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

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Abstract: Epoxy ring opening reactions with amines are efficiently and regioselectively catalyzed by high surface area graphite (G) and graphene oxide (GO) in metal- and solvent free conditions. For epoxides without aryl groups, catalytic activity is observed only for GO and is hence due to its acidic groups. For styrene oxide, instead, G and GO exhibit rather similar catalytic activities, which hence is 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 a high stereoselective control in the presence of non-racemic epoxides, providing chiral β -amino alcohols with e.e. 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 precursor of relevant molecules.

As three-membered heterocyclic rings, the epoxides are more reactive than ethers due to ring strain and are susceptible to be attacked by a range of nucleophiles, including nitrogen (e.g., ammonia, amines, azides), oxygen (e.g., water, alcohols, phenols, acids), and sulfur (thiol)-containing compounds, leading to bifunctional molecules of great industrial value.

In particular, the epoxy ring opening reaction with amines are well documented [1–49], and throughout the choice of specific physical parameters (heating [1,2], microwave [3–5], and ultrasound [5]), the use of polar reaction media (ionic liquids [6], fluoro alcohols [7] or water at different pH conditions [8,9]) or the use of catalysts or activators as homogeneous catalysts (Bronsted acids and bases [6, 9–14], several metal salts and/or complexes [15–28]), good results were achieved although are often suffering from poor regioselectivity, high temperature and/or stoichiometric amount of catalyst and the use of excess of reagents.

The use of heterogeneous catalyst as solids (silica gel [29], nano-silica [30], functionalized mesoporous silica [31–33], alumina and/or modified alumina [34–37], nano-alumino silicates

[38–42], montmorillonite-K10 clay [43], sulphated zirconia [44,45], anatase-titanium dioxides [46], heteropoly acid [47], polyoxometalate inorganic metal oxygen cluster [48], Amberlist-15 [49], nanocrystalline zirconosilicate [50], and iron oxides [51], has tried to meet the needs of more sustainable protocols assuring a good regioselective control, often lost for competitive polymerization/isomerization of epoxides. However a metal-free high regioselective procedure is still missing. One of the emerging promises in the sustainable chemistry are carbon based materials, 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], epoxide ring-opening reactions [62, 63] and in some one-pot reactions [64, 66] were successfully recorded. Recently we reported the first example of enantioselective Friedel-Crafts reaction catalyzed by graphene oxide in solvent-free conditions, proceeding with good yield and high enantioselectivity without side products and with high regioselectivity [63]. The possibility to control the stereochemical outcome of the reaction in presence of a carbon-based heterogeneous catalyst represents an important goal for green synthetic approaches, aiming to chiral molecules.

This aspect is particularly interesting considering the wide presence of chiral β -aminoalcohols unit in numerous natural products and bioactive molecules and important role to play in organic chemistry and related research fields [67]. They 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] such as asymmetric reduction of amino ketones, [73] ring-opening of enantioenriched epoxides, [74] and Sharpless asymmetric aminohydroxylation of alkenes. [75]. To the best of our knowledge, no aminolysis catalyzed by carbon based materials have been reported before.

Moreover, all the procedures reported are based on basic or acidic functionalities (as Lewis or Bronsted acids) able to activate the epoxy ring and facilitate the ring opening reaction.

Here we show the first amine epoxy ring opening reaction catalyzed by graphite as well as graphene oxide in solvent free conditions with high regioselective and enantioselective control.

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

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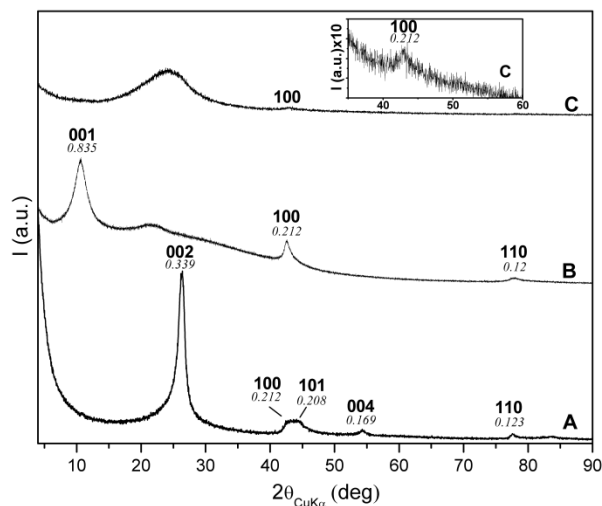
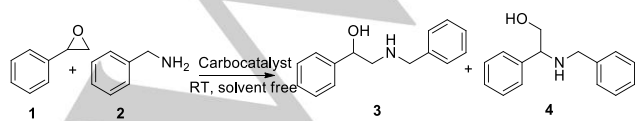


Figure 1. X-ray diffraction pattern (CuK α) of carbon based nanomaterials: (A) high surface area graphite (G); (B) graphite oxide; (C) graphene oxide obtained by ball milling.

The used high surface area graphite (G with a negligible oxygen content, Figure 1A) shows an interlayer distance of 0.339 nm and a high shape anisotropy ($D_{\parallel}/D_{\perp} = 3.1$) [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 of the interlayer distance from 0.339 nm to 0.84 nm (Figure 1B). The correlation length perpendicular to the layers (as evaluated for the first 00/ reflection) decreases from 9.8 nm to 4.2 nm, while the in-plane correlation length (as evaluated for the 100 reflection) remains almost unchanged ($D_{\parallel} \approx 30$ nm), thus leading to a shape anisotropy increase up to $D_{\parallel}/D_{\perp} = 7$. A ball-milling treatment of this graphite oxide sample leaves essentially unaltered the oxygen content (31.4 wt%, excluding water) while largely changes the X-ray diffraction pattern, with complete disappearance of the 001 reflection being replaced by a broad halo centered at $d = 0.37$ nm (Figure 1C). This indicates a complete loss of crystalline order perpendicular to the graphite oxide layers, i.e. the formation of uncorrelated graphene oxide layer. As a consequence the powder of Figure 1C will be thereafter named graphene oxide (GO). This GO sample exhibits acidic functionalities leading to 2.75 pH for GO aqueous suspension at concentration of 5 mg/ml.

The powders characterized in Figure 1 were used as possible catalysts for the ring opening reaction of styrene oxide **1** with benzylamine **2**, chosen as representative substrate. (see Table 1).



Scheme 1. Ring opening reaction of styrene oxide **1** with benzylamine **2** in solvent free conditions.

Table 1. Table 1. Catalysts screening for ring opening reaction of styrene oxide **1** with benzylamine **2**

Entry	Cat(wt%) ^a	t (hours)	Yield(%) ^b	3/4 ratio ^c
1	-	24	traces	-
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 all the reaction mixture.[b] All the yields refer to the chromatographically isolated product. [c] The 3/4 ratio was evaluated on the crude of the reaction by ¹H-NMR spectra

To verify a possible background reaction, an experiment in the absence of catalyst, under solvent-free conditions, was performed. The reaction does not work at all giving just traces of product (entry 1, table 1), thus showing the need of activation for the ring opening reaction.

Data relative to the catalytic activity of GO and G are collected in Table 1, entries 2-4 and 5-6, respectively.

Surprisingly, irrespective of the absence of acidic groups, the graphite sample exhibits a catalytic activity for the aminolysis reaction only slightly lower than for GO, i.e. a carbon material characterized by OH and COOH functional groups (cfr., entries 2 and 5 of Table1).

For both catalysts, by prolonging the reaction time to 48 hours, a very good efficiency was obtained although with a reduction of regioselectivity, possibly due to a competitive autocatalytic pathway of the aminolysis reaction (entries 3 and 6, table 1). In fact, it is quite possible that, by extending the reaction time, the formed product (amino alcohol) could activate by hydrogen bond the epoxide ring opening. This competitive activation could promote the formation of a carbocation intermediate and significantly reduce the regioselective control (for further informations see Supporting Materials).

By reducing the amount of catalyst to 1 wt% (entry 4 table 1), high yields are also reached, although for longer reaction times and by achieving rather low regioselectivity.

Because all literature procedures to activate the epoxide ring opening reaction involve basic or acidic functionalities (Lewis as well as Bronsted acids), the similar catalytic activity of the used graphite and graphene oxide powders is certainly unexpected. This result can be possibly rationalized by invoking a π -stacking interaction between styrene oxide and graphitic surface, already

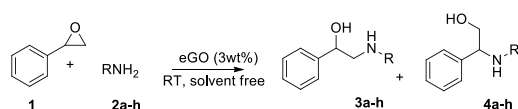
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suggested, also on the basis of DFT calculations, for Mukaiyama-Michael [58] and Friedel-Crafts reactions [63]. π -stacking interactions would be able to activate the epoxy ring opening and favor the nitrogen nucleophilic attack to generate the desired product.

To assess the scope of the procedure, a variety of alkyl and aromatic amines were reacted with styrene oxide **1**. Although

GO and G present similar catalytic activity, for the following study we have mainly used GO, which for the aminolysis reaction of Table 1 leads to slightly higher yields and regioselectivity (entries 3 and 6 of Table 1).

Table 2. Ring opening reaction of epoxide with different amines.



Entry	Epoxide	RNH ₂	t(hours)	Yield (%) ^a	3/4 ratio ^b
1			48	97	80/20
2			16	91	90/10 (3)
3			16	82	>99 (3)
4			16	94	85/15(3)
5			16	95	4/96
6			16	96	5/95(4)
7			16	97	>99(4)
8			24	98	>99(3)
9			2	85	>99(3)

[a]All the yields refer to the chromatographically isolated product.[b] The 3/4 ratio was evaluated on the crude of the reaction by ¹H-NMR spectra.

As reported in Table 2, the reaction proceeds with very good yield and excellent regioselectivity for most amines. It has to be noted that, in most cases (entry 2-3, table 2) the regioselectivity rise up to >90, while only in presence of aromatic residue on the alkyl amine (entry 1, table 2) goes down to 80/20 both in favor of the S_N2 type product. This result could be rationalized hypothesizing that a possible π -stacking interaction between benzylamine and the graphitic surface, could result in a decrease of the rate reaction and favor the less regioselective competitive autocatalytic pathway.

Interesting results were also obtained with secondary amines. In this case, in fact, the steric hindrance of the amines could slow down the nucleophilic attack and favor the competitive regioselective pathway affording to 90/10 and 85/15 **3/4** products ratio for pyrrolidine and piperidine respectively (entries 2 and 4, table 1).

It is worth adding that, as already reported in literature [8, 77], even if morpholine is a secondary amine, better regioselectivity can be obtained with graphene oxide rising up to 99% in favour of product **3c**.

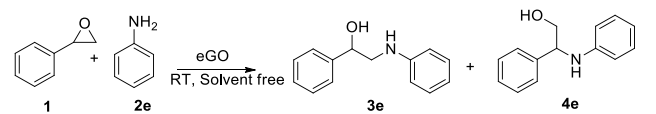
The results obtained with secondary amines are particularly interesting being higher in regioselectivity than the corresponding reactions performed in presence of other solid acid catalysts[29,30].

Moving to aromatic amines, an inversion of regioselectivity is observed as reported in entries 5-7 of table 2. The result obtained is not surprising due to the reduced nucleophilicity of aniline with respect to alkyl amines. In this instance, in fact, the electrophile has to be sufficiently activated throughout a partial carbocation formation, not involved in isomerization or polymerization of styrene oxide, ready to react with aromatic amines in the reaction mixture.

Other electrophiles were finally tested providing in good yield and regioselectivity the S_N2 type product.(entries 8 and 9). It has to be noted that while for the Bisphenol A diglycidyl ether (entry 8) the yield is quantitative, in presence of a not aromatic epoxide as epichlorohydrin, the reaction proceeds with less efficiency. In this case, in fact, no π -stacking interaction can be involved, and just 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 presence of G, proceeds with the same efficiency of the uncatalyzed reaction.(45% yield after 2h), showing the inability of graphite to activate the epoxide ring opening with alkyl substrate.

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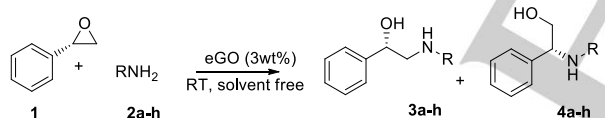
As heterogeneous catalyst, the reusability of GO was investigated by using the addition of aniline **1** to styrene oxide **2** as model reaction. The solid GO, recovered after extraction from the aqueous solution and dried at 60°C overnight, was used without any further treatment. The reaction conditions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

Table 3. Recycling test with styrene oxide **1** and aniline **2e**


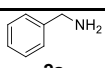

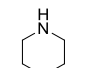
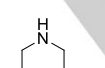

Run	T(°C)/ t(h)	Yield ^a	Regioselectivity (3/4) ^b
1	RT/16	95	4/96
2	RT/16	95	4/96
3	RT/16	96	5/95
4	RT/16	94	5/95
5	RT/16	95	4/96

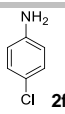
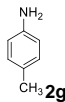
[a]All the yields refer to the chromatographically isolated product.[b] The 3/4 ratio was evaluated on the crude of the reaction by ¹H-NMR spectra.

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



Scheme 2. Enantioselective aminolysis reaction with different amines.

Entry	RNH ₂	t(hours)	Yield (%) ^a	e.e (%)	3/4 ratio ^b
1		48	97	91	80/20
2		16	91	90	90/10 (3)
3		16	82	>99	>99(3)
4		16	94	80	85/15(3)
5		16	95	>99	4/96(4)

6		16	97	95	5/95(4)
7		16	95	>99	>99(4)

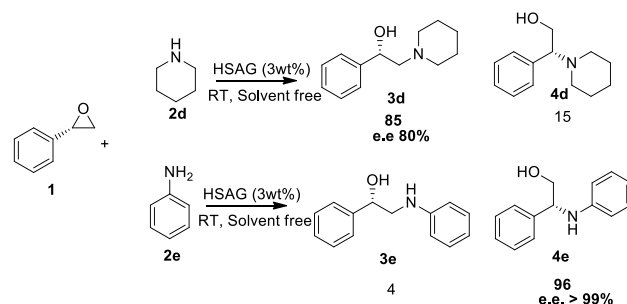
[a] All the yields refer to the chromatographically isolated product.[b]The e.e. was evaluated by HPLC analysis and refers to the major regioisomer. The absolute configuration was determined by comparison with those reported in literature. [c]The 3/4 ratio was evaluated on the crude of the reaction by ¹H-NMR spectra.

As reported in table 4, high enantioselectivity was obtained with all the amines used. The absolute configuration was determined by comparison with HPLC analysis reported in literature [51]. It is worth of adding that, as for the regioselective control, a reduced enantioselectivity for benzylamine, pyrrolidine and piperidine (entries 2 and 4, table 4) was detected, possibly due to competitive autocatalytic pathway responsible of (*S*)-styrene oxide racemization during the reaction.

Rather satisfactory are the results obtained with aromatic amines, by which high enantioselectivity was achieved. Even providing a typical product of S_N1 type reaction, the inversion of configuration detected is deriving from a S_N2 type reaction. It is reasonable to assume that the acidic activation and the π-stacking interaction of graphene oxide surface, lead to a incipient carbocation, that quickly react with aromatic amines without to be involved in racemization competitive pathway.

The slight reduction of enantioselectivity observed for 4-Cl-aniline can be attributed to a light reduction in nucleophilicity due to the presence of chlorine as substituent, while excellent result was obtained for the 4-Me-aniline where, on the contrary, very high enantioselectivity was achieved.

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



Scheme 3. Enantioselective ring opening reaction catalyzed by G

As reported in scheme 3, excellent results were obtained for both the nucleophiles used. As for GO, with alkyl amine as piperidine, the reaction proceeds providing the S_N2 type product

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with good regioselectivity (85/15) and good enantioselectivity for the major one (e.e. 80%). In presence of aromatic amine as aniline, the major product **4e**, was obtained again with excellent enantioselectivity.

It has to be noted that, although in absence of acidic functional groups, the reaction again proceeds with an excellent enantioselectivity for both the amines, alkyl and aromatic. This behavior can be explained assuming that the styrene oxide can be sufficiently activated by π -stacking interaction with graphitic surface becoming susceptible of attack by nucleophile, regardless of it is aliphatic or aromatic amine, while the nucleophilic nature determines the type product, S_N1 or S_N2 , coming from the reaction.

In conclusion, epoxy ring opening reactions by amines are efficiently catalyzed, in solvent and metal free conditions and 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 exhibits many acidic groups. In fact, most catalysts described in the literature for this kind of reaction are based on Lewis or Bronsted acids. Rather surprising instead is the very similar catalytic activity (both with aliphatic and aromatic amines) of high surface area graphite, whose content of atoms different from carbon is lower than 0.1%

These results indicate that, for both graphite and graphene oxide, their extended π system activates styrene oxide by π -stacking interactions. The presence of a large amount of OH and COOH groups on the graphene oxide surface only slightly increases yields and regioselectivities of the studied ring-opening reactions. In presence of a not aromatic epoxide as epichlorohydrin, on the contrary, only GO is catalytically active while G completely loses his activity. Hence, for not aromatic epoxides the catalytic activity only comes from acidic groups on graphene oxide layers.

These heterogeneous catalysts can be recovered and recycled without loss of both efficiency and regioselectivity, thus providing cheap and ecofriendly procedures.

Moreover, these graphite based catalysts for ring opening reactions of non-racemic styrene oxide lead to high enantioselectivity (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 m²/g. Styrene oxide, benzylamine, sulfuric acid, sodium nitrate, potassium permanganate and all the reagents used were purchased from Sigma–Aldrich and used without any further purification. TLC was performed on silica gel 60 F254 0.25 mm on 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. 120 mL of sulfuric acid and 2.5 g of sodium nitrate were introduced into a

2000 mL three-neck round bottomed flask immersed into an ice bath and 5 g of graphite were added, under nitrogen, with a magnetic stirring. After obtaining a uniform dispersion of graphite powders, 15 g of potassium permanganate were added very slowly to minimize the risk of explosion. The reaction mixture was thus heated to 35 °C and stirred for 24 h. The resulting dark green slurry was firstly poured into six liters of deionized water, and then centrifuged at 10000 rpm for 15 min with a Hermle Z 323 K centrifuge. The isolated GO powder was extensively washed with 100 mL of a 5 wt% HCl aqueous solution and subsequently with deionized water. Finally, it was dried at 60 °C for 12 h. The residue sulfur contents 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 minutes with a milling speed of 200 rpm and a ball-to-powder mass ratio of 10 to 1.

General procedure for epoxy ring opening reaction with amines. The reaction was carried out in a vial. Styrene oxide 1 (120.2 mg, 1.0 mmol) and benzylamine (131 μ l, 128.6 mg, 1.2 mmol) were added to the GO catalyst (3 wt% with respect to the mixture) at room temperature. The reaction mixture was stirred at the same temperature for the time indicated. The reaction mixture was extracted with AcOEt and the combined organic phase was dried (MgSO₄) and concentrated. The residue was purified by column chromatography on silica gel in gradient elution with Petroleum Ether/AcOEt to obtain the pure product.

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Keywords: Green • Graphite • Graphene Oxide • Aminolysis • Enantioselective

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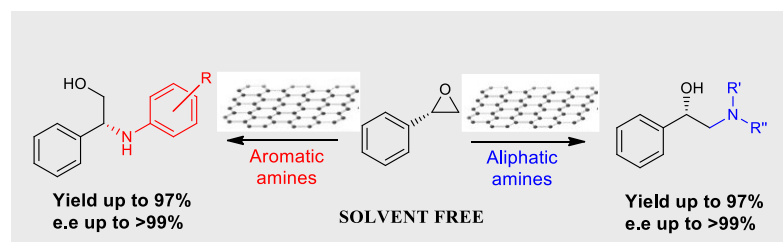
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