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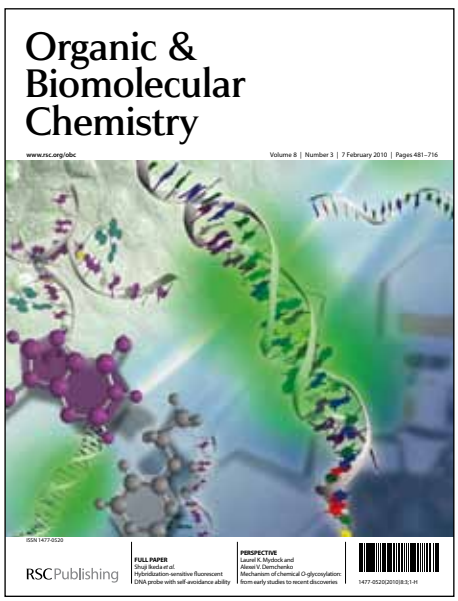

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DDQ-Promoted direct Transformation of Benzyl Hydrocarbons to Amides via a tandem reaction of CDC reaction and Backmann rearrangement

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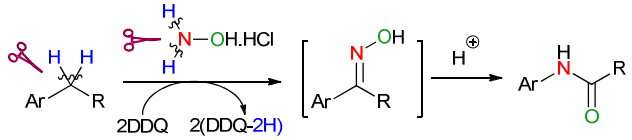
A atom-efficient and transition metal-free approach to amides from corresponding benzyl hydrocarbons through C-H and C-C bond cleavage has been developed. Mechanistic studies have shown that a DDQ-Promoted cross-dehydrogenative-coupling (CDC) reaction and the subsequent oxidation and rearrangement are involved in this transformation.

The atom-efficient and green methodologies for the construction of amide bonds is a long-standing interest and a challenge in both research and industrial chemistry due to the prevalence of this group in biologically active molecules, agrochemicals and pharmaceuticals.[1] In the past several decades, several general strategies toward the synthesis of amide bonds have been explored. The most prevalent route for amide bond formation relies heavily upon the condensation of an amine with activated carboxylic acid derivatives.[2] Other methodologies to access amides include oxidative amidation of aldehydes,[3] ketones,[4] alcohols,[5] amines,[6] Beckmann rearrangement,[7] Schmidt rearrangement,[8] aminocarbonylation of haloarenes, alkenes, and alkynes,[9] Staudinger ligation.[10] Recently, the C-H functionalization has also been employed for amide synthesis, which has attracted considerable attention and been the focus of a significant number of studies.[11] However, the development of novel methods for the preparation of amides through direct C-H or C-C bond activation (cleavage) is still an extremely attractive yet challenging task.

It is worthy of note that only a few approaches to nitrogen-containing compounds from hydrocarbon molecules have been reported.[12-17] In 2005, Chang's group[13] and Fokin's group[14] have reported copper(I) ions efficiently catalyze the direct formation of N-acylsulfonamides from alkynes and sulfonyl azides in the presence of water. In 2006, Che's group demonstrated that manganese porphyrins were efficient catalysts for the oxidation of alkynes to amides in aqueous medium.[15] Recently, Jiao Ning's group have developed a FeCl2-catalyzed cleavage of C-H or C-C bond cleavage for the direct synthesis of various arylamines from benzyl hydrocarbons.[16] In 2011, Their group also reported a FeCl2-catalyzed transformation of diarylmethane reacted with azides into corresponding amides in the presence of DDQ.[17] However, the atom-efficient and transition metal-free method for amide formation from corresponding benzyl hydrocarbons have been studied sporadically. Herein, we demonstrate a novel and direct transformation of benzyl hydrocarbons into corresponding amides via a tandem reaction of CDC reaction and Backmann rearrangement in the presence of hydroxylamine hydrochloride and DDQ (Scheme 1).



Scheme 1. DDQ-promoted transformation of benzyl hydrocarbons into amides

To begin our study, 1, 3-diphenylpropene **1a** and hydroxylamine hydrochloride were chosen as the model substrates, DDQ was used as the oxidant to examine suitable reaction conditions (Table 1). A number of solvents including CH_3CN, CH_3CN/HCOOH (1:1), DCE, 1, 4-dioxane, DMF, THF and CH_3NO_2 were screened in the presence of PPA at 80°C (Table 1, entries 1-9). Moderate yields of the desired product **2a** were obtained using Toluene, CH_3CN, DCE, 1, 4-dioxane and CH_3NO_2 as a solvent (Table 1, entries 2-5). Moreover, considerable amounts of undesired products were formed and resulted in lower yields using DMF and THF, (Table 1, entries 6 and 7). High yield of the desired product **2a** was obtained using CH_3CN as a solvent (Table 1, entry 8). Dramatically, when CH_3CN/HCOOH (1:1) instead of CH_3CN was used as the solvent, **2a** was obtained in the highest yield of 83% (Table 1, entry 9). To establish the solvent condition that improve the reactivity, Several acids such as *p*-TSA, TsCl, H_2SO_4, CF_3COOH, $MeSO_3H$, $ZnCl_2$ were tested in CH_3CN at 80°C (Table 1, entries 10-15), the desired product could be obtained in 51%-74% yield. Only 43% desired product was

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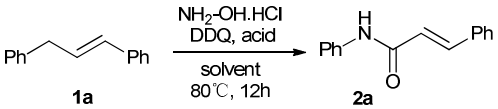
Table 1. Screening of reaction conditions.[a]



Entry	Acid	Solvent	Oxide	Yield (%)[e]
1	PPA	-[c]	DDQ	48
2	PPA	DCE	DDQ	52
3	PPA	Toluene	DDQ	45
4	PPA	1,4-Dioxane	DDQ	40
5	PPA	CH_3NO_2	DDQ	62
6	PPA	THF	DDQ	30
7	PPA	DMF	DDQ	26
8	PPA	MeCN	DDQ	78
9	PPA	MeCN/HCOOH	DDQ	83
10	-[b]	MeCN/HCOOH	DDQ	43
11	*P*-TSA	MeCN/HCOOH	DDQ	74
12	TsCl	MeCN/HCOOH	DDQ	73
13	H_2SO_4	MeCN/HCOOH	DDQ	54
14	$MeSO_3H$	MeCN/HCOOH	DDQ	71
15	$ZnCl_2$	MeCN/HCOOH	DDQ	51
16	PPA	MeCN/HCOOH	DDQ (2equiv)	61
17	PPA	MeCN/HCOOH	DDQ (1equiv)	23
18	PPA	MeCN/HCOOH	-[d]	N.D.

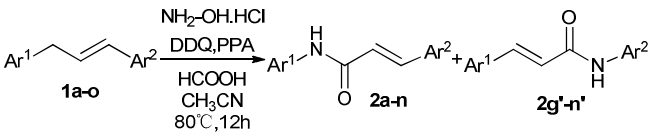
[a] Reaction conditions: **1a** (0.5 mmol), $NH_2OH.HCl$ (1.5 mmol), DDQ(1.5 mmol), acid(0.15 mmol), solvent (1.5 mL), co-solvent(1.5 mL), stirred at 80 °C over 12 h. [b] No addition of acid. [c] No addition of solvent. [d] No addition of DDQ. [e] Isolated yield. DDQ=2,3-dichloro-5,6-dicyano-1,4-benzoquinone, PPA= Polyphosphoric acid.

isolated in the absence of acid (Table 1, entry 10). PPA as the acid showed relative higher efficiency compared with other acids and thus was chosen as the acid for further optimization. The ratios of 1, 3-diphenylpropene to DDQ were also been examined. It was found that decreasing the amount of DDQ resulted in reduced yields (Table 1, entries 9, 16-18). In addition, **2a** was not observed in the absence of DDQ (Table 1, entry 18). The result was better when 1, 3-diphenylpropene/DDQ = 1:3 (Table 1, entry 9). Therefore, we chose 1, 3-diphenylpropene together with hydroxylamine hydrochloride (3 equiv) and DDQ (3 equiv) in CH_3CN/HCOOH (1:1) at 80 °C for 12 h as our optimized reaction conditions.

Based on the above study, various substrates were subjected to the reaction under the optimized conditions (Table 2). To our delight, the reaction can serve as a really general 1, 3-diarylpropene to the syntheses of various substituted acrylamides, affording moderate to excellent yields. For 1, 3-diarylpropenes bearing electron-donating substituents like methyl group on the aromatic ring, the reactions proceeded smoothly to afford the desired products with moderate to high yields (64-89%) (Table 2, entries 2, 7-8 and 13). Surprisingly, when the substrates bearing para-methoxyl groups on the aromatic ring were employed, no acrylamides products were generated and *p*-Anisonitrile was detected (Table 2, entries 3 and 9). We speculated that *p*-Anisonitrile may be generated by abnormal Beckmann Rearrangement of the intermediate oximes (Scheme 3).[18] Notably electron-withdrawing substituents at different positions of the aromatic rings (para-, meta- and ortho-) were also compatible with the process and did not affect the efficiency of the reaction (Table 2, entries 4-6, 10-12 and 14-15). However, as for the unsymmetrically substituted substrates with two different aromatic rings, the corresponding products consisting of regioisomers were formed (Table 2, entries 7-15). The regioselectivity is more likely to originate from the allylic cation rearrangement between the α- and γ-positions under the reaction conditions, and the incoming nucleophile attacked at the original allylic or γ-position to form the isomerized products.[19]

Encouraged by the above results, we further investigated the reactions between diarylmethane and hydroxylamine hydr-

Table 2. Direct transformation of 1, 3-diarylpropenes **1** into the acrylamides **2** and **2'**.[a]



entry	Ar^1, Ar^2	product	Yield (%)[b]
1	C_6H_5, C_6H_5 **1a**	**2a**	83
2	4-$CH_3C_6H_4$, 4-$CH_3C_6H_4$ **1b**	**2b**	89
3	4-$CH_3OC_6H_4$, 4-$CH_3OC_6H_4$ **1c**	**2c**	-[c]
4	4-FC_6H_4, 4-FC_6H_4 **1d**	**2d**	78
5	4-ClC_6H_4, 4-ClC_6H_4 **1e**	**2e**	85
6	4-BrC_6H_4, 4-BrC_6H_4 **1f**	**2f**	82
7	4-$CH_3C_6H_4$, C_6H_5 **1g**	**2g, 2g'**	86 (2:1)
8	2-$CH_3C_6H_4$, C_6H_5 **1h**	**2h, 2h'**	64 (1.6:1)
9	4-$CH_3OC_6H_4$, C_6H_5 **1i**	**2i**	-[c]
10	3-$CF_3C_6H_4$, C_6H_5 **1j**	**2j, 2j'**	75 (1.4:1)
11	3-BrC_6H_4, C_6H_5 **1k**	**2k, 2k'**	68 (3.3:1)
12	4-BrC_6H_4, C_6H_5 **1L**	**2l, 2l'**	83 (1.1:1)
13	C_6H_5, 4-$CH_3C_6H_4$ **1m**	**2g, 2g'**	88 (4.4:1)
14	C_6H_5, 4-FC_6H_4 **1n**	**2n, 2n'**	76 (1.1:1)
15	C_6H_5, 4-BrC_6H_4 **1o**	**2l, 2l'**	85 (1.3:1)

[a] Reaction conditions: **1** (0.5 mmol), $NH_2OH.HCl$ (1.5 mmol), DDQ(1.5 mmol), PPA(0.15 mmol), HCOOH(1.5 mL), MeCN(1.5 mL) stirred at 80 °C for 12h. [b] Yield of isolated product. [c] *p*-Anisonitrile was detected.

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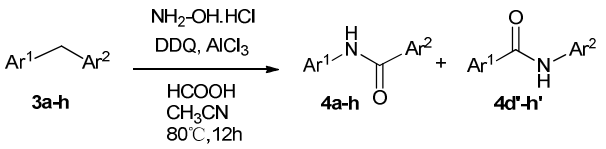
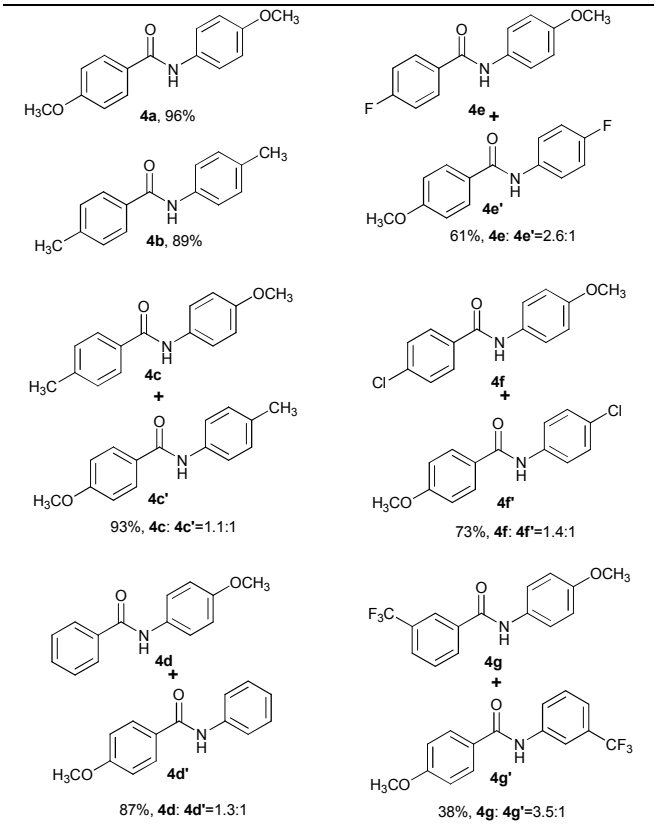
ochloride. A variety of electron-rich aromatic substrates could successfully afford the corresponding amides in moderate to good yields (Table 3). Electronic effect played an important role in the reaction. The diphenylmethane substrates bearing electron-donating groups on the phenyl ring gave the desired products with good yields, especially excellent yields were obtained when the two phenyl rings of the substrate had methyl or/ and methoxyl groups respectively (Table 3, **4a**-**4c**). Electron-withdrawing groups on the diphenylmethane decreased the yields considerably (Table 3, **4e**-**4g**), presumably because they destabilize the proposed methylenyl cation intermediate generated by oxidation. When unsymmetric diphenylmethanes were employed, two regioisomers were obtained with the regioselectivities (Table 3, **4c**-**4g**). It was found that the stronger the electron-withdrawing effect of the substituent was, the higher the ratio of the isomerized products would be.

To elucidate the mechanism and gain insight into this novel reaction, several control experiments were also conducted (Scheme 2). When the direct CDC reaction of 1, 3-diphenylpropene **1a** (0.5 mmol) and NH_2-OH.HCl (3 equiv) and DDQ (1 equiv) was carried out in room temperature, the desired C–N bond coupling product **5a** was produced in 97% yield and the C–O bond coupling product was not observed (Eq. 1). A small amount of 1, 3-diphenylpropene dimer was simultaneously detected, which implied the coupling reaction may proceed through a single-electron-transfer (SET) process.[20] In addition, when the reaction of **5a** (0.5 mmol) and DDQ (2 equiv) was carried out at 80 °C, the corresponding oxime **6a** was produced in 98% yield (Eq. 2). Then the chalcone oxime **6a** could be cleanly converted to **2a** in 91% yield at 80 °C by the Beckmann Rearrangement (Eq. 3). All of these results suggest that the pathway for the formation of acrylamide is likely to undergo a CDC reaction process with a subsequent tandem oxidation and Beckmann rearrangement rather than the oxidation of 1, 3-diphenylpropene to chalcone.

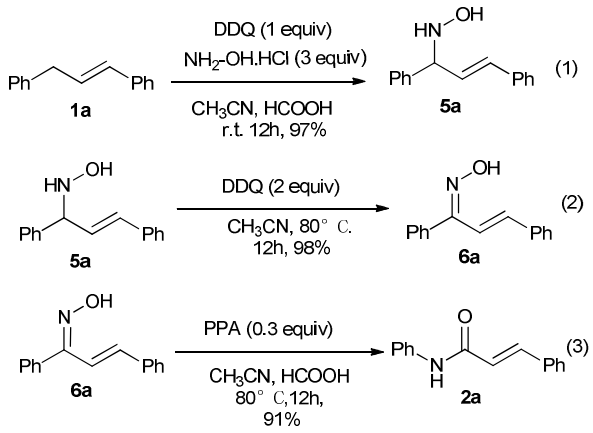
On the basis of the above experimental observations, a plausible mechanism for this transformation is hypothesized (Scheme 3).[19-21] Initially, the reaction is a single-electron transfer (SET) process between substrates **1** and DDQ to form the benzyl cation **B**. The cation **B** with a hydroxylamine anion gave rise to the C-N bond coupling products **C** and **C'** by a

Table 3. Direct transformation of the diarylmethane **3** into the amides **4** and **4'**.[a]

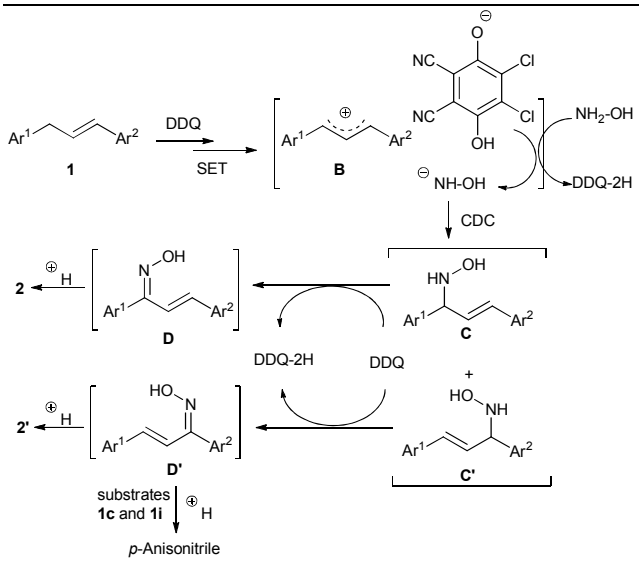




[a] Reaction conditions: **3** (1.5 mmol), $NH_2OH.HCl$ (0.5 mmol), DDQ(1.5 mmol), $AlCl_3$(0.15 mmol), HCOOH (1.5 mL), MeCN (1.5 mL) stirred at 80 °C for 12h. Yield of isolated product.



Scheme 2. Investigation of the mechanism and key intermediates.



Scheme 3. Plausible mechanism for the formation of **2** and **2'**.

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subsequent CDC reaction process, which would be oxidized to the ketoxime **D** and **D'** by the DDQ oxidative system. Subsequently, the target amides **2** and **2'** as an equilibrating mixture could be generated from the ketoxime through the Beckmann rearrangement in the presence of acid. When the substrates **1c** and **1i** were employed, *p*-Anisonitrile may be generated through the abnormal Beckmann rearrangement.

In summary, we have developed an atom-efficient and transition metal-free reaction between benzyl hydrocarbons and hydroxylamine hydrochloride using DDQ as a promoter to generate corresponding amides through sp^3 C-H and C-C bond cleavage. The mechanistic study shows that the transformation is a new process involving a hetero-CDC reaction with a subsequent tandem oxidation and Beckmann rearrangement. To the best of our knowledge, this is the first direct conversion of benzyl hydrocarbons to amides without a transition metal catalyst. Further investigation of the detailed mechanism and application of this chemistry is currently underway in our lab.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Experiment procedure and NMR data. See DOI: 10.1039/b000000x

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