Iodine catalyzed intramolecular C(sp3)–H functionalization: Synthesis of 2, 5–disubstitutedoxazoles from N –arylethylamides

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Iodine catalysed intramolecular C(sp^3)–H functionalization: synthesis of 2,5-disubstituted oxazoles from *N*-arylethylamides†

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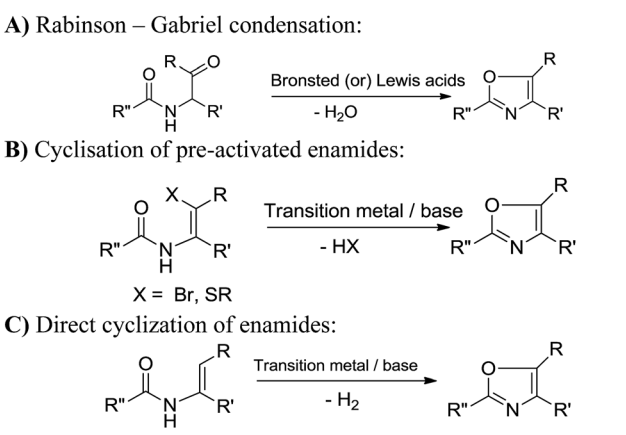
Iodine catalyzed synthesis of 2,5-disubstituted oxazoles from *N*-arylethylamides through intramolecular C(sp^3)–H functionalization under metal-free conditions is described. The method is tolerable to a wide range of substrates having a variety of functional groups with moderate to good yields of the products.

In addition to biologically active molecules for drug discovery, oxazoles are also key intermediates for the synthesis of natural products, pharmaceutical and agricultural products.[1–6] Additionally, oxazole moieties are used as fluorescent dyes,[7] in polymer industries,[8] and also serve as ligands in various metal-catalysed organic transformations.[9] As a result, the development of more facile synthetic methods to access oxazole derivatives has become of great interest to chemists.

Considering the importance of oxazole moieties, many groups have developed important methods for the synthesis of substituted oxazoles.[10–15] Among the reported methods the conversion of acyclic precursors to oxazole is the common strategy.[11–13] For example Robinson–Gabriel condensation is a versatile cyclisation strategy to synthesise a range of substituted oxazoles (Scheme 1A).[11] On the other hand enamides bearing β-vinylic carbon heteroatom (Br, and S) were subjected for the synthesis of oxazoles[12] (Scheme 1B). A step forward to the aforementioned strategies, several examples of transition metal catalyzed direct vinylic C–H functionalization of enamides have also been described (Scheme 1C).[13] Recently, Stahl and Buchwald groups were independently reported copper mediated/catalysed vinylic C–H functionalization of enamides to obtain 2,5-disubstituted oxazoles.[13h,i] Although these approaches are effective, the cyclisation of *N*-arylethylamides to oxazoles through C(sp^3)–H functionalization under transition metal-free conditions would be a convenient method to access the substituted oxazoles (Scheme 2). The separation of metal catalyst from the products is of particular importance for the synthesis of pharmaceutical fine chemicals because of their residual toxicity is a central issue to consider. Moreover, transition metal-catalyzed reactions also generate hazardous waste which is environmentally problematic and hence, should be avoided wherever possible. Very recent reports from Ghosh *et al.*, and Bathula *et al.* described the synthesis of substituted oxazoles from *N*-arylethylamides with more than stoichiometric use of *N*-bromosuccinimide (NBS),[14] these methods also suffers drawbacks such as generation of organic waste (succinimide) in the effluent and is not applicable to obtain 2,5-disubstituted oxazoles. At the outset of our interest towards the development of new strategies for the synthesis of various heterocyclic compounds,[16a–e] we wish to report herewith a metal-free synthesis of oxazoles through intramolecular C(sp^3)–H functionalization (Scheme 2). To the best of our knowledge, no such reports exist for the synthesis of 2,5-disubstituted oxazoles from *N*-arylethylamides.

We initiated our studies with *N*-phenethylbenzamide **1a** as starting substrate, which has been subjected to oxidative



Scheme 1 Reported strategies for oxazole synthesis.

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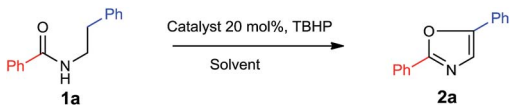
Scheme 2 Oxazole synthesis from *N*-arylethylamides.

intramolecular C–O bond formation to obtain 2,5-diphenyloxazole **2a** with catalytic amount of iodine source and TBHP as the oxidant based on our recent reports on such reactions[16f,g] and the results are illustrated in Table 1. Initially we tested the reaction with 20 mol% of KI as an iodine source, TBHP (5.0 equiv.) as an oxidant and acetonitrile as the solvent at 100 °C for 36 h, 15% of desired product **2a** was observed (Table 1, entry 1). Then we have screened out other iodine sources under these reaction conditions up to 35% yield of desired product **2a** could be obtained (Table 1, entries 2–5). When the reaction was performed under the same conditions with 20 mol% of elemental iodine, 68% of **2a** was isolated (Table 1, entry 6). By decreasing the reaction time to 24 h or reaction temperature to 80 °C the yield of **2a** was dropped to 55% and 28% respectively (Table 1, entries 7 and 8). Further, its yield was decreased by decreasing the amount of oxidant (TBHP) or I_2 (Table 1, entries 9–11) and no reaction or traces amount of **2a** was observed in the absence of I_2 or TBHP (Table 1, entries 12 and 13) or with other oxidants such as $K_2S_2O_8$, $KHSO_5$, H_2O_2 and DTBP (Table 1, entries 14–17). Then we focused on the effect of other solvents for the present transformation by fixing the temperature at 100 °C, reaction time 36 h, I_2 (20 mol%) and the oxidant TBHP (5.0 equivalents). With the several solvents tested for the reaction, the yield of **2a** was not improved (Table 1, entries 18–23). However, the best result was obtained in acetonitrile as the solvent (entry 6) for the present transformation.

In order to generalize the present transformation, we have applied this strategy to various *N*-arylethylamide derivatives (Table 2). The halogens (Br, Cl & F) present on the *para*-position of aryl ring attached to the ethylene chain of *N*-phenethylbenzamide **1a** do not affect the yield of the corresponding products (**2b–2d**). In the case of *ortho*-methoxy phenyl and pyridyl substituted amides, moderate yields of corresponding products observed (**2e** and **2f**). To extend the scope of the present transformation, we focused on the various groups attached to the carbonyl carbon of *N*-arylethylamides. The halogen (Br, Cl & F) substituents on the aryl ring irrespective of their position (either *o*/*m*/*p*) provided the corresponding products in good yields (**2g–2m**). Notably, the strong electron withdrawing groups such as nitro and fluoromethyl substituents at *para*-position of aryl ring afforded corresponding products in 74% and 76% of yield respectively (**2n** and **2o**). However, the electron donating substituents (Me and OMe) gave comparatively low yields (**2p** and **2q**). Hetero aromatic amides, such as *N*-phenethylthiophene-2-carboxamide, *N*-phenethylpicolinamide, *N*-phenethylisonicotinamide phenethylnicotinamide and *N*-phenethylisonicotinamide were also reactive under the optimised conditions and provided moderate yields of corresponding oxazoles (**2r–2u**). Amides like *N*-phenethylcyclohexanecarboxamide and *N*-phenethylpivolamide underwent to this procedure smoothly and afford the corresponding oxazoles in good yield (**2v** and **2w**). Finally the present procedure has been successfully applied for a variety of substituted aryl rings containing *N*-phenethylbenzamides and obtained respective oxazoles in good yields (**2x–2z** and **2aa–2ae**). Aliphatic amides such as *N*-octylbenzamide and *N*-decylbenzamide afforded low yield of the desired products **2af**, **2ag**. As can be seen from the yields and broad range of substituted products of Table 2, including heteroaromatic amides and aliphatic amides, the present protocol indicates its versatile nature.

To understand the mechanistic path of present transformation we performed some control experiments, in presences of TEMPO as a radical scavenger under the optimised conditions, no desired product was observed and starting material 80% recovered. But the expected intermediate **3** was detected in the reaction mixture by HRMS (ESI S52†). It indicates that, the reaction may proceed through a radical pathway. In the case of *N*-methyl-*N*-phenethylbenzamide, 75% of starting substrate was recovered (Scheme 3 (eqn (2))).

Table 1 Optimisation of reaction conditions[a]

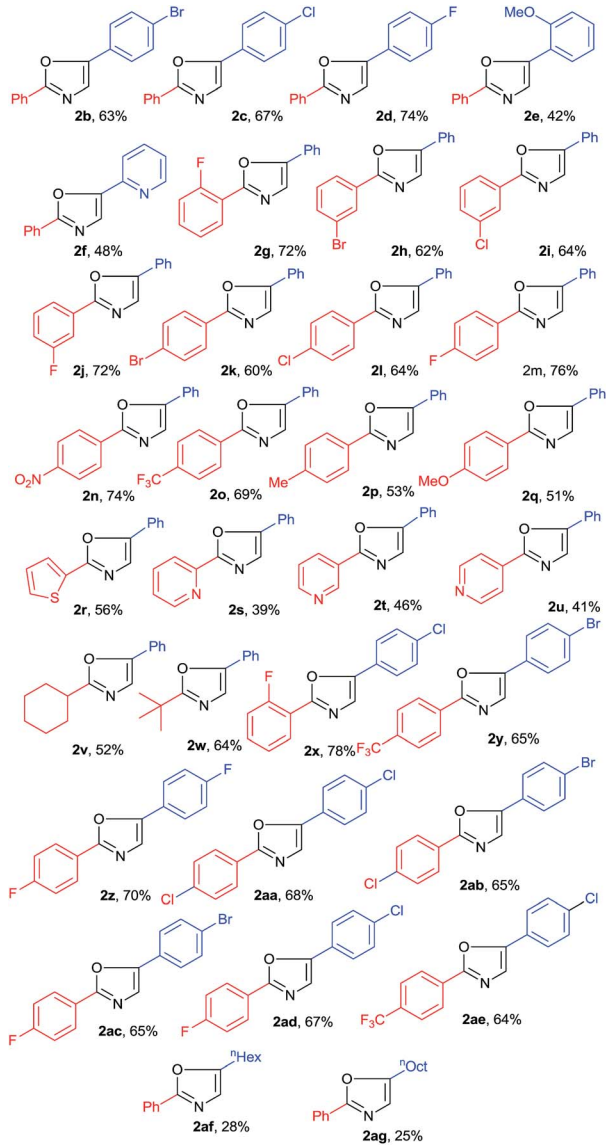


1a **2a**

Entry	Catalyst (mol%)	Oxidant (equiv.)	Solvent	Temp. (°C)	Time (h)	**2a** yields (%)
1	KI	TBHP (5)	CH_3CN	100	36	15
2	nBu_4NI	TBHP (5)	CH_3CN	100	36	10
3	NIS	TBHP (5)	CH_3CN	100	36	35
4	NaI	TBHP (5)	CH_3CN	100	36	23
5	PIDA	TBHP (5)	CH_3CN	100	36	0
6	I_2	TBHP (5)	CH_3CN	100	36	68
7	I_2	TBHP (5)	CH_3CN	100	24	55
8	I_2	TBHP (5)	CH_3CN	80	36	28
9	I_2	TBHP (4)	CH_3CN	100	36	60
10	I_2	TBHP (2)	CH_3CN	100	36	33
11[b]	I_2	TBHP (5)	CH_3CN	100	36	44
12	—	TBHP (5)	CH_3CN	100	36	Trace
13	I_2	—	CH_3CN	100	36	0
14	I_2	$K_2S_2O_8$ (2)	CH_3CN	100	36	0
15	I_2	$KHSO_5$ (2)	CH_3CN	100	36	0
16	I_2	H_2O_2 (5)	CH_3CN	100	36	0
17	I_2	DTBP (5)	CH_3CN	100	36	Trace
18	I_2	TBHP (5)	DMF	100	36	0
19	I_2	TBHP (5)	DMSO	100	36	0
20	I_2	TBHP (5)	THF	100	36	10
21	I_2	TBHP (5)	DCE	100	36	51
22	I_2	TBHP (5)	Toluene	100	36	10
23	I_2	TBHP (5)	Dioxane	100	36	36
24	I_2	O_2	CH_3CN	100	36	0

[a] Reaction conditions otherwise stated: 0.2 mmol of **1a**, 1.0 mmol of TBHP (decane), 20 mol% catalyst in 1.0 mL of CH_3CN at 100 °C for 36 h. [b] 10 mol% I_2. DTBP = di-*tert*-butyl peroxide.

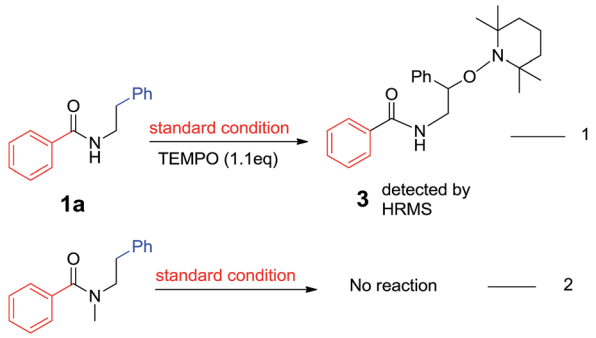
Table 2 Substrate scope for 2,5-disubstituted oxazoles[a]



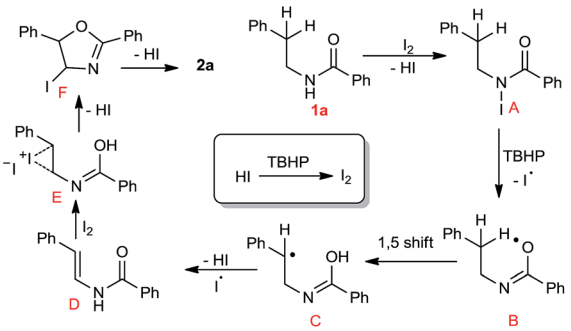
[a] Reaction conditions otherwise stated: 0.2 mmol of **1a**, 1.0 mmol of TBHP (5–6 M in decane solution), 20 mol% I_2 in 1.0 mL of CH_3CN at 100 °C for 36 h.

Further it represents that, free N–H is essential for this transformation.

On the basis of the above observations and the literature reports,[14b,17] a plausible mechanism has been proposed (Scheme 4). Initially the reaction of **1a** with iodine generates corresponding *N*-iodo intermediate **A**, it undergoes homolytic cleavage in the presence of peroxide and subsequently it generates another intermediate **B**. Through its 1, 5 proton shift forms **C**, which in the presence of iodine radical, eliminates the hydroiodic acid and converts to intermediate **D**. Further, **D** undergoes addition, substitution and elimination processes (through **E** and **F**) in the presence of iodine and provides the final product **2a**.



Scheme 3 Mechanistic experiments.



Scheme 4 Proposed mechanism.

Conclusions

In conclusion, we have developed a new approach for the synthesis of 2,5-disubstituted oxazoles employing *N*-arylethylamides with the catalytic amount of iodine and TBHP as an oxidant. Present method is appreciable as it is applicable for wide range of substrates with variety of functional group tolerance under metal-free conditions.

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