Green Regio- and Enantioselective Aminolysis Catalyzed by Graphite and Graphene Oxide under Solvent-Free Conditions

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The ring-opening reactions of epoxides with amines were efficiently and regioselectively catalyzed by high-surface-area graphite and graphene oxide under metal-free and solvent-free conditions. For epoxides without aryl groups, catalytic activity was observed only for graphene oxide, and hence, the activity must have been due to its acidic groups. For styrene oxide, instead, graphite and graphene oxide exhibited rather similar catalytic activities, and hence, the activity was mainly due to activation of the electrophilic epoxide by π -stacking interactions with the graphitic π system. The described aminolysis procedure is green and cheap because the catalyst can be recovered and recycled without loss of efficiency. Moreover, these heterogeneous catalysts exert high stereoselective control in the presence of nonracemic epoxides and provide chiral β -amino alcohols with enantiomeric excess values up to 99%.

Epoxide ring-opening reactions are useful methods to provide multifunctional compounds ready to be used as versatile intermediates in total synthesis or as precursors of relevant molecules. As three-membered heterocyclic rings, epoxides are more reactive than ethers owing to ring strain and are susceptible to attack by a range of nucleophiles, including nitrogen (e.g., ammonia, amines, and azides), oxygen (e.g., water, alcohols, phenols, and acids), and sulfur (e.g., thiols) containing compounds, and this leads to bifunctional molecules of great industrial value.

In particular, epoxy ring-opening reactions with amines are well documented,^[1-49] and with the choice of specific physical parameters (e.g., heating,^[1,2] microwave,^[3-5] and ultrasound^[5]), the use of polar reaction media (e.g., ionic liquids,^[6] fluoro al-cohols,^[7] or water under different pH conditions^[8,9]), or the use of catalysts or activators as homogeneous catalysts (e.g., Brønsted acids and bases^[6,9-14] and several metal salts and/or complexes^[15-28]), good results have been achieved, although most suffer from poor regioselectivity, high temperature, and/ or stoichiometric amounts of the catalyst and the use of excess amounts of reagents.

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The use of heterogeneous catalyst as solids (e.g., silica gel,^[29] nanosilica,^[30] functionalized mesoporous silica,^[31–33] alumina and/or modified alumina,^[34–37] nanoalumino silicates,^[38–42] montmorillonite-K10 clay,^[43] sulfated zirconia,^[44,45] annotitanium dioxides,^[46] heteropoly acids,^[47] polyoxometalate inorganic metal oxygen clusters,^[48] Amberlyst-15,^[49] nanocrystalline zircosilicate,^[50] and iron oxides^[51]) has tried to meet the need for more sustainable protocols that assure good regioselective control, often lost to competitive polymerization/isomerization of the epoxides.

However, a metal-free, highly regioselective procedure is still missing. One of the emerging promises in sustainable chemistry is carbon-based materials, which are already used in some important synthetic reactions as efficient carbocatalysts.

In particular, the use of graphite oxide and exfoliated graphite oxide as cheap and metal-free catalysts in oxidation reactions,^[52-55] Friedel–Crafts reactions,^[56] aza-Michael additions,^[57] Mukaiyama–Michael additions,^[58,59] polymerizations,^[60] crosslinking reactions,^[61] and epoxide ring-opening reactions,^[62,63] in addition to some one-pot reactions,^[64-66] have been successfully recorded. Recently, we reported the first example of the enantioselective Friedel–Crafts reaction catalyzed by graphene oxide under solvent-free conditions; the reaction proceeded to give the products in good yields with high enantioselectivities, without side products, and with high regioselectivities.^[63] The possibility to control the stereochemical outcome of the reaction in the presence of a carbon-based heterogeneous catalyst represents an important goal for green synthetic approaches that aim to prepare chiral molecules.

This aspect is particularly interesting considering the wide presence of chiral β -amino alcohol units in numerous natural products and bioactive molecules and the important role that they play in organic chemistry and related research fields.^[67] Chiral β -amino alcohols have been widely used as chiral ligands,^[68] organocatalysts,^[69] and versatile intermediates in the synthesis of various medicines^[70] and unnatural amino acids.^[71] Consequently, numerous methods for the preparation of optically active β -amino alcohols have been reported,^[72] including the asymmetric reduction of amino ketones,^[73] the ring opening of enantioenriched epoxides,^[74] and the Sharpless asymmetric aminohydroxylation of alkenes.^[75] To the best of our knowledge, aminolysis catalyzed by carbon-based materials has not been previously reported.

All of the reported procedures for the opening of epoxide rings are based on basic or acidic functionalities (as Lewis or Brønsted acids) that are able to activate the epoxy ring and to facilitate the ring-opening reaction. Herein, we show the first



examples of the opening of epoxy rings by amines catalyzed by graphite as well as graphene oxide under solvent-free conditions with high regioselective and enantioselective control.

The X-ray diffraction patterns of the graphite-based catalysts used in this study are reported in Figure 1.



Figure 1. X-ray diffraction pattern (CuK_{α}) of carbon-based nanomaterials: a) High-surface-area graphite (G); b) graphite oxide; c) graphene oxide obtained by ball milling.

The used high-surface-area graphite (G, with a negligible oxygen content, Figure 1a) shows an interlayer distance of d = 0.339 nm and a high shape anisotropy ($D_{\parallel}/D_{\perp} = 3.1$, where D_{\parallel} and D_{\perp} are the correlation lengths parallel and perpendicular to the graphitic plane, respectively).^[76] The X-ray diffraction pattern of the derived graphite oxide by Hummers oxidation (with an oxygen content of 32 wt%, excluding water) shows an increase in the interlayer distance from d = 0.339 to 0.84 nm (Figure 1 b). The correlation length perpendicular to the layers (as evaluated for the first 00L reflection) decreases from 9.8 to 4.2 nm, whereas the in-plane correlation length (as evaluated for the 100 reflection) remains almost unchanged ($D_{\parallel} \approx 30$ nm), which thus leads to an increase in the shape anisotropy up to $D_{\parallel}/D_{\perp} = 7$. Ball-milling treatment of this graphite oxide sample leaves the oxygen content essentially unaltered (31.4 wt%, excluding water), but it largely changes the X-ray diffraction pattern, and complete disappearance of the 001 reflection is replaced by a broad halo centered at d=0.37 nm (Figure 1 c). This indicates complete loss of crystalline order perpendicular to the graphite oxide layers, that is, the formation of an uncorrelated graphene oxide layer. As a consequence, the powder with the pattern shown in Figure 1 c will hereafter be named graphene oxide (GO). This GO sample exhibits acidic functionalities, which leads to pH 2.75 for an aqueous suspension of GO at a concentration of 5 mg mL $^{-1}$.

The powders characterized in Figure 1 were used as possible catalysts for the ring-opening reaction of styrene oxide (1) with benzylamine (2) (Scheme 1) as a representative example (see Table 1).

To verify a possible background reaction, an experiment in the absence of a catalyst, under solvent-free conditions, was



Scheme 1. Ring-opening reaction of styrene oxide (1) with benzylamine (2) under solvent-free conditions.

 Table 1. Catalyst screening for the ring opening of styrene oxide (1) with benzylamine (2) (see Scheme 1).

Entry	Catalyst (wt %) ^[a]	<i>t</i> [h]	Yield [%] ^[b]	Ratio (3/4) ^[c]
1	_	24	trace	-
2	GO (3)	24	55	96:4
3	GO (3)	48	97	80:20
4	GO (1)	72	95	72:28
5	G (3)	24	54	94:6
6	G (3)	48	94	75:25

[a] The wt% was calculated with respect to the entire reaction mixture. [b] All yields refer to the chromatographically isolated products. [c] The ratio **3/4** was evaluated by analysis of the crude material by ¹H NMR spectroscopy.

performed. The reaction did not proceed at all and gave only a trace amount of the product (Table 1, entry 1), which thus showed the need for activation for the ring-opening reaction. Data relative to the catalytic activity of GO and G are collected in Table 1 (entries 2–6).

Surprisingly, irrespective of the absence of acidic groups, the catalytic activity of the graphite sample for the aminolysis reaction was only slightly lower than that of GO, that is, a carbon material characterized by OH and COOH functional groups (Table 1, entries 2 and 5).

For both catalysts, by prolonging the reaction time to 48 h, very good efficiency was obtained, although with a reduction in regioselectivity, possibly as a result of a competitive autocatalytic pathway for the aminolysis reaction (Table 1, entries 3 and 6). In fact, it is possible that by extending the reaction time, the formed amino alcohol could activate the epoxide ring-opening reaction through hydrogen bonding. This competitive activation could promote the formation of a carbocation intermediate and significantly reduce the regioselective control (for further details, see the Supporting Information).

By reducing the amount of catalyst to 1 wt% (Table 1, entry 4), a high yield was also reached, although with a longer reaction time and with rather low regioselectivity.

Because all reported procedures to activate the epoxide ring-opening reaction involve basic or acidic functionalities (Lewis and Brønsted acids), the similar catalytic activities of the graphite and graphene oxide powders were certainly unexpected. This result can possibly be rationalized by π -stacking interactions between the styrene oxide and the graphitic surface, as already suggested, also on the basis of DFT calculations, for the Mukaiyama–Michael^[58] and Friedel–Crafts reactions.^[63] These π -stacking interactions would be able to activate the ring-opening reaction and favor nucleophilic attack of nitrogen to generate the desired product.

To assess the scope of the procedure, a variety of alkylamines and arylamines were treated with styrene oxide (1). Although GO and G presented similar catalytic activities, for the following study we mainly used GO, which for the aminolysis reaction depicted in Table 1 led to slightly higher yields and regioselectivities (Table 1, entries 3 and 6).

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As reported in Table 2, the reaction proceeded to give the products in very good yields with excellent regioselectivities for most amines. Notably, in most cases (Table 2, entries 2 and 3) the regioselectivity was >90, whereas only in the presence of an aromatic residue on the alkylamine (Table 2, entry 1) did it go down to 80:20 in favor of the S_N2-type product. This result can be rationalized by hypothesizing that a π -stacking interaction between benzylamine and the graphitic surface could result in a decrease in the rate reaction and favor the less regioselective competitive autocatalytic pathway.

Interesting results were also obtained with secondary amines. In this case, it is believed that steric hindrance of the amines slows down nucleophilic attack and favors the competitive regioselective pathway to afford **3/4** in product ratios of 90:10 and 85:15 for pyrrolidine and piperidine, respectively (Table 1, entries 2 and 4).

Notably, and as already reported,^[8,77] even though morpholine is a secondary amine, better regioselectivity can be obtained with graphene oxide, which gives 99% selectivity in favor of product **3***c*.

The results obtained with secondary amines are particularly interesting in that the regioselectivities are higher than those obtained for the corresponding reactions performed in the presence of other solid acid catalysts.^[29,30]

Moving to arylamines, an inversion of regioselectivity was observed (Table 2, entries 5–7). This result was not surprising because of the reduced nucleophilicity of aniline relative to that of alkylamines. In this instance, the electrophile has to be sufficiently activated throughout partial carbocation formation, which is not involved in isomerization or polymerization of styrene oxide but is ready to react with arylamines in the reaction mixture.

Other electrophiles were finally tested, and the S_N2 -type products were delivered in good yields with good regioselectivities (Table 2, entries 8 and 9). Notably, whereas the yield was quantitative for bisphenol A diglycidyl ether (Table 2, entry 8), in the presence of a nonaromatic epoxide such as epichlorohydrin, the reaction proceeded with less efficiency. In

Table 2. Ring	g opening of epoxides with different	amines.				
		+ RNH ₂ GO (3wt%)	OH H N.R	HO N ^R		
	1	2a-h	3a-h	4a-h		
Entry	Epoxide	RNH ₂		<i>t</i> [h]	Yield [%] ^[a]	Ratio (3/4) ^[b]
1		NH ₂	2a	48	97	80:20
2	C) ^A		2 b	16	91	90:10 (3)
3	\bigcirc	↓	2 c	16	82	>99 (3)
4		HN N	2 d	16	94	85:15 (3)
5	\bigcirc	NH ₂	2e	16	95	4:96
6			2 f	16	96	5:95 (4)
7		CH ₃	2 g	16	97	>99 (4)
8		NH ₂	2h	24	98	>99 (3)
9	CI CI	NH ₂	2i	2	85	>99 (3)
[3] All yields refer to the chromatographically isolated products. [b] The ratio 3/4 ratio was evaluated by analysis of the crude material by ¹ H NMP spectros.						

[a] All yields refer to the chromatographically isolated products. [b] The ratio 3/4 ratio was evaluated by analysis of the crude material by 'H NMR spectroscopy. Compound numbers in parentheses refer to the major regioisomer formed.



that case, no π -stacking interaction can be involved, and only the OH and COOH groups of graphene oxide can activate the ring-opening reaction. For the sake of comparison, it is worth adding that the same experiment performed in the presence of G proceeded with the same efficiency as that of the uncatalyzed reaction (45% yield after 2 h), which shows the inability of graphite to activate epoxide ring opening with an alkyl substrate.

As a heterogeneous catalyst, the reusability of GO was investigated in the addition of aniline (2e) to styrene oxide (1) as a model reaction. The solid GO, recovered after extraction from the aqueous solution and dried at 60°C overnight, was used without any further treatment. The reaction conditions (RT and 16 h) were kept the same in all cycles. As shown in Table 3, both the yield of the reaction and the regioselectivity remained almost unchanged after five recycling steps.



Excellent results were obtained by performing the stereoselective version of the optimized protocol (Scheme 2). In particular, we performed the ring-opening reaction of (*S*)-styrene oxide with the amines examined under the best reaction conditions.



Scheme 2. Enantioselective aminolysis with different amines.

As reported in Table 4, high enantioselectivities were obtained with all the amines. The absolute configuration was determined by comparison with reported HPLC data.^[51]

Notably, as for the regioselective control, reduced enantioselectivities for benzylamine, pyrrolidine, and piperidine (Table 4, entries 2 and 4) were detected, possibly due to the competitive autocatalytic pathway that is responsible for racemization of (*S*)-styrene oxide during the course of the reaction.

Rather satisfactory results were obtained with arylamines, by which high enantioselectivities were achieved. Even through

Table 4. Enantioselective aminolysis with different amines (see Scheme 2).						
Entry	RNH ₂		<i>t</i> [h]	Yield [%] ^[a]	ee [%] ^[b]	Ratio (3/4) ^[c]
1	NH ₂	2a	48	97	91	80:20
2	$\langle \overset{H}{\searrow}$	2b	16	91	90	90:10 (3)
3	$\left(\begin{array}{c} N \\ O \end{array} \right)$	2 c	16	82	>99	>99 (3)
4	⊢×⊂	2 d	16	94	80	85:15 (3)
5	NH ₂	2e	16	95	>99	4:96 (4)
6	NH ₂ CI	2 f	16	97	95	5:95 (4)
7	NH ₂ CH ₃	2g	16	95	>99	> 99 (4)

[a] All the yields refer to the chromatographically isolated products. [b] The *ee* was evaluated by HPLC analysis and refers to the major regioisomer. The absolute configuration was determined by comparison with those reported in the literature. [c] The ratio **3/4** was evaluated by analysis of the crude material by ¹H NMR spectroscopy. Compound numbers in parentheses refer to the major regioisomer formed.

a typical product of an S_N 1-type reaction was provided, the inversion of configuration that was detected is derived from an S_N 2-type reaction. It is reasonable to assume that acidic activation and π -stacking interactions of the graphene oxide surface lead to an incipient carbocation that quickly reacts with the arylamine without involvement in the competitive racemization pathway.

The slight decrease in the enantioselectivity was observed for 4-chloroaniline, and this can be attributed to a slight reduction in nucleophilicity owing to the presence of the chlorine substituent, whereas an excellent result was obtained for 4methylaniline, for which, on the contrary, very high enantioselectivity was achieved.

Although GO proved to be the best catalyst for the symmetric and asymmetric ring-opening reaction, very impressive results were obtained in the presence of G with (S)-styrene oxide. In particular, aniline and piperidine, an arylamine and al-kylamine, respectively, were considered for the enantioselective reaction with (S)-styrene oxide.

As reported in Scheme 3, excellent results were obtained for both nucleophiles. As for GO, with piperidine as the alkylamine, the reaction proceeded and gave the S_N2 -type product with good regioselectivity (85:15) and good enantioselectivity for the major product (80%*ee*). In the presence of an arylamine such as aniline, major product **4e** was obtained with excellent enantioselectivity.

Notably, although in the absence of acidic functional groups, the reaction proceeded with excellent enantioselectivi-



Scheme 3. Enantioselective ring opening reaction catalyzed by G.

ties for both the alkylamine and the arylamine. This behavior can be explained by assuming that styrene oxide can be sufficiently activated by π -stacking interactions with the graphitic surface and becomes susceptible to nucleophilic attack, regardless of whether it is an aliphatic or aromatic amine, whereas the nature of the nucleophile determines the type of product, $S_N 1$ or $S_N 2$, coming from the reaction.

In conclusion, the opening of epoxy rings by amines was efficiently catalyzed under solvent-free and metal-free conditions with high regioselectivity, not only by graphene oxide but also by high-surface-area graphite. The observed catalytic activity is not surprising for graphene oxide, which has many acidic groups. In fact, most catalysts described in the literature for this kind of reaction are based on Lewis or Brønsted acids. Rather surprising instead is the very similar catalytic activity (both with aliphatic and aromatic amines) of high-surface-area graphite, for which the content of atoms different from carbon is lower than 0.1 %

These results indicate that for both graphite and graphene oxide their extended π systems activate styrene oxide through π -stacking interactions. The presence of large amounts of OH and COOH groups on the graphene oxide surface only slightly increases the yields and regioselectivities of the studied ring-opening reactions. In the presence of a nonaromatic epoxide such as epichlorohydrin, on the contrary, only graphene oxide is catalytically activity, whereas graphite completely loses his activity. Hence, for nonaromatic epoxides the catalytic activity only comes from the acidic groups on the graphene oxide layers.

These heterogeneous catalysts can be recovered and recycled without loss of efficiency or regioselectivity, and thus this method is a cheap and ecofriendly procedure.

Moreover, these graphite-based catalysts for ring-opening reactions of nonracemic styrene oxide lead to high enantiose-lectivities (up to 99%) with all studied amines.

Experimental Section

Materials and methods

High-surface-area graphite (G), with Synthetic Graphite 8427 as trademark, was purchased from Asbury Graphite Mills, Inc., with a minimum carbon wt% of 99.8 and a surface area of $330 \text{ m}^2\text{g}^{-1}$. Styrene oxide, benzylamine, sulfuric acid, sodium nitrate, potassium permanganate, and all the reagents used were purchased from

Sigma–Aldrich and were used without further purification. TLC was performed on silica gel 60 F254 0.25 mm glass plates (Merck) and non-flash chromatography was performed on silica gel (0.063–0.200 mm) (Merck).

Synthetic procedures

Preparation of graphite oxide

Graphite oxide samples were prepared by Hummers' method from graphite samples. Sulfuric acid (120 mL) and sodium nitrate (2.5 g) were introduced into a 2000 mL, three-necked, round-bottomed flask immersed in an ice bath; then, graphite (5 g) was added under an atmosphere of nitrogen with magnetic stirring. After obtaining a uniform dispersion of the graphite powder, potassium permanganate (15 g) was added very slowly to minimize the risk of explosion. The mixture was then heated to 35 °C and stirred for 24 h. The resulting dark green slurry was first poured into deionized water (6 L) and then centrifuged at 10000 rpm for 15 min with a Hermle Z 323K centrifuge. The isolated GO powder was extensively washed with 5 wt% HCl aqueous solution (100 mL) and subsequently with deionized water. Finally, it was dried at 60 °C for 12 h. The residual sulfur content was less than 0.2%.

Exfoliation of graphite oxide by ball milling

Graphite oxide powders were introduced in 125 mL ceramic jars (inner diameter of 75 mm) together with stainless steel balls (10 mm in diameter) and were dry milled in a planetary ball mill (FRISCHT) for 20 min with a milling speed of 200 rpm and a ball-topowder mass ratio of 10:1.

General procedure for the epoxy ring-opening reaction with amines

Styrene oxide (1; 120.2 mg, 1.0 mmol) and benzylamine (131 μ L, 128.6 mg, 1.2 mmol) were added to a vial containing the GO catalyst (3 wt% with respect to the mixture) at room temperature. The mixture was stirred at the same temperature for the time indicated. The mixture was extracted with EtOAc, and the combined organic phase was dried (MgSO₄) and concentrated. The residue was purified by column chromatography (silica gel, petroleum ether/EtOAc, gradient) to obtain the pure product.

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