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# Graphene-Catalyzed Direct Friedel-Crafts Alkylation Reactions: Mechanism, Selectivity and Synthetic Utility

Feng Hu,[†] Mehulkumar Patel,[†] Feixiang Luo,[‡] Carol Flach,[†] Richard Mendelsohn,[†] Eric Garfunkel,[‡] Huixin He,*[,†] and Michal Szostak*[,†]

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*Supporting Information*

**ABSTRACT:** Transition-metal-catalyzed alkylation reactions of arenes have become a central transformation in organic synthesis. Herein, we report the first general strategy for alkylation of arenes with styrenes and alcohols catalyzed by carbon-based materials, exploiting the unique property of graphenes to produce valuable diarylalkane products in high yields and excellent regioselectivity. The protocol is characterized by a wide substrate scope and excellent functional group tolerance. Notably, this process constitutes the first general application of graphenes to promote direct C–C bond formation utilizing polar functional groups anchored on the GO surface, thus opening the door for an array of functional group alkylations using benign and readily available graphene materials. Mechanistic studies suggest that the reaction proceeds via a tandem catalysis mechanism in which both of the coupling partners are activated by interaction with the GO surface.

## Introduction

Transition-metal-catalyzed alkylation reactions of arenes are among the most important transformations for the production of active pharmaceutical ingredients and fine chemicals that have been extensively utilized in both academic and industrial laboratories on multi ton scale annually (Figure 1).[1] In particular, direct alkylations utilizing alkenes that proceed via an overall structural isomerization (hydroalkylation)[2] and reactions involving alcohols as atom-economic electrophilic coupling partners (Friedel-Crafts reactions)[3] represent attractive processes for direct arene functionalization. Since the seminal work by Murai,[4] remarkable progress has been achieved in direct ortho-selective C–H functionalization of arenes[5] using alkenes with the key contributions from the groups of Murai,[6] Jun,[7] Bergman/Ellman,[8] Yu,[9] and Nakamura,[10] among others.[11] Moreover, elegant Friedel-Crafts-type alkylations and hydroalkylations of unactivated arenes have been reported by the groups of Beller,[12] Rueping,[13] Niggemann,[14] and Hall,[15] among others.[16] Despite these remarkable advances, however, direct alkylation of arenes on industrial scale is currently achieved by means of transition metal catalysis,[17] which utilizes expensive metals, generates toxic waste and suffers from limited natural abundance of transition metals.[18] Transition-metal-free procedures have also been reported;[19,20] however, these methods are not general and suffer from harsh reaction conditions, further limiting their substrate scope. Given the importance of alkylarenes in chemical and pharmaceutical industry,[21] it is clear that there is an urgent need for the development of new, direct and atom-economic strategies for the alkylation reactions of arenes that would additionally meet the principles of green chemistry[22] to enable practical industrial applications.

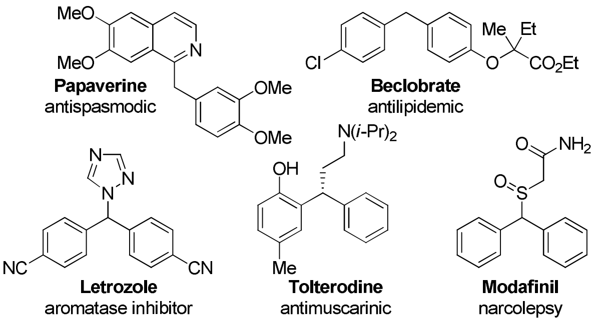


**Figure 1.** Examples of biologically-active diarylmethanes.

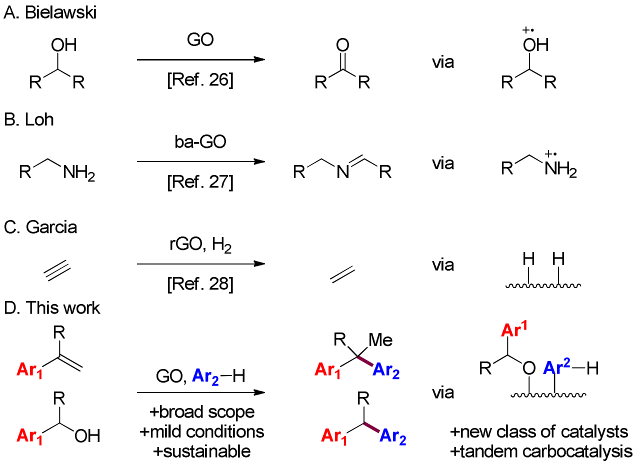


**Figure 2.** (a-c) Graphenes as carbocatalysts. (d) This work: the first graphene-catalyzed direct alkylation of arenes.

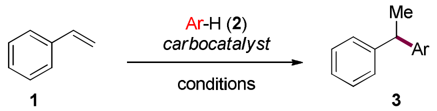
Recently, tremendous progress has been achieved in the development of new carbon-based materials as benign, abundant, and readily available catalysts for chemical synthesis (Figure 2).[23] Importantly, these carbocatalysts merge the benefits of green synthesis with heterogenous reaction conditions, which greatly simplifies work-up conditions and is particularly attractive from an industrial standpoint.[24] The importance of graphene in nanotechnology, electrochemistry, and engineering has been recognized by the 2010 Nobel Prize.[25] In 2010, Bielawski reported the landmark study on using graphene oxide (GO), a water-soluble form of graphene, as a catalyst for chemoselective oxidation of alcohols under mild conditions (Figure 2A).[26] In 2012, Loh reported oxidative dimerization of amines using base-acid treated graphene oxide (ba-GO) (Figure 2B).[27] In this study, base treatment and sequential acidification of functional groups on GO improved the catalyst efficiency in the oxidation of amines via radical cations. In 2014, Garcia reported a seminal study on using graphenes as carbocatalysts for hydrogenation of alkenes (Figure 2C).[28] The authors demonstrated the activation of $H_2$ on the graphene surface, which possibly contains frustrated Lewis acid-base sites. Other studies utilizing GO as a catalyst for oxidation reactions have been reported.[29,30] Collectively, these reports demonstrate that graphene-based materials match or even surpass the efficiency of transition metal catalysts, while at the same time offering a unique metal-free catalysis platform that can be rationally modified by heteroatom doping[31] and surface modification,[32] which heavily benefits from the natural abundance of carbon.[33] However, in contrast to the extensive progress in using graphene-based materials as catalysts for oxidation reactions,[23–30] the application of graphenes to promote synthetically useful C–C bond forming reactions utilizing functional groups on the graphene surface, including acidic sites, that employ unactivated coupling partners[12–16] are severely underdeveloped.[30]

As part of our interest in carbon-based materials,[34] we report herein the first general strategy for alkylation of arenes with styrenes and alcohols[2,3] catalyzed by functionalized graphenes, exploiting the unique property of carbon-based materials[23] to produce valuable diarylalkane products[21] in high yields and excellent regioselectivity. This process constitutes the first general application of graphenes to promote direct C–C bond formation, utilizing polar functional groups anchored on the GO surface,[23–30] which may open the door for industrial arene alkylation using benign, environmentally-friendly and readily available graphene materials. The reaction is characterized by mild conditions, wide substrate scope and excellent functional group tolerance. Mechanistic studies suggest that the reaction proceeds via a tandem catalysis mechanism,[35] in which a discrete carbocation is not formed,[36] and both of the coupling partners are activated by the interaction with the GO surface.[37] Finally, we demonstrate that another advantage of the carbocatalyzed process is its orthogonal chemoselectivity to metal-catalyzed alkylations, which should be of particular value for chemoselective manipulation of functional groups[38] beyond the reaction described herein.

## Results and Discussion

We recently developed a series of novel carbon-based materials.[34] Recognizing the importance of arene alkylation methodologies,[1–18] we questioned whether carbon-based materials can be employed as benign catalysts to promote the coupling of simple arenes with olefins and alcohols. We recognized that if such a process could be developed, it would represent a significant advancement in the synthesis of unsymmetrical diarylalkanes[20,21] via a direct and atom-economical method[22] as well as it would open the door for numerous related transformations using the carbocatalysis platform.[23–30]

**Table 1. Optimization of the Reaction Conditions**[a]

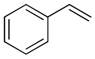
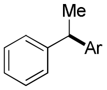
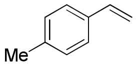
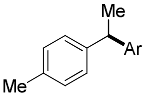
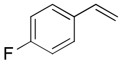
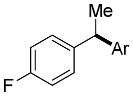
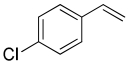
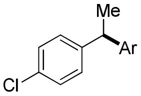
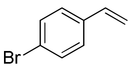
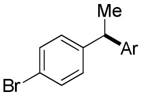
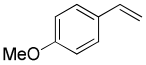
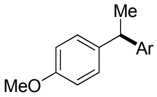
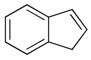
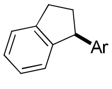
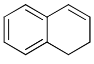
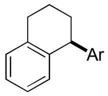
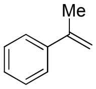
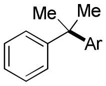
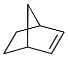
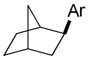


| entry | catalyst | solvent | T (°C) | conv (%) | yield (%) |
|---|---|---|---|---|---|
| 1 | graphite | $CHCl_3$ | 100 | <2 | <2 |
| 2 | h-GO | $CHCl_3$ | 100 | <2 | <2 |
| 3 | r-GO | $CHCl_3$ | 100 | >98 | 37 |
| 4 | GO | $CHCl_3$ | 100 | >98 | >98 |
| 5 | GO | toluene | 100 | >98 | 63 |
| 6 | GO | dioxane | 100 | >98 | 26 |
| 7 | GO | $CH_3CN$ | 100 | 28 | <2 |
| 8 | GO | DMF | 100 | 19 | <2 |
| 9 | GO | $CH_2Cl_2$ | 100 | >98 | 59 |
| 10 | GO | $CHCl_3$ | 75 | >98 | 90 |
| 11 | GO | $CHCl_3$ | 50 | <2 | <2 |
| 12[b] | GO | $CHCl_3$ | 100 | 90 | 88 |
| 13[c] | GO | $CHCl_3$ | 120 | 93 | 22 |
| 14[c,d] | GO | $CHCl_3$ | 120 | >98 | 90 |
| 15[e] | GO | $CHCl_3$ | 100 | >98 | >98 |

[a] Conditions: 1,3-dimethoxybenzene (3.0 equiv), graphene (200 wt%), solvent (0.20 M), 25-120 °C. [b] 50 wt%. [c] 20wt%. [d] 1.0 M [e] Arene (1.2 equiv). See SI for full details.

We initiated our investigations by screening a range of conditions for the alkylation of 1,3-dimethoxybenzene[14] with styrene in the presence of various graphene-based materials (Table 1 and SI). After extensive optimization, we were delighted to find that the proposed alkylation reaction proceeded in an excellent 98% yield in the presence of GO (modified Hummers method, 200 wt%)[34,39] in $CHCl_3$ at 100 °C (branched/linear >98:2; mono-/dialkylation >98:2). Interestingly, utilization of other graphene-based materials, such as microwave-enabled holey-GO (h-GO, which refers to GO with nanoholes existing in its basal plane),[34] and reduced GO (r-GO) provided inferior results (entries 1-4). As expected, no reaction was observed using natural flake graphite. However, to our surprise, h-GO which features similar functionalities as GO also gave low conversion (vide infra). Extensive optimization of the reaction temperature and solvents indicated that the reaction ensues at lower temperatures, but the process is less efficient (entries 4-11). Other solvents could be used, but $CHCl_3$ was found to provide the best results in terms of yield and selectivity. Remarkably, the activator loading could be decreased to 20 wt% with no decrease in the reaction efficiency (entries 12-14). The observed turnover number compares very favorably with the GO-catalyzed oxidation of alcohols.[26] This is noteworthy as the latter process utilizes the carbon-based material as an electron-acceptor rather than proton-donor. Furthermore, high yield and excellent selectivity was observed with an equimolar ratio of the coupling partners, indicating that olefin polymerization[40] does not compete with arene alkylation under these conditions (entry 15). In line with the critical role of carbocatalyst, alkylation products were not detected in the absence of GO (see SI for additional control experiments).

**Table 2. Olefin Scope in the GO-Catalyzed Alkylation of Arenes[a]**

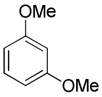
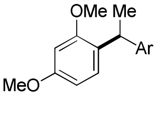
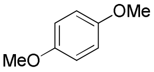
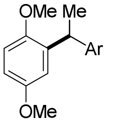
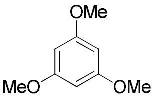
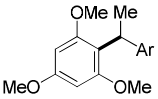
| entry | 1 | olefin | product | yield (%) | regioselectivity (%) |
|---|---|---|---|---|---|
| 1 | **1a** |  |  | 98 | 9:1 |
| 2 | **1b** |  |  | 98 | >20:1 |
| 3 | **1c** |  |  | 99 | 12:1 |
| 4 | **1d** |  |  | 98 | 9:1 |
| 5 | **1e** |  |  | 65 | 10:1 |
| 6 | **1f** |  |  | 60 | >20:1 |
| 7 | **1g** |  |  | 51 | 15:1 |
| 8 | **1h** |  |  | 88 | >20:1 |
| 9 | **1i** |  |  | 62 | >20:1 |
| 10 | **1j** |  |  | 81 | 3:1 |

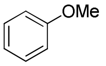
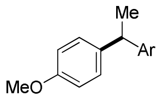
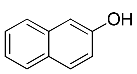
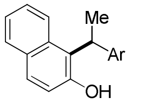
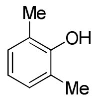
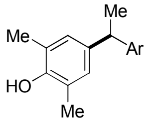
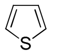
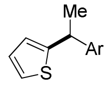
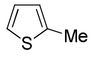
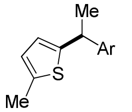
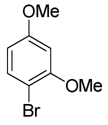
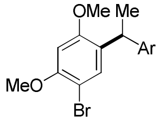
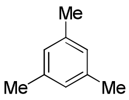
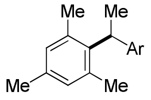
[a] Conditions: olefin (1.0 equiv), 1,3-dimethoxybenzene (3.0 equiv), GO (200 wt%), $CHCl_3$ (0.20 M), 100 °C. See SI for full details.

With the optimized conditions in hand, the preparative scope was next investigated using 1,3-dimethoxybenzene[14] as a standard arene (Table 2). As shown in Table 2, a wide variety of olefins featuring diverse functional groups can be readily arylated. Functional group tolerance is a particularly noteworthy feature of our protocol, including a number of deactivating substituents (**1c**-**1e**)[41] and functional groups poised for further functional group manipulation (**1e**-**f**).[42] Arenes containing neutral (**1b**), electron-deficient (**1c**), halide (**1d**-**1e**) and electron-rich substituents (**1f**) at the para-position give the alkylated products in high yields. Efficient alkylation with indene (**1g**) and dihydronapthalene (**1h**) coupling partners demonstrates that the current protocol can be used to selectively install arenes at the benzylic positions in cyclic ring systems. Disubstituted olefins serve as efficient coupling partners (**1i**). Moreover, we were pleased to find that the reaction is not limited to styrenyl olefins as norbornene underwent coupling to deliver the alkylated product in high yield (**1j**).[43] We note, however, that terminal aliphatic alkenes are quantitatively recovered from the reaction (vide infra), attesting to the high chemoselectivity of the current protocol.[38]

Next, we explored the scope of the arene coupling partner using styrene as a standard olefin (Table 3). As shown, the nucleophile scope is also very broad. As expected, a variety of electron-rich arenes, such as 1,4-dimethoxybenzene (**2b**), 1,3,5-trimethoxybenzene (**2c**), and anisole (**2d**) furnished the desired products in excellent yields. It is worthwhile to note that the use of these nucleophiles provides an efficient route to methoxy-substituted unsymmetrical diarylmethanes which constitute the core of diverse bioactive natural products.[44] Naphthalenes can be coupled in excellent regioselectivity (**2e**). Furthermore, steric-hindrance on the arene component is well-tolerated (**2f**). The synthetic utility of our protocol is further highlighted by the coupling of heteroaromatic rings relevant in pharmaceutical and materials industry (**2g**-**h**).[45] Moreover, high yields are achieved in the alkylation of functionalized aromatic rings featuring aryl bromides poised for cross-coupling functionalization (**2i**),[42] and even non-activated substrates, such as mesitylene (**2j**).[12] High yields and excellent regioselectivity are noteworthy features of our protocol and compare favorably with metal-catalyzed arene alkylations.[12–16] Notably, the products feature unsymmetrical diarylalkane motifs that have found numerous applications as drug pharmacophores.[21]

**Table 3. Arene Scope in the GO-Catalyzed Alkylation of Arenes[a]**

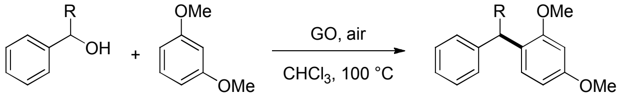
| entry | 2 | arene | product | yield (%) | regioselectivity (%) |
|---|---|---|---|---|---|
| 1 | **2a** |  |  | 98 | 9:1 |
| 2 | **2b** |  |  | 98 | - |
| 3 | **2c** |  |  | 90 | - |

| | | | | | |
|---|---|---|---|---|---|
| 4 | **2d** |  |  | 81 | 11:1 |
| 5 | **2e** |  |  | 71 | >20:1 |
| 6 | **2f** |  |  | 73 | - |
| 7 | **2g** |  |  | 61 | >20:1 |
| 8 | **2h** |  |  | 66 | 11:1 |
| 9 | **2i** |  |  | 78 | >20:1 |
| 10 | **2j** |  |  | 63 | - |

[a]See Table 2. See SI for full details.

On the basis of the results in Tables 2-3, we hypothesized that the alkylation protocol could be extended to alcohols as coupling partners. Friedel-Crafts alkylation with alcohols is regarded as one of the current top research priorities due to beneficial, environmentally-friendly profile of the reaction.[22] In the event, we were pleased to find that the coupling of 1,3-dimethoxybenzene with benzyl alcohols proceeded with excellent efficiency under our optimized conditions (see SI for detailed studies), providing alternative disconnection to the diarylalkane products.

**Scheme 1. GO-Catalyzed Direct Friedel-Crafts Alkylation of Arenes with Alcohols**



**5a**, R = H
**5b**, R = Me
**2a**
**3t**, R = H, 82%
**3a**, R = Me, 95%

To confirm the critical role of graphene in this novel alkylation reaction, extensive characterization of the GO before and after the reactions (referred to in the section below as 'GO' and 'recovered GO') were conducted. (1) To determine if trace quantities of transition metals were involved in these alkylation reactions, the GO material was analyzed by XPS (X-ray photoelectron spectroscopy) and AAS (atomic absorption spectroscopy). XPS analysis indicated less than 50 ppm of trace metal contaminants (detection limit). AAS analysis indicated less than 20 ppb of trace metal contaminants (Mn, Fe, Cu, Cd, Zn, Ni, Pb, Au; detection limit), supporting the metal-free carbocatalyzed alkylation. In addition, our extensive purification process excludes the presence of metallic impurities.[34] (2) Surface area analysis of the recovered GO (methylene blue adsorption method) is calculated to have a surface area (SA) of 367.29 m$^2$ g$^{-1}$, indicating an increase of π-stacking interactions as compared to the parent GO material (SA of 1371.62 m$^2$ g$^{-1}$), consistent with partial reduction to rGO during the reaction.[46] (3) UV-Vis experiments with the GO material used in the alkylation reactions indicated a significant increase of near infrared absorption (at 800 nm, recovered GO, absorption of 0.3055, c = 20 mg mL$^{-1}$, ε = 15.3 mL mg$^{-1}$ cm$^{-1}$; GO, absorption of 0.0634, c = 40 mg mL$^{-1}$; ε = 1.6 mL mg$^{-1}$ cm$^{-1}$) (Figure SI-4). Moreover, compared to the GO starting material, the peak at 236 nm corresponding to the $\pi-\pi^*_{C-C}$ transition has been red-shifted (254 nm), further suggesting recovery of aromatic properties of the GO material (partial reduction to rGO).[47] (4) pH measurements of the GO material used for the alkylation reactions (pH = 3.91 at 0.29 mg mL$^{-1}$) and the recovered GO (pH = 3.95 at 0.29 mg mL$^{-1}$) indicated the slightly acidic nature of the GO carbocatalyst, and no changes in the acidity after the reaction.[48] (5) EDXS analysis (energy-dispersive X-ray spectroscopy) of the GO material before the reaction showed C/O atomic ratio of 1.95, which increased to C/O atomic ratio of 3.46 after the reaction, indicating that some oxygen functionalities have been removed from the GO surface during the reaction (Figure SI-1). (6) Detailed XPS analysis of the GO material before the reaction showed C/O atomic ratio of 1.97, which increased to C/O atomic ratio of 2.96 after the reaction (Figure 3 and Figure SI-2). Furthermore, C1s spectrum of the GO material before and after the reaction indicated a substantial decrease of C–O/C=O functional groups on the GO surface (from 49.4% to 40.9%) with a concomitant increase of the intensity of peaks corresponding to C=C bonds (from 37.0% to 52.0%). Notably, these changes include loss of C=O and C–O functions from the GO surface (epoxide, hydroxyl) during the reaction, as well as the reduction of anhydride and carboxylic acid functional groups on the GO surface (from 13.6% to 7.2%). (7) Film conductivity measurements indicated a substantial increase in conductivity of GO (below the detection limit, 8.7 10$^{-3}$ S m-$^{1}$, 100 MΩ) and recovered GO (3.2 10$^{-2}$ S m$^{-1}$, 27.8 MΩ). (8) FTIR measurements were also performed to analyze the changes in functional groups on the GO surface during the alkylation reactions (Figure SI-3).[49] Compared to the GO starting material, the intensity of signals at 1225, 1204 and 1730 cm$^{-1}$ attributed to C–O (C–OH/C–O–C, hydroxyl/epoxide) and C=O (carbonyl groups), respectively, has significantly decreased. Moreover, complete disappearance of signals at 1413 and 1817 cm$^{-1}$, attributed to carboxylic acid RCOO-H bending vibrations and anhydride C=O stretching vibrations, respectively, was observed. The FTIR spectrum also revealed that the signal at 1633 cm$^{-1}$, attributed to the presence of sp$^2$ C=C bonds, has shifted to 1560 cm$^{-1}$, further indicating the loss of electron withdrawing functional groups from the GO surface. Thus, in agreement with other data, the FTIR spectral information suggests that polar functional groups are removed from the GO surface during the alkylation reactions. (9) Calculation of the carboxylic acid content in the GO starting material used for the alkylation reactions indicated that GO contains 0.66 mol of C/0.34 mol of O, with 13.6% of C (0.090 mol) in the form of carboxylic acid functional groups based on the XPS data.[50] Moreover, the GO material recovered after the alkylation reactions contains 0.75 mol of C and 0.25 mol of O, with 7.2% of C (0.054 mol) in the form of carboxylic acid functional groups. This represents a 2.32 mmol $g^{-1}$ loss of carboxylic acid functional groups during the catalysis (TON ca. 20 based on the carboxylic acid functional groups), consistent with a proton switch mechanism on the graphene surface.[51] It is worthwhile to note that the calculated TON corresponds to the quantity of the catalytically-active functional groups on the material surface rather than to the overall mass of the graphene catalyst as is the case with the wt% descriptor. Overall, the structural changes on the GO surface suggest that GO undergoes partial reduction to rGO during the process, and point towards the importance of oxygen-containing functionalities anchored on the GO surface (hydroxyl, epoxide and carboxylic acid groups).

Based on this consideration, it is reasonable to observe the low conversion efficiency in the presence of rGO and graphite due to dramatically decreased oxygen-containing functionalities (Table 1).[52] On the other hand, holey GO and GO contain similar functional groups. Besides, it was widely reported that holey graphene materials exhibit much improved performance compared to its non-holey counterpart.[27,34a,53] The existence of nanoholes in the basal plane of holey GO not only provides a “short-cut” for efficient mass transport, but also provides more catalytic centers due to increased edges. Thus, in the beginning we were surprised by the low conversion when holey GO was used as the catalyst for the alkylation reaction. However, careful comparison of the detailed XPS and FTIR analysis of GO and h-GO was performed, and we found that holey GO has higher graphitic carbon (46% vs. 37%) and total C/O ratio (2.38 vs. 1.97) than GO as described above. The carboxylic acid content in holey GO is also much higher (23% vs. 13.6%), possibly due to much larger amount of edges in holey GO, where carboxylic acid groups are normally located. However, the relative content of C–O/C=O functional groups is much lower in holey GO (31% vs. 49%).[34a]

In general, the molecular structure of GO is described as defect-free graphitic domains (aromatic regions), which are separated by amorphous-like regions (polar regions), and sometimes feature nanoholes in its basal plane.[47a,54] The high content of graphitic carbon with low percentage of C–O/C=O functional groups indicate that holey GO features larger graphitic domains. Therefore, even though larger amounts of carboxylic acid groups are present on the holey-GO surface, the spatial arrangement of these functional groups is not optimal for the catalytic reaction. In contrast, the smaller aromatic domains and relatively higher density of functional groups on the GO material as described above appear to be beneficial to promote the catalytic C–C coupling.[34b]

We conducted additional studies to gain insight into the mechanism of the alkylation reaction of arenes (Figure 4 and SI). (1) Hammett study performed using differently substituted 4-arylalkene electrophiles showed an excellent correlation (a small $\rho^+$ value of -0.68, $R^2$ = 0.99; $\rho$ value of -1.12, $R^2$ = 0.90),[55] indicating build-up of a partial positive charge at the benzylic carbon in the transition state, which can be compared with a $\rho^+$ value of -5.6 for a classical solvolysis of aryl tosylates via an $S_N1$ mechanism.[56] (2) Moreover, Hammett correlation obtained by plotting the regioselectivity of alkylation of 1,3-dimethoxybenzene with 4-substituted styrenes showed an excellent correlation ($\rho^+$ value of -1.16, $R^2$ = 0.98; $\rho$ value of -1.79, $R^2$ = 0.79), indicating an increase of regioselectivity with a faster reaction rate, which may be characteristic of a diffusion-controlled reaction rate.[57] (3) Intermolecular competition experiments with differently substituted styrenes revealed that steric hindrance plays an important role in these reactions, consistent with coordination to the GO surface. (4) Intermolecular competition experiments with benzylic alcohols revealed that 1° alcohols are intrinsically more reactive substrates than 2° alcohols, which is opposite to the trend observed in the classical Friedel-Crafts reactions.[3] (5) Initial rate measurements revealed that the overall reaction rate does not change significantly over the course of the reaction,[58] and that benzylic alcohols are coupled preferentially to olefins (**1a**, $v_{\text{inital}} = 1.40 \times 10^{-1}$ mM $s^{-1}$; **5b**, $v_{\text{inital}} = 8.03 \times 10^{-1}$ mM $s^{-1}$), consistent with dispersion kinetics and the presence of carbinol as an intermediate in the reaction.[59] No intermediates were detected by careful monitoring of the reaction with either alkene or alcohol coupling partners. (6) Examination of different leaving groups in the alkylation, indicates fully chemoselective reaction for the coupling of alcohol in the presence of acetate, consistent with coordination to the graphene surface.[37] Importantly, this chemoselectivity is opposite from that expected of the classical alkylations mediated by transition metals,[1–16] and should be of particular value for chemoselective manipulation of alcohols by carbon-based materials.[38]

A proposed mechanism for the alkylation of arenes is presented in Scheme 1. The mechanistic studies are consistent with activation of both of the coupling partners by transient anchoring to the graphene surface.[23] The key step involves activation of the olefin coupling partner by hydration, generated in situ from the reduction of graphene, and a transition state in which the arene nucleophile is prepositioned for a concerted C–C bond forming step[60,61] by π-stacking interactions with the carbon-based material to give the alkylated product and regenerate the catalyst after the release of water. Single carbon-based material promotes two distinct steps in the catalytic cycle owing to the presence of polar and aromatic functional groups on a single surface. The fact that the

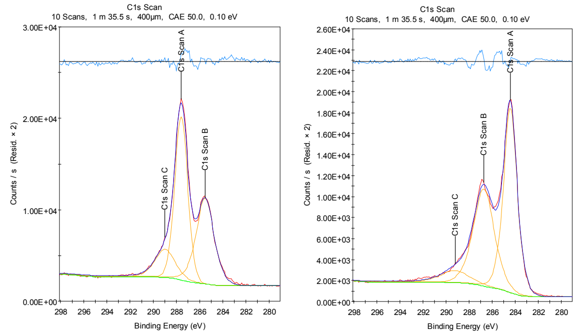


**Figure 3.** (a) X-ray photoelectron spectroscopy C1s spectrum of GO. (b) X-ray photoelectron spectroscopy C1s spectrum of GO after alkylation of 1,3-dimethoxybenzene with styrene.

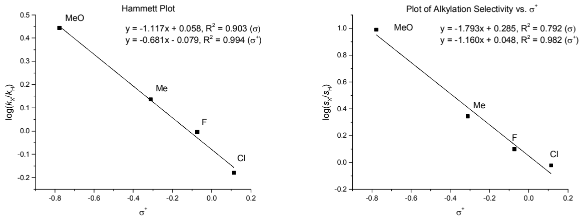
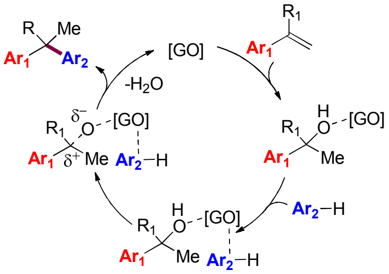


**Figure 4.** (a) Plot of log *k* vs. $\sigma^+$ for the alkylation of 1,3-dimethoxybenzene with styrene. (b) Plot of log *s* (*s* = selectivity) vs. $\sigma^+$ for the alkylation of 1,3-dimethoxybenzene with styrene. [olefin] = 0.20 M. [arene] = 0.60 M. [GO] = 40 mg/mL. *T* = 100 °C.

chemical structures including the spatial arrangement of functional groups on GO surfaces exert significant impact on the catalytic efficiency soundly supports this hypothesis. In this scenario, olefin hydration appears to be a kinetically relevant step in the reaction. An alternative mechanism, involving arene addition to the carbocation cannot be excluded; however, this mechanism is less likely based on the relative reactivity data. A possible mechanism when alcohols are used as substrates involves activation of the alcohol by a transient coordination to the carbocatalyst surface to give a stabilized cation. This mechanism is supported by the relative reactivity in the alkylation using benzylic alcohols and olefins, as well as by the relative reactivity of 1° and 2° alcohols observed in the mechanistic studies. Further studies to elucidate the mechanism are ongoing.

**Scheme 2. Mechanism for the GO-Catalyzed Alkylation of Arenes**



## Conclusions

In conclusion, we have developed a highly efficient alkylation of arenes to give valuable diarylmethanes catalyzed by graphenes. Our data show that graphenes in the absence of any transition metals are effective and general catalysts for the formation of C–C bonds via a novel catalysis mechanism, in which activation of both coupling partners is possible owing to the presence of polar and aromatic functional groups on the graphene surface. Considering the importance of Friedel-Crafts alkylation reactions as well as a wide variety of coupling manifolds for arene functionalization, our study provides a conceptual framework for the use of GO-based materials for large scale industrial catalysis. Notably, our study shows that reactions catalyzed by graphene oxide display orthogonal regio- and chemoselectivity to transition metals, which allows to distinguish between functional groups with similar reactivity. We expect that doping with heteroatoms and control of the polar sites on the surface will result in further enhancement of selectivity and catalytic activity of carbon-based materials. Further mechanistic studies and the extension to a wide variety of π-systems are underway in our laboratories, and these results will be reported shortly.[62]

## ASSOCIATED CONTENT

### Supporting Information

Characterization of catalysts, elemental analysis, experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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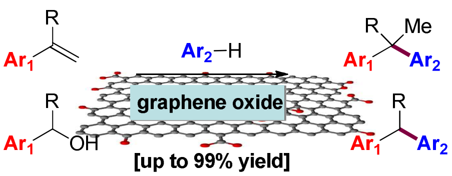
(62) At the present stage of reaction development, the reaction is not compatible with carboxylic acids (full recovery of the starting material); aldehydes (oxidation to carboxylic acids); esters (polymerization). Processes that involve additional functional groups are currently being optimized. The functional group compatibility compares favorably with other recently reported reactions mediated by carbon-based materials.[23,26,27] We believe that further improvement in catalyst efficiency will be achieved by structure modifications and surface engineering of the graphene-based catalyst,[31,32] and these studies will be reported in due course.

*Catalytic alkylation of arenes via tandem carbocatalysis*



- ■***broad scope***
- ■***mild conditions***
- ■***sustainable***
- ■***carbocatalyzed***