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Graphite oxide mediated oxidative aromatization of 1,4-dihydropyridines into pyridine derivatives

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ABSTRACT

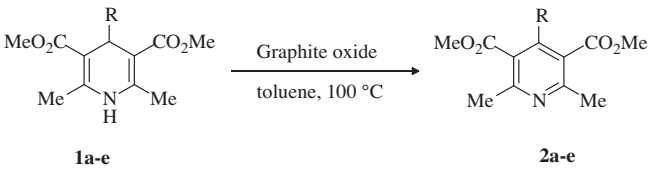
A new approach utilizing graphite oxide as an oxidizing agent is applied for the oxidative aromatization of 1,4-dihydropyridines. Graphite oxide efficiently aromatized Hantzsch 1,4-dihydropyridines into their corresponding pyridine derivatives in excellent yields. The reaction was carried out in toluene at 100 °C.

Due to their low cost and wide variety of reasonably well-defined physicochemical properties and morphologies, carbon-based materials are desirable catalytic agents. However, little systematic attention has been given to their use and behavior as catalysts. Carbon-based materials catalyze a variety of reactions in solution.[1] Medina et al. reported that carbon samples (carbon black, activated carbon, non-activated charcoal, and graphite) catalyzed nitrobenzene reduction with hydrazine.[2] Carbon nanotubes have been shown to dehydrogenate *n*-butane,[3] while C_{60} has successfully been used to catalyze the hydrogenation of nitrobenzene.[4] Graphite oxide (GO) and other chemically modified graphene-based materials (CMGs) have not been explored extensively as catalysts for facilitating synthetically useful transformations. In a recent patent, Lizhu et al. investigated the reduction of graphite oxide to graphene using 1,4-dihydropyridines as hydrogen donors.[5] GO impregnated with palladium nanoparticles displayed very high turnover frequencies in Suzuki–Miyaura coupling reactions.[6] More recently, GO was applied for the oxidation of alcohols and alkenes, and the hydration of various alkynes into their respective aldehydes and ketones in good to excellent yields. The reactions proceed under relatively mild conditions and simple filtration was shown to be a convenient and effective method for catalyst recovery.[7]

The pyridine nucleus is of substantial significance as it is the key component in a variety of bioactive compounds, both naturally occurring and synthetic.[8] Thus, the synthesis of highly substituted pyridines has attracted much attention, and a number of procedures have been developed.[9] Among these, a very convenient approach which attracted our attention was the oxidative aromatization of 1,4-dihydropyridines (1,4-DHPs). These compounds generally undergo oxidative metabolism in the liver by the action of cytochrome P450 to form the corresponding pyridine derivatives.[10] A variety of reagents and methods such as tetrakis-(pyridine)cobalt(II) dichromate,[11] electrochemical catalysis,[12] peroxydisulfate-Co(II),[13] $H_6PMo_9V_3O_{40}$,[14] MnO_2,[15] silica modified sulfuric acid/$NaNO_2$,[16] and silica chromate[17] have been utilized for this oxidative conversion.

Herein, we report on the use of graphite oxide (GO), a readily available and inexpensive material, as a mild and efficient agent for the oxidative aromatization of Hantzsch 1,4-dihydropyridines (Schemes 1 and 2).

The synthesis of graphite oxide typically involves the oxidation of graphite using a modified Hummers method.[18] The relatively



1a-e **2a-e**

R= Ph, *p*-Me-C_6H_4, *p*-Br-C_6H_4, *m*-HO-C_6H_4, *p*-O_2N-C_6H_4

Scheme 1. Graphite oxide mediated oxidative aromatization of symmetrical 1,4-dihydropyridines.

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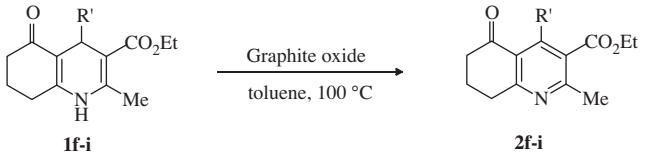

R'=*p*-Cl-C_6H_4, *p*-HOC_6H_4, *p*-MeO-C_6H_4, *m*-EtO-*p*-HO-C_6H_3

Scheme 2. Graphite oxide mediated oxidative aromatization of unsymmetrical 1,4-dihydropyridines.

harsh conditions used in this synthetic protocol introduce a variety of oxygen-containing functionalities (e.g., alcohols, epoxides, and carboxylates) into the material. As a result, GO is slightly acidic[19] and has long been recognized as having strong oxidizing properties.[20]

The GO used in this work was synthesized according to a modified Hummers method.[21,22] The prepared GO was characterized using powder XRD, and UV, and FT-IR spectroscopy to establish its authenticity.[23]

In a typical experimental procedure, a solution of 1,4-dihydropyridine **1a** (1 mmol) in $CHCl_3$ as solvent was heated under reflux for six hours in the presence of graphite oxide (200 wt %). Under these conditions, dimethyl 2,6-dimethyl-4-phenylpyridine-3,5-dicarboxylate (**2a**) was obtained in 32% yield (entry 1, Table 1). It should be noted that increasing the oxidant concentration from 200 to 300 wt % had a negligible effect on the yield of the corresponding pyridine **2a** in $CHCl_3$ (entry 2, Table 1). Performing the reaction in the absence of solvent at 100 °C gave the corresponding pyridine in a high 75% yield (entry 3, Table 1). A high yield was obtained when $CHCl_3$ was replaced by toluene as the solvent. Indeed, the reaction of 1 equiv of 1,4-dihydropyridine **1a** in the presence of 200 wt % GO in toluene at 100 °C gave the corresponding pyridine **2a** in 93% yield after three hours (entry 4, Table 1).

In a similar fashion, various symmetrical and unsymmetrical 1,4-dihydropyridines **1a–e** and **1f–i** reacted smoothly with GO under similar reaction conditions to give the corresponding symmetrical pyridines **2a–e** and unsymmetrical pyridine derivatives **2f–i**, respectively, in 90–96% yields (Schemes 1 and 2). The results are summarized in Table 2. Symmetrical and unsymmetrical 1,4-dihydropyridines containing electron-withdrawing or electron-donating groups on the 4-aryl substituent gave the corresponding pyridine derivatives in excellent yields.

The results obtained using GO as the oxidizing agent are comparable to those previously reported using other oxidants, but with several advantages including short reaction times, high yields, and avoidance of the use of toxic transition metals. Furthermore, GO is easily synthesized from inexpensive and readily available graphite. The utility of this methodology should make this simple technique an attractive addition to the range of procedures already known for this transformation.[11–17]

We also investigated the reusability of the oxidizing agent. After completion of the reaction, the solvent was evaporated, methylene chloride was added and the mixture was filtered through a sintered funnel. GO is insoluble in methylene chloride and could be removed by filtration. The dried recycled oxidant was used three times in consecutive reactions of **1a** with only a 20% loss in the yield, compared to the original experiment, for each run.

Table 1
Effect of the solvent and temperature on the oxidative aromatization of dimethyl 2,6-dimethyl-4-phenyl-1,4-dihydropyridine-3,5-dicarboxylate (**1a**)

Entry	GO (wt %)	Solvent	Time (h)	Yield[a] (%)
1	200	$CHCl_3$ (reflux)	6	32
2	300	$CHCl_3$ (reflux)	6	40
3	200	Solvent-free[b] (100 °C)	7	75
4	200	Toluene (100 °C)	3	93

[a] Isolated yield.
[b] 1,4-Dihydropyridine **1a** was dissolved in $CHCl_3$ and added to GO; the solvent was evaporated from the mixture which was then heated at 100 °C.

Table 2
Synthesis of pyridine derivatives

Entry	R or R′	Product[a]	Yield (%)[b]	Mp (°C)	
				Found	Reported
1	C_6H_4	**2a**	93	136	136–138[24]
2	*p*-Me-C_6H_4	**2b**	90	137–138	137–138[25]
3	*p*-Br-C_6H_4	**2c**[17]	96	139	136–140[17]
4	*m*-HO-C_6H_4	**2d**	92	191–192	—
5	*p*-O_2N-C_6H_4	**2e**	95	148	148[26]
6	*p*-Cl-C_6H_4	**2f**	91	151–152	—
7	*p*-HO-C_6H_4	**2g**[c]	94	134–135	—
8	*p*-MeO-C_6H_4	**2h**[27]	95	196–198	153[27]
9	*p*-HO-*m*-EtO-C_6H_3	**2i**[c]	92	121–122	—

[a] All products were characterized by ^1H NMR and mass spectrometry.[28]
[b] Isolated yields.
[c] When the 1,4-dihydropyridine was not completely soluble in toluene, one drop of DMF was added.

In conclusion, we have developed a novel method using graphite oxide, a cheap and easily available material, for the oxidative aromatization of symmetrical and unsymmetrical 1,4-dihydropyridine derivatives. The reaction is carried out at 100 °C and affords excellent yields of products in short reaction times. The present method has many advantages, including simplicity and generality. Graphite oxide was synthesized from inexpensive graphite using readily available reagents. Further investigations using graphite oxide for other chemical transformations are currently in progress.

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22. Synthesis of graphite oxide using the modified Hummers method[21]: graphite (8 g) was added to a mixture of 98% H_2SO_4 (14 mL), $K_2S_2O_8$ (4 g), and P_2O_5 (4 g), and the mixture was stirred and the solution was kept at 80 °C for 6 h. The resulting preoxidized product was washed with H_2O and dried. CAUTION: The preoxidized product (8 g) was added to 98% H_2SO_4 (180 mL), followed by the slow addition of $KMnO_4$ (24 g) with the temperature kept at <20 °C in order to avoid overheating and explosion. The solution temperature was increased to 35 °C and maintained for 2 h. Next, H_2O (400 mL) was added over 15 min. Further H_2O (1.1 L) was added to dilute the solution, and 30% H_2O_2 (20 mL) was injected into the solution to completely react with the excess $KMnO_4$. A brown solution was obtained which was washed with 1:10 37% HCl: H_2O solution (2 L) in order to remove metal ions and H_2O (2 L). Dried graphite oxide was obtained by centrifugation followed by dehydration on a rotary evaporator under vacuum.
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28. Typical procedure for the oxidation of 1,4-dihydropyridines using graphite oxide: A mixture of symmetrical or unsymmetrical 1,4-dihydropyridine **1a**–**e** or **1f**–**i** (1 mmol) and GO (200 wt %) was stirred at 100 °C in toluene (2 mL) for 3 h. After completion of the reaction as indicated by TLC, the solvent was evaporated and the residue dissolved in CH_2Cl_2 and filtered through a sintered funnel. The filtrate was purified by recrystallization from EtOH.

Dimethyl 4-(3-hydroxyphenyl)-2,6-dimethylpyridine-3,5-dicarboxylate (**2d**), Mp: 191–192 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 2.56 (s, 6H, $2CH_3$), 3.55 (s, 6H, $2OCH_3$), 6.67 (d, J = 7.6 Hz, 1H, Ar), 6.73 (s, 1H, Ar), 6.83 (d, J = 7.6 Hz, 1H, Ar), 7.17 (t, J = 7.8 Hz, 1H, Ar), 8.75 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.86, 52.78, 115.13, 116.48, 120.04, 127.42, 130.11, 137.93, 146.89, 155.95, 156.68, 168.70; MS (EI) (70 eV), m/z (%): 315 (35) $[M]^+$, 284 (20), 252 (100), 224 (42), 196 (24), 59 (24), 29 (22), 15 (18); IR (KBr) ν = 3500, 2953, 1735, 1654, 1558, 1444, 1288, 1031 cm^{-1}; Anal. Calcd for $C_{17}H_{17}NO_5$: C, 64.75; H, 5.43; N, 4.44. Found: C, 64.54; H, 5.40; N, 4.32.

Ethyl 4-(4-chlorophenyl)-2-methyl-5-oxo-5,6,7,8-tetrahydroquinoline-3-carboxylate (**2f**), Mp: 151–152 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.02 (t, J = 7.1 Hz, 3H, CH_3), 2.21 (m, 2H, CH_2), 2.60 (s, 3H, CH_3), 2.64 (t, J = 6.2 Hz, 2H, CH_2), 3.23 (t, J = 6.2 Hz, 2H, CH_2), 4.04 (q, J = 7.1 Hz, 2H, OCH_2), 7.10 (d, J = 8.5 Hz, 2H, Ar), 7.37 (d, J = 8.5 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.08, 21.77, 23.67, 34.04, 40.43, 61.99, 124.17, 128.39, 129.40, 130.61, 134.21, 136.38, 148.01, 158.61, 165.04, 167.68, 197.43; MS (EI) (70 eV), m/z (%): 343 (10) $[M]^+$, 315 (6), 298 (6), 270 (7), 139 (8), 29 (100), 27 (3); IR (KBr) ν = 3425, 3356, 3078, 2887, 1726, 1681, 1544, 1487, 1265, 1219, 1080 cm^{-1}; Anal. Calcd for $C_{19}H_{18}ClNO_3$: C, 66.38; H, 5.28; N, 4.07. Found: C, 65.89; H, 5.12; N, 4.01.

Ethyl 4-(4-hydroxyphenyl)-2-methyl-5-oxo-5,6,7,8-tetrahydroquinoline-3-carbo-xylate (**2g**), Mp: 134–135 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.04 (t, J = 7.1 Hz, 3H, CH_3), 2.20 (m, 2H, CH_2), 2.65 (s, 3H, CH_3), 2.67 (t, J = 6.7 Hz, 2H, CH_2), 3.25 (t, J = 6.1 Hz, 2H, CH_2), 4.06 (q, J = 7.1 Hz, 2H, OCH_2), 6.81 (d, J = 8.5 Hz, 2H, Ar), 7.03 (d, J = 8.5 Hz, 2H, Ar), 8.25 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.13, 21.75, 23.36, 33.81, 40.56, 61.92, 115.43, 124.86, 128.74, 129.31, 131.28, 149.79, 157.22, 158.05, 164.77, 168.17; 197.91; MS (EI) (70 eV), m/z (%): 325 (10) $[M]^+$, 296 (3), 280 (5), 77 (5), 43 (72), 29 (100); IR (KBr) ν = 3091, 3066, 2991, 2947, 1726, 1693, 1602, 1552, 1510, 1442, 1373, 1273, 1224, 1006 cm^{-1}; Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.31. Found: C, 69.66; H, 5.70; N, 4.29.

Ethyl 4-(3-ethoxy-4-hydroxyphenyl)-2-methyl-5-oxo-5,6,7,8-tetrahydroquinoline-3-carboxylate (**2i**), Mp: 121–122 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.03 (t, J = 7.1 Hz, 3H, CH_3), 1.46 (t, J = 6.9 Hz, 3H, CH_3), 2.22 (m, 2H, CH_2), 2.64 (s, 3H, CH_3), 2.65 (br s, 2H, CH_2), 3.24 (t, J = 6.1 Hz, 2H, CH_2), 4.04 (q, J = 7.1 Hz, 2H, OCH_2), 4.10 (br s, 2H, OCH_2), 6.65 (d, J = 8.0 Hz, 1H, Ar), 6.68 (s, 1H, Ar), 6.94 (d, J = 8.0 Hz, 1H, Ar), 7.30 (br s, 1H, OH); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.18, 15.18, 21.82, 23.54, 34.04, 40.59, 61.90, 64.87, 112.20, 114.33, 121.10, 124.69, 129.47, 131.14, 145.66, 146.01, 149.23, 158.15, 164.83, 168.19, 197.49; MS (EI), (70 eV) m/z (%): 369 (10) $[M]^+$, 313 (15), 267 (15), 43 (25), 29 (100); IR (KBr) ν = 3360, 2985, 2937, 2885, 1730, 1699, 1647, 1598, 1512, 1429, 1269, 1222, 1035 cm^{-1}; Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.28; H, 6.28; N, 3.79. Found: C, 67.79; H, 6.06; N, 3.68.