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Pinacol Rearrangement and Direct Nucleophilic Substitution of Allylic Alcohols promoted by Graphene Oxide and Graphene Oxide-CO$_2$H

Melania Gómez-Martínez, Alejandro Baeza,* and Diego A. Alonso*

Dedication ((optional))

Abstract: Graphene oxide (GO) and carboxylic acid-functionalized GO (GO-CO$_2$H) have been found to efficiently promote the heterogeneous and environmentally friendly pinacol rearrangement of 1,2-diols and the direct nucleophilic substitution of allylic alcohols. In general, high yields and regioselectivities are obtained in both reactions using 20 wt% of catalyst loading and mild reaction conditions.

Introduction

Graphene (G) is considered as one of the most promising materials in nanotechnology, electrochemistry, and engineering.[1] The significance of graphene in recent years has involved an exponential increase in the number of studies into graphene-based materials. Consequently, remarkable progress has been accomplished in the development of new graphene derivatives as benign, abundant, and readily available catalysts and supports for organic transformations. Among graphene derivatives, highly oxidized graphene oxide (GO),[2] usually produced from the exfoliation of graphite oxide, has emerged as a new class of carbonaceous water-compatible heterogeneous catalyst that promises green and economically viable routes to different families of organic compounds. This is mainly due to its unique aromatic nanostructure with a high surface area and the presence of different oxygen-containing functional groups which can be considered as the active sites operating as soft acids or mild green oxidants. Furthermore, GO is easily functionalized[3] providing to the synthetic chemist a wide variety of graphene-like carbocatalysts.[4] Typical GO-catalyzed organic reactions are substitutions, additions, hydrolyses, condensations, and redox processes.[5]

Graphene oxide's usefulness as a solid state acid catalyst comes from its high acidity (pKa 3-4 in water)[6] as a consequence of the sulfate or sulfonic acid groups present on its surface. Prompted by previously studies on the use of GO as acid catalyst[7] and as a part of our recent interest in carbon-based materials,[8] we report herein the successful use of few-layer GO and a carboxylic acid-functionalized GO (GO-CO$_2$H)[9]

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as heterogeneous carbocation chemistry[10] catalysts, in particular, for the pinacol rearrangement of 1,2-diols and the direct nucleophilic substitution of allylic alcohols. This study constitutes the first general application of graphene-like catalysts to promote these reactions.

Results and Discussion

The pinacol rearrangement is a valuable process for the synthesis of aldehydes or ketones through the elimination of water and skeletal rearrangement of 1,2-diols.[11] The reaction is usually performed employing harsh Brønsted acids, such as H$_2$SO$_4$ or HClO$_4$ although Lewis acids[12] as well as solid catalysts such as zeolites[13] and silicoaluminophosphates,[14] have been also successfully used in this interesting organic transformation. Table 1 shows the properties and materials employed in the present study.

Table 1. Carbonaceous materials.

Material	O/C atomic ratio[a]	%Mn[b]	%S[c]
GO[d]	0.655	0.09	0.8
rGO[d]	0.142	0.16	0
GO-CO$_2$H[d,e]	0.664	0.003	0.2
GiO[f]	1.37	0.05	5.2

[a] Determined by XPS. [b] Determined by ICP-MS. [c] Determined by elemental analysis. [d] Provided by NanoInnova Technologies S.L. [e] 0.7 mmol CO$_2$H/g. [f] Provided by Applynano Solutions S.L.

The GO-catalyzed (20 wt%) pinacol rearrangement of 2,3-diphenylbutane-2,3-diol was selected as model reaction in order to perform the reaction conditions study (Table 2). Using toluene (0.20 M) as solvent at 100 ˚C, only pinacol rearrangement with phenyl migration was observed affording 3,3-diphenylbutan-2-one (1) in a 95% isolated yield. Interestingly, the rearrangement was highly chemoselective and no other side reactions, such as the Nametkin rearrangement,[15] were observed in the crude reaction mixture. The yield of the reaction clearly decreased when reducing the temperature (Table 2, entries 2 and 3). The reaction could also be performed under solvent-less conditions to afford **1** in an 80% yield. No conversion towards **1** was detected when using H$_2$O as reaction medium, being only acetophenone formed (8% conversion by GC) from the retro-

pinacol coupling of the starting diol. This reaction is probably catalyzed by traces of metal oxides, such as MnO_2, contained in the carbocatalyst.[16] Interestingly, microwave irradiation showed a significant reduction in reaction time without compromising performance (Table 2, entry 6). Regarding catalyst study, no conversion was observed in the absence of GO (Table 2, entry 7). The importance for catalysis of the functionality of GO was demonstrated using rGO as catalyst in toluene, which resulted inactive in the pinacol rearrangement (Table 2, entry 8). The carboxylic acid-functionalized GO-CO_2H (0.7 mmol CO_2H/g) was also unproductive as catalyst in the rearrangement. In fact, only acetophenone was detected (10% conversion by GC) as a consequence of the retro-pinacol coupling of the starting material (Table 2, entry 9).
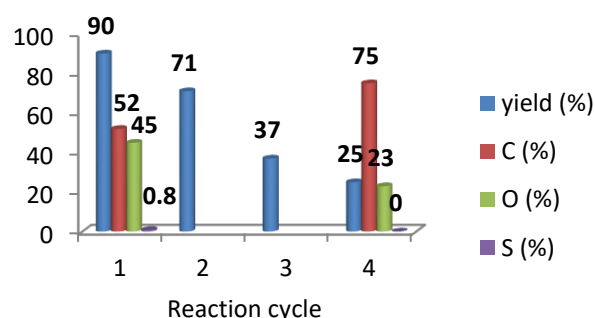
carbocatalyst,[17] this material was not effective in the pinacol rearrangement of 2,3-diphenylbutane-2,3-diol (Table 2, entry 10), probably due to the markedly smaller specific surface area and the absence of reactive sites to be a viable carbocatalyst. This result was confirmed when graphite oxide (GiO)[18] was used as catalyst, which afforded **1** in a 80% isolated yield (Table 2, entry 11). Given the analytical properties of the employed GiO (see Table 1), this result clearly indicated the important contribution to the process of both appropriate acidic sulfate groups (C-OSO_3H) and a high surface area. Catalytic contributions from metallic contaminants must be excluded.[19] To discard the impact in GO of residual manganese originated from its preparation process (0.09% by ICP-MS, see Table 1), the model reaction was carried out in the presence of an excess (0.1 mg) of MnO_2 and $MnCl_2$ (Table 2, entries 12 and 13). The obtained results illustrate that manganese species have no obvious catalytic activity for the pinacol rearrangement under the optimized reaction conditions. Furthermore, rGO (0.16% Mn by ICP-MS, 0% S by elemental analysis, Table 1) had shown no activity in the reaction (Table 2, entry 8) which definitively excluded any metal-catalyzed contribution to the studied process and reinforced the role of the sulfate groups as catalytic active sites in the material.

Table 2. Carbocatalyzed pinacol rearrangement of 2,3-diphenylbutane-2,3-diol. Conditions study.

Entry	Catalyst	Solvent	T (ºC)	Conv. (%)[a]
1	**GO**	**Toluene**	**100**	**95 (93)**
2	GO	Toluene	50	82
3	GO	Toluene	rt	< 5
4	GO	–	100	80
5	GO	H_2O	100	< 5 [8][b]
6	GO	Toluene	100[c]	92
7	–	Toluene	100	< 5
8	rGO	Toluene	100	< 5
9	GO-CO_2H	Toluene	100	< 5 [10][b]
10	Graphite	Toluene	100	< 5
11	GiO	Toluene	100	80
12	MnO_2[d]	Toluene	100	< 5 [15][b]
13	$MnCl_2$[d]	Toluene	100	< 5 [28][b]

[a] Conversion towards **1** determined by ^{1}HNMR. In brackets, isolated yield after flash chromatography. [b] In square brackets, reaction conversion towards acetophenone detected by GC analysis in the crude reaction mixture. [c] Reaction performed under MW irradiation (100 °C, 150 W, 1 h). [d] 0.1 Milligrams were used as catalyst.


Figure 1. GO recyclability and elemental analysis.

To test the recyclability of the catalyst, GO was recovered after centrifugation, washed, and reused in four consecutive reaction runs. As depicted in Figure 1, under the optimized loading reaction conditions, a progressive deactivation of the carbocatalyst was observed. Elemental analysis the GO promoter after the fourth run showed a strong decrease in O and S contents. Since GO-CO_2H did not show any catalytic activity in the rearrangement, this result confirmed the central role of the -OSO_3H groups as active sites for a good catalytic activity in the pinacol rearrangement. In fact, some

These results clearly showed the importance for catalytic activity of a high-surface few-layer system with the appropriate functionality. Although graphite has often been cited as effective

partially nonspecific reduction of GO was observed during the catalytic cycle by XPS.[20,21]

The importance for catalysis of the presence in the material of attached hydrogen sulfate groups was confirmed performing different tests. The first study consisted of the preparation of sulfonated reduced graphene oxide[22] (rGO-SO$_3$H, 3.29 %S by elemental analysis, see SI) from rGO (inactive catalytic material in the pinacol rearrangement). The freshly prepared rGO-SO$_3$H showed good catalytic activity in two reaction cycles under the optimized reaction conditions (Scheme 1).

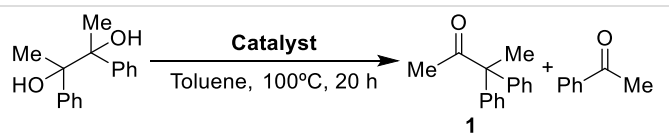| Run **1** (Yield, %)	
1	79
2	72
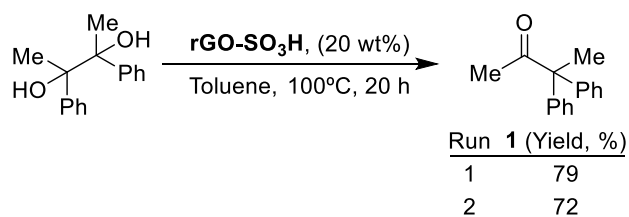
Scheme 1. rGO-SO$_3$H-catalyzed pinacol rearrangement.

We also studied the activity of GO (25 mg) after three washings/extraction cycles with ultrapure water (3 × 10 mL) to remove sulfuric acid impurities. The catalytic activity of the washed GO was tested in the pinacol rearrangement of 2,3-diphenylbutane-2,3-diol resulting an 80% conversion in 20 h. This result demonstrated that water removed some of the not so strongly bonded active OSO$_3$H sites from GO sheets.[23] Overall, the performed control experiments are compatible with the presence of hydrogen sulfate catalytic units bound to GO, as previously demonstrated for other organic transformations.[5f,g]

In order to assess how important was the presence of OSO$_3$H groups for the reaction to proceed, we decided to test the reaction using H$_2$SO$_4$ and pTsOH as homogeneous catalysts in equivalent amounts to that estimated from the elemental analysis of GO (see Table 1).[24] Thus, 2,3-diphenylbutane-2,3-diol was allowed to react under the optimized conditions using sulfuric acid (1.2 mol%) as catalyst. After 20 h no rearranged product was observed (<5% conversion by GC), being only detected a 17% of acetophenone from the retro-pinacol reaction (Table 3, entry 1). On the other hand, pTsOH (1.2 mol%) afforded a 15% conversion of **1** along with a 55% of acetophenone (Table 3, entry 2). Interestingly, when this last reaction was carried out in the presence of 20 wt% of rGO, only starting material was detected by GC analysis, being no retro-pinacol product observed. Thus, the role of the carbonaceous surface on the selectivity of the process was then clearly demonstrated. Finally, good conversion towards **1** were only observed when the reaction was perfomed using 25 mol% of pTsOH as homogeneous catalyst (Table 3, entry 4). All the obtained results seems then to suggest a synergistic effect involving, apart from the anchored OSO$_3$H groups, other active sites present on the GO surface.

Table 4. GO-catalyzed pinacol rearrangement. Substrate scope.

Entry	Starting diol	Structure **No**., yield (%)[a]
1		**1**, 92%
2		**2**, 96%[b]
3		**3**, 95%[c]
4		**4** + **5** 90%[c] (87/13)[d]
5		**6** + **7** 93%[c] (84/16)[d]
6		**8** + **9** 80%[b],[e] (90/10)[f]
7		**10**, 99%[c],[g]
8		**11**, 80%

[a] Isolated yield after flash chromatography. [b] 50 wt% of GO was used. [c] Isolated crude yield, >95% pure by ^{1}HNMR. [d] Ratio determined by ^{1}HNMR over the crude reaction mixture. [e] A 10% of benzophenone was also obtained. [f] Ratio determined by GC over the crude reaction mixture. [g] Reaction performed under neat conditions. An 87% yield of **10** was obtained using toluene as solvent.

Table 3. Pinacol rearrangement of 2,3-diphenylbutane-2,3-diol. Role of the OSO₃H active sites.

| Entry	Catalyst (mol%)	1 (%) / Acetophenone (%)[a]
1	H₂SO₄ (1.2)	3 / 17
2	pTsOH (1.2)	15 / 55
3	pTsOH (1.2) + rGO[b]	0 / 0
4	pTsOH (25)	90 / 0

[a] Reaction conversion determined by GC analysis. [b] 20 wt% of rGO (0% S content, see Table 1) was used.

Next, we tested the pinacol rearrangement of a range of structurally different 1,2-diols under the optimized reaction conditions (Table 4). In general, good to excellent isolated yields were obtained, being in many cases (compounds **3**-**7**, **10**) unnecessary a purification step, since the rearranged crude products were highly pure (>95% by ¹HNMR). As expected when using weak acidic conditions such as those generated by GO, we obtained those products formed from the most stable carbocation involving the expected migration, as in the case of 2-methyl-1,1,3-triphenylpropane-1,2-diol and 3-methoxy-2-methyl-1,1-diphenylpropane-1,2-diol that afforded compounds **2** and **3** in 96 and 95% yield, respectively (Table 4, entries 2 and 3). 2-Methyl-1,1-diphenylpropane-1,2-diol afforded as major product 3,3-diphenylbutan-2-one (**4**) although small amounts of ketone **5** were also detected as a consequence of the good migratory aptitude of the phenyl group (Table 4, entry 4).

Similarly, ketones **6** and **7** were obtained in a 78 and 15% yield, respectively, from the rearrangement of 1,1,2-triphenylethane-1,2-diol (Table 4, entry 5). 1,2,2,2-Tetraphenylethan-1-one was isolated from benzopinacol in a 72% yield through a phenyl 1,2-shift (Table 4, entry 6). In this case benzophenone (10%) and 2,2,3,3-tetraphenyloxirane **9** (8%) were also detected in the crude reaction mixture.[25] Finally, ring-expansion of [1,1'-bi(cyclopentane)]-1,1'-diol and 1-(hydroxydiphenylmethyl)cyclopentan-1-ol afforded spiro[4.5]decan-6-one (**10**) and 2,2-diphenylcyclohexan-1-one (**11**) in 99 and 80% isolated yield, respectively.

Alkene oxides such as **9**, have been proposed as possible intermediates in the pinacol rearrangement of sterically hindered substrates as a consequence of the formation of a transient carbocationic intermediate.[11a] This type of substrates are also starting materials for the Meinwald rearrangement, reaction which is usually catalyzed by Brønsted or Lewis acids.[26] As depicted in Scheme 2, GO also promotes the synthesis of

carbonyl compounds from epoxides. Thus, treatment of 1-phenyl-7-oxabicyclo[4.1.0]heptane with GO (50 wt%) under the optimized conditions led to the formation of 1-phenylcyclopentanecarbaldehyde (**12**) in a 56% isolated yield.
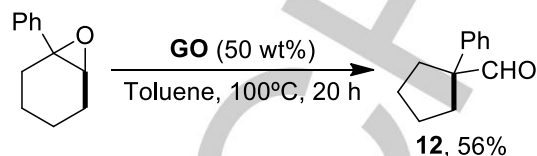
Scheme 2. Meinwald rearrangement.

The assumption of the formation of epoxide **9** as intermediate in the pinacol rearrangement was reinforced performing the GO-catalyzed rearrangement of benzopinacol in the presence of two soft nucleophiles such as TsNH₂ and acetylacetone under the optimized conditions. As depicted in the Scheme 3, apart from unreacted starting material, benzophenone and the rearranged product **8**, we could also detect by GC and ¹H-NMR analyses of the crude reaction mixture compounds **13** and **14** in a 1:1 ratio. The presence of such products can be explained from the direct attack of the nucleophile onto a transient carbocation and/or from the epoxide **9** ring opening (Scheme 3), both possibilities pointing towards the formation of a carbocationic intermediate.
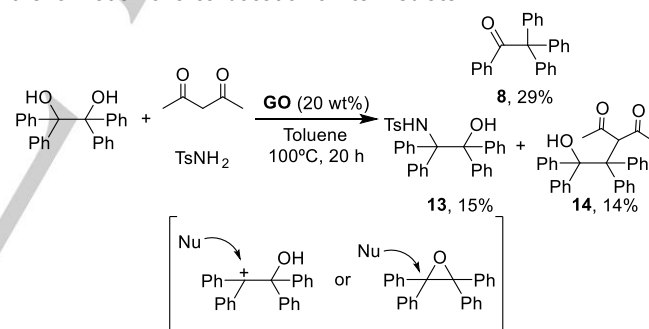
Scheme 3. Pinacol rearrangement mechanism elucidation experiments.

We next turned our attention to the use of the graphene-based carbocatalysts in the intermolecular direct nucleophilic substitution of activated allylic alcohols.[27] This well-known transformation has been studied using different Lewis and Brønsted acids but as far as we know it has no precedent using such carbocatalysts. The reaction, which normally proceeds via a carbocationic intermediate (S_N1 pathway), can be considered as a straightforward and environmentally benign way to get access to new allylic entities, generating water as the sole by-product.[28] As starting point, the reaction between (*E*)-1,3-diphenylprop-2-en-1-ol and *p*-toluensulfonamide as nucleophile in water as solvent[29] was chosen as model reaction in the search for the optimal conditions (Table 5). Firstly, GO (20 wt%)

was selected as catalyst and at 80 °C the corresponding amination product **15** was obtained in good yield (Table 5, entry 1). Attempts to reduce the temperature resulted in detriment of the yield (Table 5, entries 2 and 3). Good yields can be also achieved at 50 °C but using 50 wt% of catalyst. It is worth to say that in the absence of catalyst, the reaction did not work at all (Table 5, entry 4). Next, other carbocatalysts were examined under the above mentioned conditions. Thus, whereas rGO or graphite gave rise to **15** in low yields (Table 5, entries 5 and 7), $GO-CO_2H$ rendered the allylic substitution product in 83% yield (Table 5, entry 6). The fact that rGO produced a low yield in the process, somehow ruled out a possible Mn-catalyzed process, in agreement with the result observed in the pinacol rearrangement. The solvent-free allylic amination reaction was also taken into account using the most active GO-derived catalysts (Table 5, entries 8 and 9). In concordance with the previous results in water, $GO-CO_2H$ turned out to be the best catalyst yielding the corresponding product in 88% yield. The better performance of this catalyst under both reaction conditions can be ascribed to the presence of more Brønsted acidic functionalities on the

Table 5. Carbocatalyzed direct allylic substitution of (*E*)-1,3-diphenylprop-2-en-1-ol with 4-methylbenzenesulfonamide. Conditions study.[a]

Entry	Catalyst	Solvent	T (ºC)	Yield (%)[b]
1	GO	H_2O	80	81 (75)[c]
2	GO	H_2O	50	28/88[d]
3	GO	H_2O	rt	< 5
4	–	H_2O	80	< 10
5	rGO	H_2O	80	30
6	*GO-CO₂H*	*H_2O*	*80*	*83 (82)[c]*
7	Graphite	H_2O	80	20
8	GO	–	80	64
9	*GO-CO₂H*	*–*	*80*	*88 (69)[c]*

[a] Unless otherwise stated the reaction conditions were: alcohol (0.08 mmol), $TsNH_2$ (2 equiv.) in H_2O (0.5 mL). [b] Isolated yield after flash chromatography. [c] In brackets isolated yields using 1.25 equiv. of $TsNH_2$. [d] Reaction performed using 50 wt% of GO.

surface of graphene which facilitates the allylic alcohol activation. The reaction optimization study clearly showed that $GO-CO_2H$ performed the best when using water as solvent and solvent-free conditions (Table 5, entries 6 and 9, respectively). Therefore, these were the conditions of choice for testing other

nucleophiles using (*E*)-1,3-diphenylprop-2-en-1-ol as π-activated allylic alcohol (Table 6). Firstly, 1,3-dicarbonyl compounds were taken into account. Thus, acetyl acetone rendered the corresponding allylic substitution product **16** in high yield even when 1.25 equiv. of nucleophile were employed using both approaches (Table 6, entries 1 and 2). Similarly, 1,3-diphenyl-1,3-propanedione behaved well in both medias producing in moderate yields (*E*)-2-(1,3-diphenylallyl)-1,3-diphenylpropane-1,3-dione (**17**) (Table 6, entries 3 and 4). Asymmetrically substituted 1-phenylbutane-1,3-dione gave rise to the desired product **18** in high yields and a 58:42 diastereomeric mixture, regardless the conditions employed (Table 6, entries 5 and 6).

Next, β-ketoesters were essayed starting with ethyl benzoylacetate. In this case, product **19** was achieved in moderate yields at the best under both conditions (Table 6, entries 7 and 8). Better results were obtained with a cyclic β-keto ester, reaching for compound **20** 80% and 81% yield, respectively (Table 6, entries 9 and 10). Electron-rich aromatics were next evaluated as nucleophiles in a Friedel-Crafts type reaction. Thus, when *N,N*-dimethylaniline was tested, product **21** was obtained as a sole regioisomer in high yields, especially when water was employed as solvent (83%) (Table 6, entries 11 and 12). However, phenol showed an opposite trend. Thus, whereas the reaction barely worked in water (<25%), high yield was obtained under neat conditions (76%) (Table 6, entries 13 and 14).

On the other hand, when allyltrimethylsilane was allowed to react under the optimized conditions, low conversions at best were observed even when higher amounts (3 equiv.) of nucleophile were employed. Intrigued by these results we decided to switch to another carbocatalyst since we speculate a possible consumption of the nucleophile by means of the reaction of some of the multiple oxygen atoms present in the $GO-CO_2H$ surface with the organosilicon species. The assumption seemed to be true, since the reaction employing GO (20 wt%) rendered the corresponding allylation product in high yields under solvent-free conditions (Table 6, entries 15 and 16). In addition, rGO was also tested but no reaction was observed, which point towards the need of acidic functionalities within the graphene surface able to activate both the substrate and the nucleophile and again rules out a possible metal catalyzed process.

In order to study the regiochemical outcome of the reaction, (*E*)-4-phenylbut-3-en-2-ol was submitted to the allylic substitution using acetyl acetone as nucleophile under the above mentioned optimal reaction conditions (Scheme 4). When this more challenging substrate, due to formation of a less stable carbocation, was allowed to react under solvent free conditions, a good 76% yield of a 70:30 regioisomeric mixture was obtained, being the isomer with the most stable olefin **24** (conjugated with the aromatic ring) the major regioisomer. Unfortunately, the reaction in water gave very low yields.
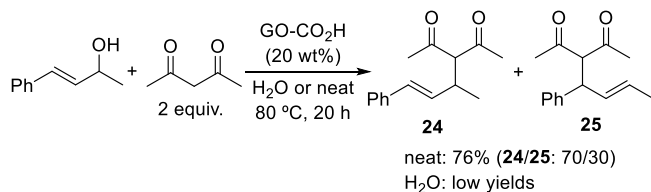
Scheme 4. Allylic substitution. Regiochemical study

Although the direct allylic substitution reaction over allylic alcohols is a well-studied process which proceeds through the formation of the corresponding allylic carbocation,[27] we studied the substitution of (*E*)-1,3-diphenylprop-2-en-1-ol in the presence of equimolecular amounts of 4-methylbenzenesulfonamide and acetylacetone. As depicted in Scheme 5, under the optimized reaction conditions, a 37/63 mixture of compounds **15**/**16** was observed in the crude mixture (^{1}HNMR), supporting that also in the case of GO-CO$_2$H as catalyst, the allylic substitution reaction occurs through fully developed carbocations.
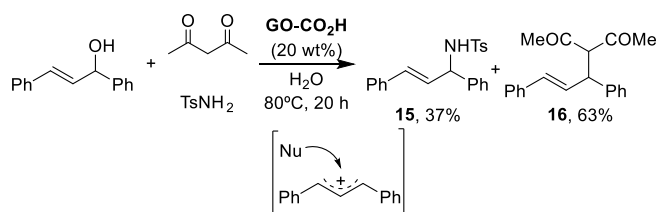
Scheme 5. Allylic substitution mechanism elucidation experiments

The recyclability of the carbonaceous catalyst in the direct allylic substitution was next tackled. For this purpose, the reaction between model allylic alcohol, (*E*)-1,3-diphenylprop-2-en-1-ol and acetyl acetone without solvent and under the optimized conditions (Table 6, entry 2) was chosen. As can be observed in Figure 2, the yield of the product remained almost unaltered until the third cycle. In the fourth run a slight decrease in yield was obtained, which was more accused after the fifth one. As in the case of the pinacol rearrangement, elemental analysis of GO-CO$_2$H after the last fifth run also showed a strong decrease in S contents, and hence a loss of acidic sulfur-containing groups on the catalyst surface, but almost no change on the oxygen content. These results could explain the partial reduction of the catalytic activity, which is by far less accused than in the pinacol rearrangement.
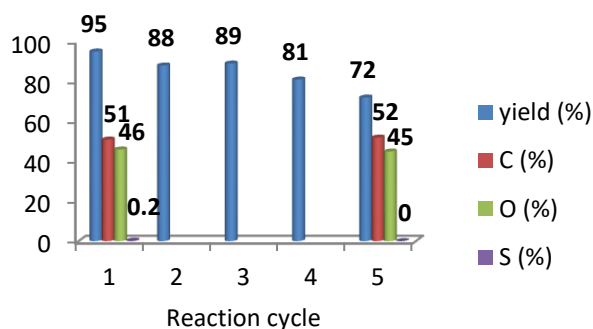
Figure 2. GO-CO$_2$H recyclability and elemental analysis.

Next, we decided to explore the role of the OSO$_3$H and COOH groups in the reaction mechanism of the pinacol rearrangement. For that purpose, we carried out 3 parallel experiments consisting on the optimized reaction between (*E*)-1,3-diphenylprop-2-en-1-ol and acetyl acetone, using the equivalent amount of PhCOOH, H$_2$SO$_4$, and *p*TsOH as homogeneous catalysts according to the calculated carboxylic acid and sulfur contents of GO-CO$_2$H (see Table 1). After 20 h, when using PhCOOH (2.93 mol%) as acid catalyst, the allylation product was obtained in a 18% conversion (GC analysis).[30] By the contrary, H$_2$SO$_4$ (0.26 mol%) and *p*TsOH (0.26 mol%) were able to catalyse the allylation of (*E*)-1,3-diphenylprop-2-en-1-ol in a 68 and 97% conversion, respectively. These results are somehow in concordance with the behaviour observed in the recyclability test, in which the loss of OSO$_3$H groups did not decrease considerably the catalyst activity. From all the performed tests, both sulfonic and carboxylic acid moieties seem

Table 5. Allylic substitution. Nucleophiles scope study.[a]

Entry	Nu	Solvent	Product	Yield (%)[b]
1		H$_2$O	**16**	74
2		neat		90
3		H$_2$O	**17**	60
4		neat		60
5		H$_2$O	**18** (*dr* = 58:42)[c]	91
6		neat		90
7		H$_2$O	**19** (*dr* = 54:46)[c]	60
8		neat		56
9		H$_2$O	**20** (*dr* = 54:46)[c]	80]
10		neat		81
11		H$_2$O	**21**	83
12		neat		75
13		H$_2$O	**22** (*o/p* = 17:83)[c]	<25
14		neat		76
15		H$_2$O	**23**	38[d]
16		neat		85[d]

[a] Unless otherwise stated the reaction conditions were: alcohol (0.3 mmol), nucleophile (1.25 equiv.) in H$_2$O (when corresponding, 2 mL). [b] Isolated yield after flash chromatography. [c] Determined by ^{1}H NMR analysis from the crude reaction mixture. [d] The reaction was performed using GO as catalyst.

to be involved as active sites in the process with the former as main actor.

Conclusions

In summary, we have demonstrated that few-layers GO and functionalized GO-CO$_2$H are able to catalyze the pinacol rearrangement and the direct nucleophilic substitution of allylic alcohols, respectively. Generally good yields and regioselectivities are observed in both processes. Several studies about the active sites of the carbocatalysts revealed no-metal species involvement in these transformations. Instead, analytical and experimental data suggest that the sulfate groups, introduced spontaneously during Hummers oxidation, and the carboxylic acids play a decisive catalytic role in the studied reactions. Only GO-CO$_2$H has shown good recyclability when used in the direct nucleophilic substitution.

Experimental Section

Typical procedure for the carbocatalyzed pinacol rearrangement

A 10 mL glass vessel was charged with GO (20 wt%), the corresponding diol (0.1 mmol) and toluene (0.5 mL). The vessel was sealed with a pressure cap, and the mixture was stirred and heated at 100 ºC for 20 h. Then, the mixture was cooled at room temperature and the mixture was filtered using a syringe equipped with a 4 mm/0.2 µm PTFE filter. The solvent was removed under reduced pressure. The crude residue was purified by flash chromatography (silica gel, Hexane/EtOAc mixtures) to give the pure compound.

Typical procedure for catalyst recovery

Once the reaction was finished, 10 mL of Et$_2$O were added and the resulting mixture was stirred for 5 minutes. After centrifugation (6000 rpm, 15 minutes), the solvent was separated using a syringe equipped with a 4 mm/0.2 µm PTFE syringe filter. The washing/centrifugation sequence was repeated five additional times until no product was detected in the liquid phase by TLC. Then, the residual solvent was completely removed from the carbocatalyst under reduced pressure, being the material further dried at room temperature under vacuum for 12 h. The recovered catalyst was directly used in the next run after adding fresh reagents and solvent. This procedure was repeated for every cycle, being the conversion of the cycles determined by GC chromatography.

Typical procedure for the carbocatalyzed allylation reactions

A 10 mL glass vessel was charged with carbocatalyst GO-CO$_2$H (12.61 mg, 20 wt%), (*E*)-1,3-diphenylprop-2-en-1-ol (63.07 mg, 0.3 mmol, 1eq), and the corresponding nucleophile (0.375 mmol, 1.25 eq), and H$_2$O (2 mL). The vessel was sealed with a pressure cap, and the mixture was stirred and heated at 80 ºC for 20 h. Then, the mixture was cooled at room temperature and EtOAc (4 mL) was added. The resulting two-phase mixture was filtered using a 4 mm/0.2 µm PTFE syringe filter. Then, after phase separation, the aqueous phase was further extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over MgSO$_4$ and concentrated under reduced pressure. The crude residue

was purified by flash chromatography (silica gel, Hexane/EtOAc mixtures) to obtain the corresponding pure allylation products.

The same procedure was carried out under neat conditions.

Typical procedure for catalyst recovery

For the catalyst recovery experiment, acetyl acetone was chosen as nucleophile under solvent-free conditions. Once the reaction was finished, the mixture was diluted with 10 mL of EtOAc and it was stirred for 5 minutes. This mixture was then centrifuged (6000 rpm, 15 minutes) and the solvent was eliminated using a syringe equipped with a 4 mm/0.2 µm PTFE filter. The washing/centrifugation sequence was repeated five additional times until no product was detected in the liquid phase by TLC. The residual solvent present in the catalyst was completely removed under reduced pressure. The recovered carbocatalyst was further dried under vacuum at room temperature and it was directly used in the next reaction cycle after adding fresh reagents. This procedure was repeated for every reaction cycle, being the reaction conversion determined by GC chromatography.

Characterization Data

The physical and spectroscopic data shown below can be taken as representative. For the whole catalysts and products characterization data along with general and other experimental details and NMR charts see supporting information.

3,3,4-triphenylbutan-2-one (2).
Yellow oil; 96% yield; IR: 1703, 1594, 1495, 1446 cm^{-1}; ^{1}HNMR (300 MHz, CDCl$_3$): δ = 2.04 (s, 3H), 3.65 (s, 2H), 6.60 (d, *J* = 7.2 Hz, 2H), 6.92-7.02 (m, 3H), 7.18-7.28 (m, 10H); ^{13}CNMR (75 MHz, CDCl$_3$): δ = 27.4, 43.5, 68.7, 125.9, 127.1, 127.3, 128.0, 129.8, 130.9, 137.7, 140.3, 207.4; MS (EI): *m/z* 301 (*M*$^+$ + 1, 0.2%), 300 (*M*$^+$, 0.6), 258 (22), 257 (100), 209 (14), 179 (65), 178 (46), 165 (27); HRMS: Calcd for C$_{20}$H$_{17}$ (*M*$^+$-MeCO): 257.3484; Found 257.1329.

4-methoxy-3,3-diphenylbutan-2-one (3).
Yellow solid; 95% yield; m.p. 78 ºC; IR: 1709, 1599, 1495, 1484, 1446, 1119, 1109, 1091 cm^{-1}; ^{1}HNMR (300 MHz, CDCl$_3$): δ = 2.15 (s, 3H), 3.33 (s, 3H), 4.20 (s, 2H), 7.18-7.21 (m, 4H), 7.25-7.37 (m, 6H); ^{13}CNMR (75 MHz, CDCl$_3$): δ = 28.1, 59.4, 66.2, 77.5, 127.1, 128.2, 129.0, 140.8, 207.4; MS (EI): *m/z* 255 (*M*$^+$ + 1, 0.1%), 254 (*M*$^+$, 0.3), 220 (4), 211 (25), 181 (21), 179 (48), 178 (33), 166 (11), 165 (55), 105 (17), 77 (12); HRMS: Calcd for C$_{15}$H$_{15}$O (*M*$^+$-MeCO): 211.1117; Found 211.1121.

(*E*)-*N*-(1,3-diphenylallyl)-4-methylbenzenesulfonamide (15).[26]
White solid; 82% yield; ^{1}HNMR (300 MHz, CDCl$_3$): δ = 2.35 (s, 3H), 5.06 (d, *J* = 7.2 Hz, 1H), 5.14 (t, *J* = 6.7 Hz, 1H), 6.10 (dd, *J* = 15.8, 6.6 Hz, 1H), 6.37 (d, *J* = 15.9 Hz, 1H,) 7.15-7.29 (m, 12H), 7.68 (d, *J* = 8.3 Hz, 2H); MS (EI): *m/z* 364 (*M*$^+$ + 1, 0.5%), 363 (*M*$^+$, 2), 208 (100), 193 (12), 130 (11), 115 (18), 104 (35), 103 (10), 91 (42), 77 (13).

(*E*)-3-(1,3-diphenylallyl)pentane-2,4-dione (16).[26]
Off-White solid; 90% yield; ^{1}HNMR (300 MHz, CDCl$_3$): δ = 1.93 (s, 3H), 2.25 (s, 3H), 4.33-4.35 (m, 2H), 6.19 (ddd, *J* = 15.8, 5.1, 2.8 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H,) 7.20-7.34 (m, 10H); MS (EI): *m/z* 249 (*M*+-COCH$_3$, 91%), 274 (44), 232 (30) 231 (11), 194 (11), 193 (29), 191 (17), 189 (10), 178 (25), 128 (11), 115 (68), 91 (100).

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Carbocatalysts for Carbocations. The use of graphene oxide and graphene oxide-CO_2H as readily available carbonaceous materials in processes involving carbocationic intermediates, such as the Pinacol rearrangement and direct nucleophilic substitution is herein disclosed. In general, high yields are obtained in both transformations, being the heterogeneous catalyst recycled up to five times in the case of the allylic substitution reaction.
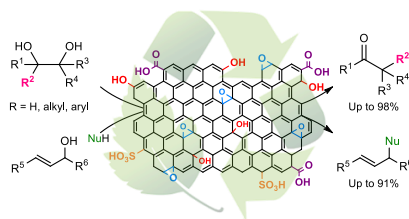
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Pinacol Rearrangement and Direct Nucleophilic Substitution of Allylic Alcohols promoted by Graphene Oxide and Graphene Oxide-CO_2H