



C–H oxidation using graphite oxide

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ABSTRACT

Graphite oxide was found to be an effective oxidant for use in a broad range of reactions, including the oxidation of olefins to their respective diones, methyl benzenes to their respective aldehydes, diaryl-methanes to their respective ketones, and various dehydrogenations. The temperatures used in the reactions were typically mild (100–120 °C), and the heterogeneous nature of the oxidant facilitated isolation and purification of the desired products. In most cases, no by-products were observed and the desired products were isolated in good to excellent yields.

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1. Introduction

The oxidation of organic substances has received significant attention as it represents an important functional group transformation, from both fundamental and practical perspectives.¹ Thus far, a wide range of homogeneous transition metal-based catalysts has been developed for this purpose.² Unfortunately, many metals are not widely available and/or are toxic, which presents sustainability and environmental challenges. Moreover, homogenous catalysts can be difficult to separate from the reaction mixtures in which they are used.³ Although soluble, metal-free superoxides and peroxides may offer solutions to some of the aforementioned challenges, stoichiometric quantities of these reagents are required and they lack the selectivity inherent to some of the aforementioned catalysts.⁴ Herein we report the use of graphite oxide (GO)⁵ as a heterogeneous reagent for oxidizing various hydrocarbons. Compared to other oxidants used for similar purposes, GO offers several advantages, including low cost, ease of synthesis, and high stability to ambient conditions (e.g., resistance to hydrolysis and oxidative degradation, etc.).

GO is typically prepared from natural sources of flake graphite using strongly acidic and oxidizing conditions. The most commonly employed synthetic protocol is often called the ‘Hummert method,’ where graphite is treated with KMnO_4 in concentrated H_2SO_4 , followed by workup in aqueous H_2O_2 .^{5a} Though the precise structure of GO is still uncertain, it is generally accepted that a wide

range of functional groups, including alcohols, epoxides, and carboxylic acids, are introduced during the synthesis of GO, both to its surface as well as to its periphery (Fig. 1). As a result, GO tends to be highly acidic and strongly oxidizing,^{5f} and exhibits a high propensity to undergo reduction when exposed to hydrazine,⁶ borohydride,⁷ hydroquinone,⁸ alcohols,⁹ and other reagents.¹⁰ Indeed, GO is commonly used as an intermediate in the preparation of graphene and graphene-like materials.¹¹

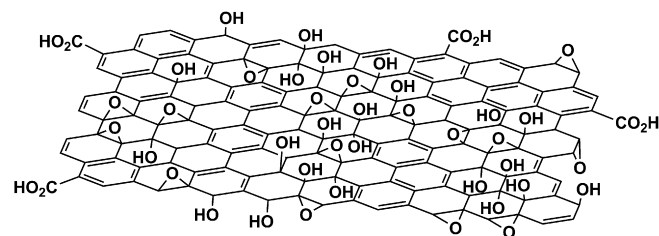


Fig. 1. Proposed structure of graphite oxide (GO) based on the Lerf–Klinowski model.^{5f}

2. Results and discussion

Exploiting the reactivity intrinsic to GO, our previous studies have identified this material as a powerful reagent for oxidizing various alcohols and alkenes, as well as hydrating alkynes, to their corresponding aldehyde or ketone compounds.¹² Additionally, it was discovered that these transformations could be performed simultaneously in a single reaction vessel to form advanced substrates, such as chalcones.^{12b} Although the mechanism of the

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forementioned reactions remains elusive, the structure of GO suggested to us that the presence of the surface bound oxygen-containing functionalities may play an important role in the observed reactivities and govern product formation (see below).

In our preliminary report,^{12a} GO was found to be capable of oxidizing *cis*-stilbene to benzil (see Fig. 2); a transformation, that is, similar to a Wacker oxidation, which invariably requires the use of transition metals.¹³ As summarized in Tables 1 and 2, we have since optimized the oxidation of *cis*-stilbene to benzil with respect to the loading of GO and the reaction temperature. In general, increasing the loading of GO used in the reaction was found to increase the yield of the benzil product, though no improvement was observed beyond 400 wt %. At low temperatures (≤ 60 °C), minimal conversion was observed, regardless of GO loading; however, lower yields of product were obtained at temperatures above 100 °C, presumably due to thermal degradation of the GO substrate.^{5f} The use of a nitrogen atmosphere, in lieu of air, was also explored although minimal effects on the product yield were observed.

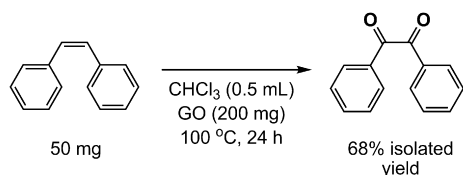


Fig. 2. Oxidation of *cis*-stilbene using graphite oxide (GO).

Table 1

Optimization of the oxidation of *cis*-stilbene to benzil: effect of GO loading and atmosphere^a

Entry	GO Loading(wt %)	Atmosphere	Isolated yield (%)
1	200	Ambient	49
2	300	Ambient	57
3	400	Ambient	68
4	800	Ambient	52
5	200	Nitrogen	44 ^b
6	400	Nitrogen	58 ^b

^a All reactions were performed using 50 mg of *cis*-stilbene and 0.5 mL of CHCl₃ heated at 100 °C for 24 h.

^b Yield determined by ¹H NMR spectroscopy.

Table 2

Optimization of the oxidation of *cis*-stilbene to benzil: effect of temperature^a

Entry	Temperature °C	Isolated yield (%)
1	60	7
2	80	10
3	100	60
4	120	55

^a All reactions were performed using 50 mg of *cis*-stilbene (neat) and 200 mg GO (400 wt %) and were heated at the indicated temperature for 24 h.

Ultimately, optimized conditions were determined (50 mg *cis*-stilbene, 400 wt % GO, 0.5 mL CHCl₃, 100 °C, 24 h, air) and benzil was obtained in 68% isolated yield (improved from 49% in our earlier report).^{14,15} Under these optimized conditions, the reactivity of GO toward a range of functionalized *cis*-stilbenes was explored.¹⁶ As summarized in Table 3, the highest yields of oxidized product were obtained from substrates that featured electron-donating or moderately electron-withdrawing groups (entries 1–4; 38–68%). Only a modest yield (25%) of oxidized product was obtained from 4,4'-dinitro-*cis*-stilbene, which features strongly electron-withdrawing nitro groups (entry 5).¹⁷ Nevertheless, these results are remarkable as the oxidation of stilbenes or similar 1,2-disubstituted olefins to

Table 3

Oxidation of various substituted *cis*-stilbenes using GO^a

Entry	Starting material	Product	Isolated yield
1			50%
2			38%
3			68%
4			48%
5			25%
6			12%

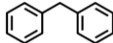
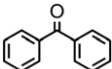
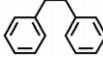
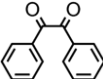
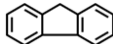
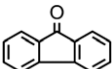
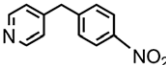
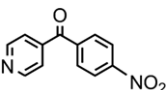
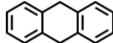
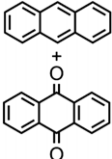
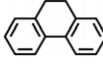
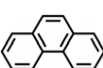
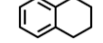



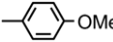
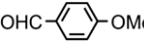


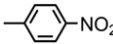
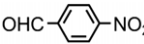
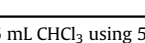
^a All reactions were performed in 0.5 mL CHCl₃ using 50 mg of the substrate and 200 mg (400 wt %) of GO at 100 °C for 24 h in Teflon-sealed vials.

their corresponding diones typically requires the use of metal catalysts, such as selenium(IV) oxide or chromate-containing species.¹⁸

After this initial success, we explored the ability of GO to oxidize more challenging substrates, including hydrocarbons possessing sp³-hybridized C–H bonds. As summarized in Table 4, various substrates with benzylic methylene groups were successfully converted to their corresponding ketone and unsaturated products using GO (conditions: 50 mg substrate, 200 wt % GO,¹⁹ 0.5 mL CHCl₃, 120 °C, 24–48 h, air). For some substrates, such as diphenylmethane (entry 1), oxidation resulted in the formation of the respective ketone.²⁰ In other cases, such as that of dihydrophenanthrene (entry 6), dehydrogenative aromatization was observed.²¹ In general, the oxidation of substrates with doubly activated benzylic positions afforded the corresponding ketone products in good yield (e.g., 72% in the case of diphenylmethane).²² Conversely, substrates, such as bibenzyl (entry 2), wherein each methylene is only activated by a single phenyl substituent, afforded decreased yields of product (17%). The reduced yield of benzil from bibenzyl may be due to the substrate's relatively high conformational freedom, although diphenylmethane (entry 1) was oxidized to its respective carbonyl in higher yield than fluorene (entry 3). Collectively, these results suggested to us that benzylic activation may be a primary factor in determining a substrate's susceptibility to C–H oxidation when GO is used as the oxidant.

¹H NMR spectroscopic analysis of the crude reaction mixtures showed no by-products for nearly all the substrates explored in this study. The only exception was 9,10-dihydroanthracene (Table 4, entry 5), which revealed a mixture of anthracene and anthraquinone (isolated in 49% and 31% yield, respectively). In comparison, Su and co-workers observed the oxidative dehydrogenation of 9,10-dihydroanthracene to anthracene when multi-walled carbon nanotubes (MWCNTs), another carbon-based material used to

Table 4
Oxidation of various hydrocarbons using GO^a

Entry	Starting material	Product	Isolated yield (%)
1			72%
2			17%
3			59%
4			80%
5			49%
6			31%
7			85%
8			24%
9			26%
10			16%
11			6% ^b
			4% ^b

^a All reactions were performed in 0.5 mL CHCl₃ using 50 mg of the substrate and 100 mg (200 wt %) of GO at 120 °C for 24 h in Teflon-sealed vials.

^b Yield determined by ¹H NMR spectroscopy.

facilitate synthetic transformations, were used as the oxidation catalyst.²³ Virtually no anthraquinone was detected in the product mixture obtained from the MWCNT-catalyzed reaction, a result, which suggested to us that GO's reactivity extends beyond that of MWCNTs. For example, using GO, two substrates related to 9,10-dihydroanthracene, tetralin (entry 7) and 1,2-dihydronaphthalene (entry 8), were subjected to identical reaction conditions as those described above (50 mg substrate, 100 mg GO, 0.5 mL CHCl₃, 120 °C, 24–48 h). Naphthalene was isolated as the sole product in 24% and 26% yield, respectively, in both reactions; the corresponding dione (naphthaquinone) was not observed.²⁴

In addition to the conversion of diaryl methylenes to their respective ketones, GO was also found to oxidize substituted methyl benzenes to their corresponding aldehydes (entries 9–11), albeit in relatively low yields. In general, the incorporation of strongly electron-donating groups, such as 4-methylanisole (entry 9), afforded the corresponding aldehyde product in higher isolated yields compared to methyl benzenes bearing neutral or electron-withdrawing groups.

3. Conclusions

In summary, GO was found to facilitate the oxidation of olefins, diarylmethanes, and methyl benzenes, as well as the dehydrogenation of various hydrocarbons. The reactions were performed under mild conditions and without the need for additional oxidants or metal co-catalysts. The methodology described herein has several advantages compared to analogous metal-based systems that have been previously used for similar purposes,²⁵ including: ready accessibility of GO, operational simplicity, and increased environmental compatibility. However, relatively large quantities of GO were required to obtain reasonable yields of the desired oxidized products. Hence, in addition to expanding the scope of reactivity displayed by GO, future efforts will be directed toward the development of methodologies that utilize lower quantities of this material.

4. Experimental section

4.1. General considerations

All chemical reagents were purchased from commercial sources and used without additional purification. Unless otherwise noted, all experiments were performed under ambient conditions. ¹H and ¹³C NMR data were collected on Varian Unity INOVA 400 MHz and Varian Mercury 300 MHz spectrometers. Chemical shifts (δ) are referenced downfield from (CH₃)₄Si using the residual solvent peak as an internal standard (CDCl₃, 7.24 ppm for ¹H and 77.0 ppm for ¹³C NMR, respectively). FT-IR spectra were recorded using a Perkin–Elmer Spectrum BX spectrometer.

4.2. Preparation of graphite oxide (GO)

A modified Hummers method was used to prepare the graphite oxide.^{5a} A 100 mL reaction flask was charged with natural flake graphite (3.0 g; SP-1, Bay Carbon Inc. or Alfa Aesar [99%; 7–10 μ m]), concentrated sulfuric acid (75 mL), sodium nitrate (1.5 g), and a stir bar, and then cooled on an ice bath. The flask was then slowly charged with KMnO₄ (9.0 g) over 2 h, which afforded a dark colored mixture. The rate of addition was controlled carefully to prevent the temperature of the suspension from exceeding 20 °C. After stirring at 0 °C for 1 h, the mixture was heated at 35 °C for 0.5 h. The flask was then cooled to room temperature and the reaction was quenched by pouring the mixture into 150 mL of ice water and stirred for 0.5 h at room temperature. The mixture was further diluted to 400 mL with water and treated with a 30% aqueous solution of hydrogen peroxide (7.5 mL). The resulting vibrant yellow mixture was then filtered and washed with an aqueous HCl solution (6.0 N) (800 mL) and water (4.0 L). The filtrate was monitored until the pH value was neutral and no precipitate was observed upon the addition of aqueous barium chloride or silver nitrate to the filtrate. The filtered solids were collected and dried under high vacuum to afford the desired product (5.1 g) as a dark brown powder. Spectral data matched literature values.⁵

4.3. Oxidation of *cis*-stilbenes

In a typical preparation, a 7.5 mL vial was charged with GO (200 mg), *cis*-stilbene (50 mg), CHCl₃ (0.5 mL) and a magnetic stir bar. The vial was then sealed with a Teflon-lined cap under ambient atmosphere and heated at 100 °C for 24 h. After the reaction was complete, the mixture was cooled to room temperature and washed with CH₂Cl₂ (50 mL). The filtrate was collected and the solvent was evaporated to obtain the crude product, which was then purified by silica chromatography (CH₂Cl₂ or CH₂Cl₂/hexanes as the eluent) and the solvent was removed under reduced pressure

to obtain the desired product. All isolated products matched spectroscopic data reported previously in the literature (see ESI).

4.4. Oxidation of hydrocarbons possessing methyl or methylene groups

In a typical preparation, a 7.5 mL vial was charged with GO (100 mg), substrate (50 mg), CHCl_3 (0.5 mL) and a magnetic stir bar. The vial was then sealed with a Teflon-lined cap under ambient atmosphere and heated at 70 °C, 120 °C or 120 °C for 24 h. The reaction mixture was then cooled to room temperature and washed with CH_2Cl_2 (50 mL). The filtrate was collected and the solvent was removed under vacuum to obtain the crude product, which was then purified by silica chromatography (CH_2Cl_2 , hexanes, $\text{EtOAc}/\text{CH}_2\text{Cl}_2$ or CH_2Cl_2 /hexanes as the eluent). The oxidation reactions involving toluene, 4-nitrotoluene, cyclohexadiene, cyclohexene, and cyclohexane were performed using CDCl_3 instead of CHCl_3 and conversions were determined directly by ^1H NMR spectroscopy. All products matched spectroscopic data reported previously in the literature (see ESI).

Acknowledgements

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2011.02.065.

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- In order to determine whether a transition metal impurity in the GO was responsible for the observed reactivity, the as-prepared GO was analyzed by atomic absorption (AA) spectrometry and inductively coupled plasma mass spectrometry (ICP-MS). No measurable manganese (used in the preparation of GO) was observed via AA, and the Mn content (analyzed at a concentration of 0.05 mg mL⁻¹ in a 1% aqueous HNO₃ solution) was measured to be 76 ppb via ICP-MS. Other metal impurities found in low concentrations include: Al (25 ppb), Ba (1 ppb), and Pb (1 ppb).
- In addition to the desired product, analysis of the resulting crude reaction mixture via ^1H NMR spectroscopy revealed the presence of *cis*-stilbene, *trans*-stilbene (7%), a small amount of benzaldehyde (4%) and benzoic acid (<2%) as by-products.
- trans*-Stilbene was found to be unreactive under the conditions described herein.
- Under these conditions, we surmise that the increased yields of unfunctionalized stilbenes may be due to side reactions of GO with the functional groups present on the derivatives of *cis*-stilbene. The use of lower GO loadings or lower temperatures may minimize these side reactions, though such variations have not been exhaustively explored.
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- GO loadings of less than 200 wt % were found to be ineffective in the oxidation of the hydrocarbons bearing methyl or methylene groups shown in Table 4.
- Analysis by FT-IR (KBr) and powder conductivity of the GO recovered after reaction with diphenylmethane revealed that the carbon material was reduced, consistent with our previous results (see the Supplementary data, Figs. S1–S3.).¹¹
- Similar reactivity was observed when multi-walled carbon nanotubes (MWCNTs) were used to effect the oxidative dehydrogenation of 9,10-dihydroanthracene.^{23,26}
- No reaction was observed when GO was substituted with natural flake graphite or hydrazine-reduced graphene oxide,²⁷ indicating the functionalized surface intrinsic to GO was necessary for the oxidation reaction to occur.
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- The decreased yield of naphthalene from dihydronaphthalene or tetralin, relative to anthracene from 9,10-dihydroanthracene, may be due to reduced activation of the C–H bonds as a result of mono-benzylic substitution, as compared to di-benzylic substitution. We surmise that the preferential dehydrogenative aromatization of dihydronaphthalene and tetralin over oxygenation may be rationalized by the 1,2 relationship of the hydrogen atoms being lost, which may facilitate the loss of diatomic H₂,²⁸ in contrast to the 1,4 relationship in anthracene. Moreover, dehydrogenation of anthracene may be followed by the addition of water to the aromatized species, forming a dihydroxyl intermediate, which may then be oxidized to the dione.
- For examples of selenium(IV) oxide and zinc dichromate used in stilbene oxidations, see Ref. 18. For examples of manganese-containing species and cerium salts used in diarylmethylene oxidations, see: (a) Lai, S.; Lee, D. G. *Tetrahedron* **2002**, *58*, 9879–9887; (b) Park, K. K.; Tsou, L. K.; Hamilton, A. D. *Synthesis* **2006**, 3617–3620. For examples of potassium chlorate and manganese dioxide species used for the aromatization of di- or tetrahydrogenated aryl species, see: (c) Patai, R.; Rajbenback, L. *J. Am. Chem. Soc.* **1951**, *73*, 862–863; (d) Radtke, R.; Hintze, H.; Rösler, K.; Heising, A. *Chem. Ber.* **1990**, *123*, 627–633. For examples of iron, copper, and cobalt-containing species used in the oxidation of substituted methyl benzenes, see: (e) Wang, F.; Xu, J.; Li, X.; Gao, J.; Zhou, L.; Ohnishi, R. *Adv. Synth. Catal.* **2005**, *347*, 1987–1992; (f) Saussine, L.; Brazi, E.; Robine, A.; Mimoun, H.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1985**, *107*, 3534–3540.
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