table 2 prior to GC/MS analysis. The mixture was filtered through a sintered funnel and evaporated under reduced pressure. Purification was achieved by column

chromatography using hexane as the eluent. The spectroscopic data of the obtained aldehydes were compared with authentic samples.[16] Other products were also known compounds[10–12] and were characterized by ^{1}H NMR, mass spectrometry, and FT-IR spectroscopy.

2-(2,3-Dihydro-1*H*-inden-3-yl)-1*H*-indene, Mp: 59 °C; ^{1}H NMR ($CDCl_3$, 80 MHz): $\delta = 2.23$ (m, 2H, CH_2), 2.94 (m, 2H, CH_2), 3.34 (s, 2H, CH_2), 4.35 (t, $J = 7.6$ Hz, 1H, CH), 6.57 (s, 1H, CH), 7.26 (m, 8H, Ar), MS (EI) (70 eV), m/z (%): 232 (55) $[M]^+$, 217 (18), 202 (8), 141 (4), 117 (100), 91 (9); IR (KBr) $\nu = 3067$, 3018, 2939, 2845, 1609, 1478, 1459, 1390, 1203, 1017, 912, 748, 554 cm^{-1}.

4-(Prop-1-en-2-yl)-1,1′-biphenyl Mp: 117 °C; ^{1}H NMR ($CDCl_3$, 80 MHz): $\delta = 2.83$ (s, 3H, CH_3), 4.84 (br s, 1H, CH_2), 5.15 (d, $J = 1.6$ Hz, 1H, CH_2), 7.20 (m, 9H, Ar); MS (EI) (70 eV), m/z (%): 194 (100) $[M]^+$, 179 (28), 152 (8), 115 (5); IR (KBr) $\nu = 3435$, 2938, 2364, 1910, 1615, 1482, 832, 763, 731, 691 cm^{-1}.

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