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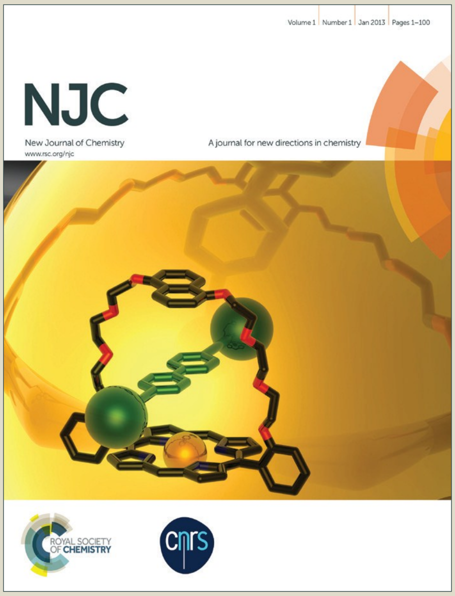

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Graphene oxide: a promising carbocatalyst for the regioselective thiocyanation of aromatic amines, phenols, anisols and enolizable ketones by hydrogen peroxide/KSCN in water

Dariush Khalili[a]

Graphene oxide (GO), as a heterogeneous carbocatalyst catalyzes the direct thiocyanation of a variety of arenes including aromatic amines, phenols, anisols and carbonyl compounds that possessing α-hydrogen in the presence of hydrogen peroxide and KSCN in water as a green media. This procedure is chemoselective, avoids the use of precious metals and toxic solvents and has broad substrate scope. Easy removal from the reaction mixture and recyclability with no loss of activity are the key features of graphene oxide in this catalytic system.

Dedicated to my Doctoral mentor Professor Nasser Iranpoor for celebriting 34 years efforts in organic chemistry

Introduction

Sulfur-containing molecules rank among the most imperative motifs in natural products and biologically important compounds;[1-3] particularly thiocyanates that play a pivotal role in organic synthesis.[4] This functional group serves as precursor for the preparation of many valuable heterocycles including agrochemicals, drugs and dyes.[5-7] Furthermore, thiocyanates could be readily transformed into a more versatile sulfur-bearing groups for the additional structure modification.[8-11] Therefore, the synthesis of thiocyanate compounds is attractive in the view of organic and medicinal chemistry researchers. Arene and α-keto thiocyanates are two main class of thiocyanates which have been more investigated in recent researches in this area. A number of synthetic methods have been developed for the thiocyanation of arenes[12-20] and ketones[21-26] using a variety of reagents under different reaction conditions. However, many of these methods associated with some disadvantages including long reaction time, unsatisfactory yield, use of a large excess of expensive and strong oxidizing agents and toxic solvents. Although these subjects still represent a real challenge, to overcome these issues, the concept of heterogeneous systems can be helpful. Graphene oxide (GO) prepared by exhaustive oxidation of graphite, consists of a variety of oxygen functional groups, including epoxy, hydroxyl, carbonyl, and carboxyl groups.[27] Due to the introduction of these functional groups, GO tends to have acidic (pH 4.5 at 0.1 mg/mL) and be an oxidant.[28, 29] It holds full potentials as a heterogeneous metal-free catalyst or support for several organic transformations[27, 30-39] and therefore this carbocatalyst can be ideal candidate for this purpose. Continuing our studies in developing novel system reagents for construction of thiocyanates[40-42] it was interesting to develop a green protocol for the thiocyanation reaction. Herein an eco-friendly method for the direct thiocyanation of arenes and ketones with H_2O_2/KSCN in water in the presence of graphene oxide as a catalyst is presented.

Results and discussion

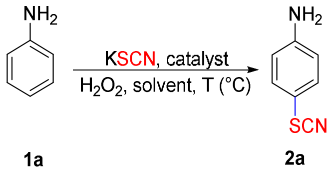
Graphite oxide obtained by oxidation of graphite using the modified Hummers method.[43] Then the graphite oxide aqueous suspension was ultrasonicated to form graphene oxide. The prepared GO was characterized using FT-IR, UV/Vis and Raman spectroscopy and also with AFM and XRD study to establish its authenticity. The FTIR spectrum of GO shows a broad peak appeared at 3429 cm^{-1} in the high frequency area attributed to the stretching mode of O-H bond, reveals the presence of hydroxyl groups in graphene oxide. The band observed at 1720 cm^{-1} was assigned to the carboxyl group. The sharp peak found at 1615 cm^{-1} is a resonance peak that can be assigned to the stretching and bending vibration of OH groups of water molecules adsorbed on graphene oxide. The peak at 1356 cm^{-1} arises from C-OH group. The peak at 1225 cm^{-1} denotes C-O-C stretching and the peak at 1056 cm^{-1} corresponds to the vibrational mode of the C-O group.

The UV-Vis spectrum of graphene oxide has an strong absorption peak at 233 nm, attributed to π-$\pi*$ transition of the C–C conjugated aromatic domains and weak absorption (shoulder) at 305 nm due to n-π $*$ transition of C=O bond (See supporting information). Raman spectroscopy is a standard non-destructive technique that is widely used to obtain structural information about carbon-based materials. Raman spectra of the graphene oxide shows an intense tangential mode (G band) at 1587 cm^{-1}, with a disordered-induced peak (D band) at 1355 cm^{-1}. The G band of graphene oxide broadens and up-shifts in comparison to those observed in graphite (strong G band at 1577 cm^{-1} due to first order scattering of the E_{2g} mode). A possible explanation of this behavior is the presence of isolated double bonds which resonate at higher frequencies. Furthermore, the D band at 1355 cm^{-1} becomes prominent, indicating that the oxidation process influences the size of the in-plane sp^2 domains. On the other hand, because of the breaking of the stacking order which is due to the oxidation reaction, the intensity of the 2D band is smaller after oxidation. The surface image and height profiles of AFM for graphene oxide show the existence of irregularly sheet like morphology and lateral dimension of a few micrometers with the presence of mono layers and few layered of graphene oxide. The presence of a few layers in the sample is due to the aggregation or self assembly of two or three layers of graphene oxide during the drying process in the specimen preparation. The height profiles along the straight line depicted in Figure 4 (supporting information) show that the height of graphene oxide is about 1.45 nm, compatible well with the reported value.

XRD analysis was used to characterize the crystalline nature and phase purity of the as-synthesized graphene oxide. Pure graphite has a strong and sharp diffraction peak at $2\theta = 26.55°$, corresponds to the (002) plane of hexagonal graphite structure with the interlayer spacing of 0.34 nm. After the chemical oxidation and exfoliation into graphene oxide, the 26.55° peak disappeared and a wide diffraction peak at 11.78° appeared instead, revealing a d-spacing of 0.83 nm. An increased interlayer distance between consecutive carbon basal planes is attributed to the intercalation of oxygen functional groups and water molecules into carbon layer structure.

We then started our study by investigating the electrophilic thiocyanation of aniline **1a** (1 mmol) with H_2O_2 (3 mmol)/GO in the presence of KSCN (2.5 mmol) as the model reaction. As graphene oxide can be easily dispersed in H_2O,[44] therefore our initial goal was to use this green media for the thiocyanation reaction. In fact, the use of water as the solvent has gained distinctive importance in the past few years due mainly to the economic and environmental advantages. In the absence of graphene oxide as a catalyst, when aniline was treated with hydrogen peroxide and KSCN at 80 °C, no significant thiocyanation of aniline was observed (Table 1, entry 1). Other carbon promoters, such as natural flake graphite(Table 1, entry 2), hydrazine-reduced graphene oxide[45] (Table 1, entry 3) and activated carbon[46] (Table 1, entry 4) were also examined in this reaction, but the yield of product **2a** were lower after 6 h. A large increase in yield of **2a** was observed using the graphene oxide as catalyst (90%, entry 5). To clarify the role of GO, an experiment was performed. When the model reaction was carried out in the absence of H_2O_2 and in the presence of GO at 80 °C, only trace amounts of product **2a** was obtained (Table 1, entry 6). This result clearly highlight the specific role of GO in this transformation. Decreasing the reaction temperature also resulted in the yield decline of the desired product (entry 7). Compared to other screened solvents such as acetonitrile, THF, ethanol, chloroform and diethyl ether, water appeared to be the best one (entries 5-12). The amount of catalyst was also screened, and 10 mol% loading of GO was found to be optimal; a lower yield was observed when the amount of the catalyst was decreased to 5 mol% (entry 13). Increasing the amount of GO did not increase the yield of **2a** (entry 14). Notably, the employment of NH_4SCN instead of KSCN resulted in a less efficient transformation (entry 15).

Table 1: Optimization of the reaction condition[a]



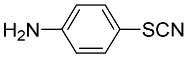
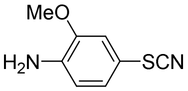
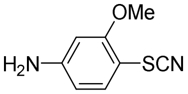
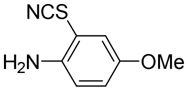
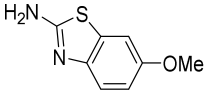
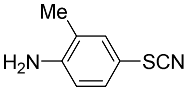
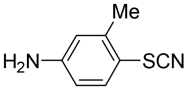
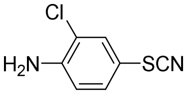
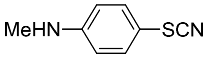
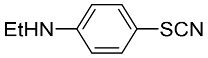
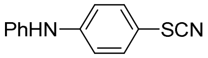
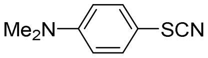
Entry	Catalyst (mol%)	Solvent (condition)	Time	Yield (%)[b]
1[c]	-	H_2O, 80 °C	6 h	<5
2	Graphite (10)	H_2O, 80 °C	6 h	18
3[d]	r-GO (10)	H_2O, 80 °C	6 h	33
4	Activated carbon (10)	H_2O, 80 °C	6 h	56
5[e]	**GO (10)**	**H_2O, 80 °C**	**1 h**	**90**
6[f]	GO (10)	H_2O, 80 °C	1 h	trace
7	GO (10)	H_2O, r.t.	1 h	61
8	GO (10)	CH_3CN, reflux	1 h	85
9	GO (10)	THF, reflux	1 h	71
10	GO (10)	EtOH, reflux	1 h	85
11	GO (10)	$CHCl_3$, reflux	1 h	58
12	GO (10)	Et_2O, reflux	1 h	36
13	GO (5)	H_2O, 80 °C	1 h	74
14	GO (15)	H_2O, 80 °C	1 h	89
15[g]	GO (15)	H_2O, 80 °C	1 h	77

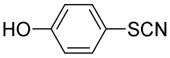
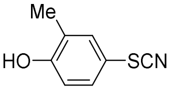
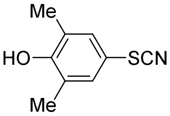
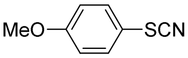
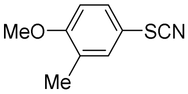
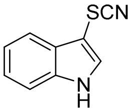
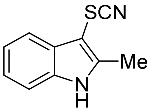
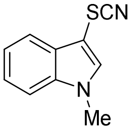
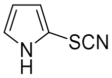
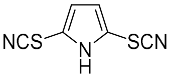
[a]The reactions were performed with aniline (1 mmol), H_2O_2 (35%, 3 mmol), KSCN (2.5 mmol) and carbon promoter (type indicated), solvent (3 mL). [b]Isolated yield. [c]Blank experiment in H_2O without graphene oxide. [d]r-GO = reduced graphene oxide. [e]Bold value signifies best reaction conditions. [f]In the absence of H_2O_2. [g]Reaction performed using NH_4SCN as thiocyanates source.

Comparison of the obtained results confirmed the unique promoting activity of graphene oxide. Under optimal reaction conditions, a study on the substrate scope was carried out, and the results are summarized in Table 2.

To evaluate the amine scope, the preparation of thiocyanate products from aniline derivatives was explored using our standard reaction conditions.

Table 2: Thiocyanation of arenes[a]

Entry	Substrate	Product		Time	Yield (%)[b]
1	Aniline (**1a**)		**2a**	3 h	90
2	2-Methoxyaniline (**1b**)		**2b**	2 h	93
3	3-Methoxyaniline (**1c**)		**2c**	2 h	87
4	4-Methoxyaniline (**1d**)		**2d**	2 h	11
			**2d'**		81
5	2-Methylaniline (**1e**)		**2e**	2 h	89
6	3-Methylaniline (**1f**)		**2f**	2 h	85
7	2-Chloroaniline (**1g**)		**2g**	5 h	80
8	*N*-methylaniline (**1h**)		**2h**	3 h	86
9	*N*-ethylaniline (**1i**)		**2i**	3 h	88
10	*N*-phenylaniline (**1j**)		**2j**	5 h	83
11	*N,N*-dimethylaniline (**1k**)		**2k**	3 h	85

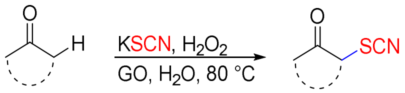
12	Phenol (**1l**)		**2l**	8h	79
13	2-Methylphenol (**1m**)		**2m**	6 h	82
14	2,6-dimethylphenol (**1n**)		**2n**	6 h	86
15	Anisole (**1o**)		**2o**	7 h	78
16	2-Methylanisole (**1p**)		**2p**	6 h	83
17	Indole (**1q**)		**2q**	1 h	90
18	2-Methylindole (**1r**)		**2r**	45 min	95
19	*N*-methylindole (**1s**)		**2s**	2 h	91
20[c]	Pyrrole (**1t**)		**2t**	1 h	83
			**2t'**		9

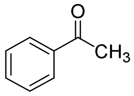
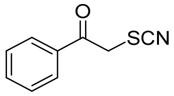
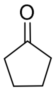
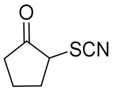
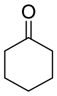
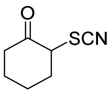
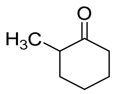
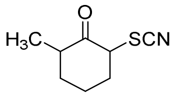
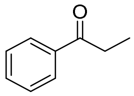
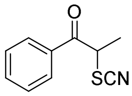
[a]Reagents and conditions: arene (1 mmol), GO (10 mol%), H_2O_2 (35%, 3 mmol), KSCN (2.5 mmol), water (3 mL), 80 °C. [b]Isolated yields after flash column chromatography on silica gel. [c] After 10 h, 9% yield of the bis-adduct was obtained.

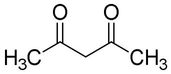
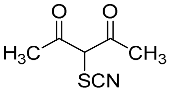
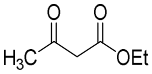
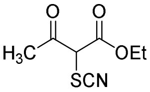
Aniline (**1a**), anilines having electron-donating (**1b-f**) or withdrawing groups (**1g**) can be successfully used in this system reagent (Table 2, entries 1-7). Generally, electron-rich anilines such as 2-methoxy- (**1b)** or 2-methyl- (**1e**) aniline are more prone to electrophilic thiocyanation than electron-deficient substrates such as 2-chloroaniline (**1g**). Utilizing *para*-substituted anilines which contains a blocked 4-position, *ortho* thiocyanation occurred. For example thiocyanation of 4-Methoxyaniline (**1d**) led to the formation of two products, the normally thiocyanated product (**2d**) as a minor product along with cyclization product of **2d** (**2d'**) in a 1:8 ratio (entry 4). This observation is not unprecedented.[47, 48] A range of *N*-substituted anilines such as *N*-methyl- (**1h**), *N*-ethyl- (**1i**), *N*-phenyl- (**1j**) and *N*,*N*-dimethyl (**1k**) anilines also underwent thiocyanation efficiently (Table 2, entries 8-11). These substrates thiocyanated exclusively at their *para* position indicating that this method provides regioselective monothiocyanation. However, treatment of phenols and anisols such as phenol (**1l**), 2-methyl- (**1m**), 2,6-dimethylphenol (**1n**), anisol (**1o**) and 2-methylanisole (**1p**) with KSCN in the presence of H_2O_2/GO resulted in the formation of thiocyanated phenols and anisols (Table 2, entries 12-16). Furthermore, the reactions of indole derivatives (**1q-s**) with this reagent system proceeded efficiently and generated the desired products **2q-s** in 90, 95 and 91% yields, respectively. Pyrrole was also easily transformed into 2-thiocyanato pyrrole **2t** in 1 h (entry 20). In this case a minor amount of 2,5-dithiocyanatopyrrole **2t'** was obtained along with the 2-thiocyanato derivative. We also checked the possibility of the selective synthesis of 2,5-dithiocyanatopyrrole **2t'** under the optimal reaction conditions. In this case, by changing the ratio of KSCN to oxidant (H_2O_2) no improvement in the yield of **2t'** was observed. Prolonged reaction time may also help to increase the yield of 2,5-dithiocyanatopyrrole **2t'**. Therefore the effect of this parameter on the yield of **2t'** was investigated. When the reaction time was extended to 72 h, the yield of the desired product **2t'** reached to 29%. Further increasing the reaction time failed to improve the outcome. Additionally, the effect of temperature was also examined by increasing the reaction temperature to refluxing point of H_2O. At this temperature, product **2t'** was obtained in 37% yield even after a 72 h reaction time. Generally, the possibility of performing the reactions in water, the simple filtration for recycling of the catalyst and using H_2O_2 as an oxidant make this protocol a valid candidate towards the goal of green chemistry.

After establishing the activity of the methodology for thiocyanation of arenes, we attempted to further apply this protocol to the thiocyanation of enolizable ketones. The procedure for synthesizing thiocynated arenes that was described above was expanded to the thiocyanation of ketones (Table 3). Initially, we have attempted the thiocyanation of acetophenone (**3a**) with potassium thiocyanate using H_2O_2 as a green oxidant and graphene oxide as a catalyst in water at 80 °C. The reaction proceeded smoothly to afford the 1-phenyl-2-thiocyanatoethanone (**4a**) in 80% yield (Table 3, entry 1). Similarly, cyclic ketones such as cyclopentanone (**3b**) and cyclohexanone (**3c**) underwent smooth thiocyanation to furnish the corresponding α-thiocyanoketones **4b-c** in good yields (Table 3, entries 2 and 3).

Table 3: Graphene oxide (GO) catalyzed thiocyanation of carbonyl compounds[a]



Entry	Substrate	Product	Time (h)	Yield (%)[b]
1	**3a** 	 **4a**	4	80
2	**3b** 	 **4b**	4	86
3	**3c** 	 **4c**	5	83
4	**3d** 	 **4d**	5	83
5	**3e** 	 **4e**	5	86

6	**3f**			**4f**	4	-[c]
7	**3g**			**4g**	4	-[d]

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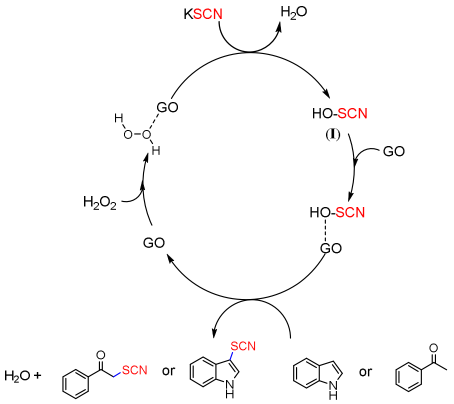
[a]Reaction conditions: carbonyl compound (1 mmol), GO (10 mol%), H_2O_2 (35%, 3 mmol), KSCN (2.5 mmol), water (3 mL) at 80 °C. [b]Isolated yields reported. [c]The product readily decomposed. [d]A mixture of decomposed products was obtained.

Other cyclic ketones, such as 2-methylcyclohexanone (**3d**) also participated well in this reaction (entry 4). Similarly, enolizable acyclic ketones such as 1-phenylpropan-1-one (**3e**) (Table 1, entry 5,) also reacted readily with potassium thiocyanate to give the corresponding α-thiocyanated product **4e** in good yield. The good reactivity of H_2O_2/GO in the thiocyanation of aryl methyl ketones and cyclic ketones prompted us to extend this thiocyanation method for β-dicarbonyl compounds. Thus, pentane-2,4-dione (acetylacetone) (**3f**), upon treatment with our system, afforded a complex mixture of products and our efforts to isolate the product was not successful. This observation is in accordance with those reported for the thiocyanation of β-dicarbonyl compounds.[49] We ratiocinate that since these catalytic reactions must be performed at 80 °C, the product 3-thiocyanatopentane-2,4-dione (**4f**) decomposed readily to a black semisolid. The possibility of applying this catalytic system in the reaction of pentane-2,4-dione (**3f**) with KSCN at 0 °C (at which product **4f** is more stable) was examined. Unfortunately, it was found that the yield of 3-thiocyanatopentane-2,4-dione (**4f**) decreased dramatically to <10% when the reaction temperature was decreased from 80 °C to 0 °C. Under the same condition (80 °C), the transformation of ethyl acetoacetate (**3g**) went to completion at 80 °C in water (as indicated by TLC and IR of the crude product) but attempts to isolate product ethyl α-thiocyanatoacetoacetate (**4g**) using H_2O_2/GO (even at 0 °C) proved to be unsuccessful, yielding a viscous oily mixture of several compounds (Table 3, entry 7). This behavior is due to the rapid decomposition of the product into a complex mixture and is known in the literature.[26, 49] Therefore, we made no further endeavors to purify this mixture.

To the best of our knowledge, thiocyanation of a wide range of substrates including aromatic amines, phenols, anisols and enolizable ketones have not yet been reported and therefore effectiveness for thiocyanation of broad range of substrates is the unique feature of our system. Based on the existing literature[17, 40] and our observations, a plausible mechanism is outlined in Scheme 1. In the recent years, the acidic nature of GO has been ascribed to the presence of surface attached carboxylic functions[29, 33, 39, 50] and also organosulfate group being originated during the oxidation of graphite using Hummers method. These active functional groups specially carboxylic acid groups[50] facilitate the proton transfer reactions due to their acidic properties. The reaction pathway begins with the activation of H_2O_2 by GO as a solid acid. Then, reaction of activated H_2O_2 with KSCN generates HO-SCN[17, 51, 52] which is activated again on subsequent reaction with GO and able to produce thiocyanium ion SCN^+. Eventually, this electrophile is attacked by arene/enolizable ketone to produce the target product and water as a byproduct.



Scheme 1: Plausible reaction mechanism

To confirm this hypothesis we performed a reaction sample in the absence of indole and isolated a yellow precipitate after the removal of GO which could be due to the formation of OH-SCN (**I**). IR analysis of this precipitate shows the characteristic -SCN and -OH bands at 2190 and 3383 cm^{-1}, respectively. Besides, in order to show thiocyanating ability of this precipitate, the reaction of indole (**1q**), with 10 mol% of GO and 2.5 eqiv of this yellow precipitate (**I**) in water was examined. The desired product (**2q**) was obtained in 85% yield at 80 °C. In addition, to prove that the observed reactivity of GO in thiocyanation reaction was not mediated by the residual Mn, which used in the preparation of GO, inductively coupled plasma atomic emission spectroscopy (ICP-AES) was performed on an aqueous dispersion of GO. In particular, the manganese content was measured to be <40 ppb (approximately equivalent to other native metal contaminants found in the material).[53, 54]

We also checked the reusability of the catalyst for the thiocyanation of aniline under optimized conditions (Table 4). It was found that the catalytic system can be effectively reused for up to five cycles without much loss in catalytic activity. It should be noted that during the recycling experiments, the GO catalyst was filtered off after previous run, washed with diethyl ether and warm ethanol for several times and dried in vacuum before starting the next test.

Table 4: Reusability of GO for the thiocyanation of aniline with H_2O_2 and KSCN[a]

Run	1	2	3	4	5
% Yield[b] of **2a**	90	89	89	88	87

[a]Conditions: Aniline (1 mmol), GO (10 mol%), H_2O_2 (35%, 3 mmol), KSCN (2.5 mmol) in water (3 mL) at 80 °C. [b]Isolated yield.

Conclusions

In summary, we have developed a useful, and simple method for the regioselective thiocyanation of wide range of substrates including aromatic amines, phenols, anisols and enolizable ketones using graphene oxide as a reusable catalyst and H_2O_2 as a green oxidant in the presence of KSCN in water. High stability, easy separation from the reaction mixture, and reusability of the catalyst with minimal loss of activity are the major advantages of the catalyst. It can be envisioned that such a cost effective solid acid catalyst holds great potential for a wide range of acid-catalyzed reactions.

Experimental

General information

All chemicals used in this study were analytical grade, commercially available and used without further purification. Graphite (CAS No. 7782-42-5, particle size: <50µm) was purchased from Merck. Most of the products were purified by column chromatography from appropriate solvents and were identified by ^{1}H NMR, ^{13}C NMR and elemental analyses. Progress of the reactions was monitored by TLC using silica gel polygrams SIL G/UV 254 plates. FT-IR spectra were recorded on Shimadzu DR-8001 Spectrometer. NMR spectra were recorded on a Bruker Avance DPX 250 MHz Instrument in $CDCl_3$ or DMSO-*d6* solvents using TMS as internal standard. Chemical shifts were reported in ppm (δ), and coupling constants (*J*), in Hz. Elemental analyses were determined in our department using ThermoFinnigan Flash EA 1112 Series. The surface morphology of graphite and graphene oxide was analyzed by using a Field emission scanning electron microscopy (FESEM, SIGMA, ZEISS, Germany) and Atomic force microscope (AFM, DUALSCOPE^{TM} DS 95-50-E, DME, Denmark). X-ray diffraction (XRD) patterns were recorded on a XRD-D8 (BRUKER, Germany) employing a scanning rate of 0.05° s^{-1} from 10° to 90° with CuKα radiation. The absorbance of graphene oxide solutions was detected by UV-Vis Spectrophotometer (Pharmacia Biotech Ultraspec 4000). Dispersive Raman Microscope (SENTERRA, BRUKER, Germany) was used to characterize functional groups and structural information. The analysis system was equipped with high-energy laser diodes. Melting points were determined in open capillaries with a Galen-Kamp melting point apparatus and are not corrected.

Synthesis of graphene oxide (GO): natural flake graphite (1g, particle size: <50µm; from Merck), $NaNO_3$ (fine mesh, 1.0 g) and H_2SO_4 (48 ml, 98%) was cooled to 0 °C by stirring in an ice bath for 15 min. 3.0 g finely meshed $KMnO_4$ powder was added slowly with vigorous stirring while keeping the temperature below 20 °C (a dark colored mixture was obtained). After 1.5 h, the mixture was warmed to 35±3 °C for 30 min. Then 180 ml water was added slowly, the temperature rose gradually and was kept in 95 °C for another 30 min. Then 400 ml water was added. Finally aqueous solution of hydrogen peroxide (H_2O_2, 35%, 10 mL) was added to convert the unreacted permanganate and manganese dioxide into soluble sulfates. The vibrant yellow mixture was then filtered and the precipitate washed with an aqueous HCl solution (5%, 200 mL). The prepared GO was dialyzed in a dialysis bag for 1 week to ensure the complete removal of acid and residual metal ions. The final precipitate was kept in the dark until further use. For using in the reactions, the graphite oxide aqueous suspension was ultrasonicated (200 mL, 10 mg mL^{-1}) for 1 h to form graphene oxide.

General procedure for the thiocyanation of arenes/enolizable ketones: To a solution of graphene oxide (10 wt%) in H_2O (3 mL), hydrogen peroxide (30%, 3 mmol, 0.26 mL) was added and stirred for 5 min at 80 °C. Then arene/ketone (1 mmol) and KSCN (2.5 mmol, 243 mg) were added to the resulting mixture and stirring was continued at 80 °C until TLC analysis showed the completion of the reaction. After completion of the reaction, the stirring was stopped and the graphene oxide was separated by simple filtration. Then the solution was extracted with ethyl acetate (3×10 mL). The combined extracts were washed sequentially with brine, dried over anhydrous Na_2SO_4 followed by concentrated in vacuo. The resulting crude was purified with column chromatography on silica gel to afford the thiocyanato derivatives. All the products are known compounds and were characterised by the comparison of their spectral data with those reported in the literature (see supporting information).

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Notes and references

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† Electronic Supplementary Information (ESI) available: FT-IR, UV-Vis. Raman spectrum, XRD and AFM image of graphene oxide (GO). The spectral data of all the products are enclosed. See DOI: 10.1039/x0xx00000x

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Graphene oxide: a promising carbocatalyst for the regioselective thiocyanation of aromatic amines, phenols, anisols and enolizable ketones by hydrogen peroxide/KSCN in water

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Graphene oxide as a heterogeneous carbocatalyst catalyzes the direct thiocyanation of a variety of arenes and enolizable carbonyl compounds