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Copper(I) Iodide-Catalysed Aerobic Oxidative Synthesis of Imidazo[1,2-*a*]pyridines from 2-Aminopyridines and Methyl Ketones

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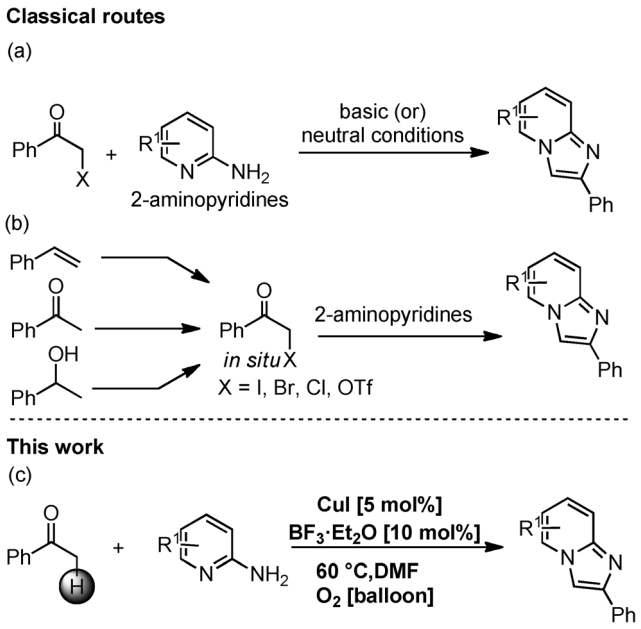
Abstract: We report here an operationally simple copper-catalysed synthesis of imidazo[1,2-*a*]pyridines through C–H activation with oxidative linkage of two C–N bonds under very mild conditions using molecular oxygen as a sole oxidant. The process allows the quick assembly of imidazo[1,2-*a*]pyridines including the antiulcer drug zolimidine from inexpensive and readily available 2-aminopyridines and methyl ketones with broad range of functional group tolerance.

Keywords: aerobic oxidation; C–H activation; copper; imidazo[1,2-*a*]pyridines; zolimidine synthesis

The transition metal-catalysed direct C–N bond formation through C–H activation by the formal loss of H_2 or H_2O would enhance the existing toolbox of synthetic methods to build complex nitrogen heterocycles.[1] Such strategies offer a highly atom-economical approach to enable the efficient construction of a broad range of C–N bonds in synthetic chemistry,[2] compared to metal-catalysed C–N bonds *via* cross-coupling reactions of organic halides with amines.[3] The use of molecular oxygen for copper-catalysed aerobic oxidative C–N bond formations is highly attractive[2–4] due to its large abundance, low cost and the lack of toxic by-products.[5]

Imidazo[1,2-*a*]pyridine (IP) scaffolds are found in many pharmacologically important compounds.[6] Such compounds exhibit antiviral, antibacterial, fungicidal and anti-inflammatory properties.[7] Many commercially available drugs (Supporting Information, Figure S1) including alpidem,[8] olprinone,[9] minodronic acid[10] (to treat anxiety, heart failure and osteoporosis), zolimidine (peptic ulcer),[11] necopidem, saripidem[12] (sedative and anxiolytic) and optically active GSK812397 candidate (HIV infection)[13] are derived from imidazo[1,2-*a*]pyridine core entities. In this context, significant contributions have been made by various groups[14] including our own.[15] However, the preparation of the starting substrates comprises a multistep procedure. Consequently, a practical and atom-economical synthesis of IPs from simple starting materials remains as a challenging task. Compared to pre-activated ketones[16] (Scheme 1), the use of unactivated methyl ketones as starting substrates for IP synthesis is highly desirable. We report herein the synthe-



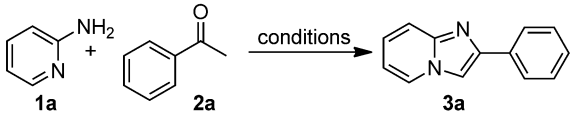
Scheme 1.

sis of substituted imidazo[1,2-*a*]pyridines using CuI/$BF_3{\cdot}Et_2O$[17] as catalyst, through C–H activation in the presence of O_2 as a sole oxidant. This method affords good selectivity, yields, functional group compatibility and thereby circumvents the aforementioned issues in the traditional synthesis of imidazo[1,2-*a*]pyridines. To the best of our knowledge, a copper-catalysed aerobic oxidative synthesis of imidazo[1,2-*a*]pyridines through C–H activation of methyl ketones has not been reported previously.

Initially, we investigated the dehydrogenative annulation of 2-aminopyridine **1a** with acetophenone **2a** as a model system (Table 1). After reaction of **1a** (5 mmol) and **2a** (7.5 mmol) with 20 mol% of copper iodide as a catalyst under neat conditions at room temperature for 24 h, **3a** was not observed (Table 1,entry 1). On using O_2 as the oxidant, a trace amount of **3a** was observed (Table 1, entry 2). On adding $BF_3{\cdot}Et_2O$ as an additive at room temperature, 7% of **3a** was isolated (Table 1, entry 3). A clear improvement of the yields was observed when the reaction temperature was raised from room temperature to 80 °C (Table 1, entries 4–6). By using DMF as solvent, **3a** was obtained in 72% at 60 °C in 10 h (Table 1, entry 7). After increasing the amount of **2a** to 10.0 mmol (2 equiv.), **3a** was obtained in 74% yield (Table 1,entry 8). When the catalyst loading (CuI) was decreased to 10 and 5 mol%, the yield of **3a** was increased to 76% and 82%, respectively (Table 1, entries 9 and 10). To uphold the reaction yield we screened out other additives, solvents, oxidants and copper salts but they were found to be less effective (entries 11–16). Reactions performed with other copper salts [CuBr, CuCl, $Cu(OAc)_2$ and $Cu(OTf)_2$] and without catalyst were either poorly effective or entirely ineffective (entries 17–21). These observations are in line with the literature methods.[17,18]

As listed in Table 2, the copper-catalysed dehydrogenative annulation of **1a** with various methyl ketones **2** was found to afford the substituted IPs **3** in moderate to good yields under aerobic oxidative conditions. The presence of a variety of electron-donating and

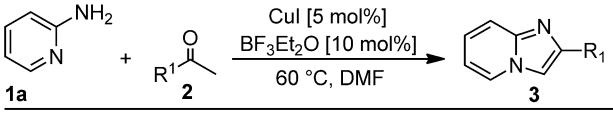
Table 1. Optimization of reaction conditions for **3a**.[a]

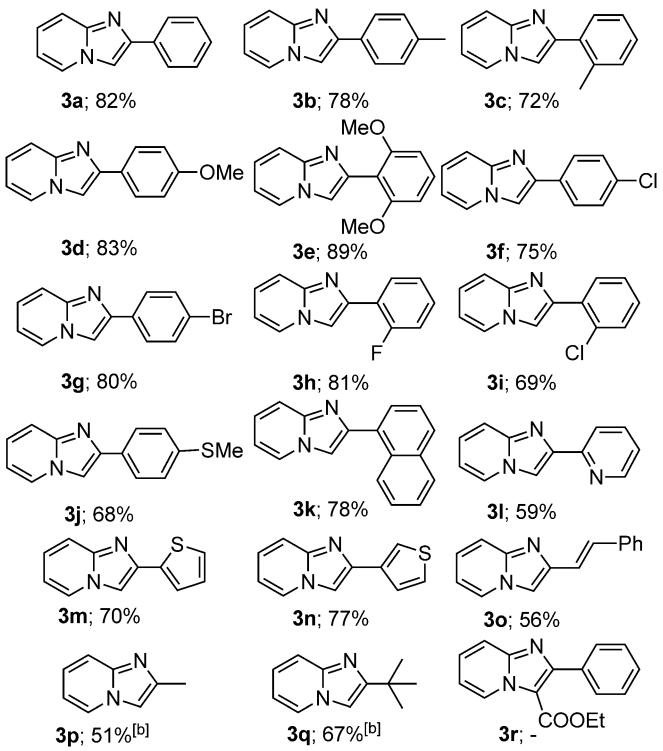


Entry	Catalyst [mol%]	Additive [mol%]/ Oxidant	Solvent	Temp [°C]	Time [h]	Yield [%][b]
1[c]	CuI (20)	--	--	r.t.	24	nr
2[c]	CuI (20)	--/O_2	--	r.t.	24	trace
3[c]	CuI (20)	$BF_3{\cdot}Et_2O$ (10)/O2	--	r.t.	24	7
4[c]	CuI (20)	$BF_3{\cdot}Et_2O$ (10)/O_2	--	45	24	53
5[c]	CuI (20)	$BF_3{\cdot}Et_2O$ (10)/O_2	--	60	24	55
6[c]	CuI (20)	$BF_3{\cdot}Et_2O$ (10)/O_2	--	80	24	58
7[c]	CuI (20)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	10	72[d]
8	CuI (20)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	10	74[d]
9	CuI (10)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	20	76[d]
10	CuI (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	24	82
11	CuI (5)	PivOH (10)/O_2	DMF	60	24	66
12	CuI (5)	TFA (10)/O_2	DMF	60	24	68
13	CuI (5)	$BF_3{\cdot}Et_2O$ (10)/air	DMF	60	24	50
14	CuI (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	CH_3CN	60	24	46
15	CuI (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	NMP	60	24	78
16	CuI (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	CH_3OH	60	24	68
17	CuBr (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	24	8
18	CuCl (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	24	2
19	$Cu(OAc)_2$ (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	24	nr
20	$Cu(OTf)_2$ (5)	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	24	nr
21	--	$BF_3{\cdot}Et_2O$ (10)/O_2	DMF	60	24	nr

[a] *Reaction conditions:* **1a** (5 mmol), **2a** (10 mmol), CuI, additive (10 mol%), DMF (2 mL), 60 °C in an oil bath under O_2 (balloon) 24 h, unless otherwise stated.
[b] Isolated yields.
[c] **2a** (7.5 mmol) used.
[d] 15% and 8% of 3-iodo-2-phenylimidazo[1,2-*a*]pyridine were isolated in entries 7, 8 and 9, respectively (nr = no reaction).

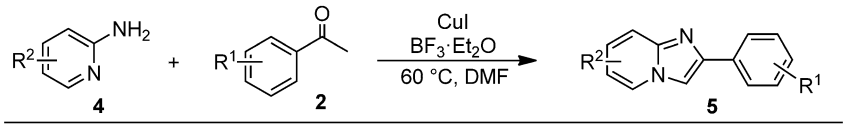
Table 2. Reaction of 2-aminopyridine with various ketones.[a]

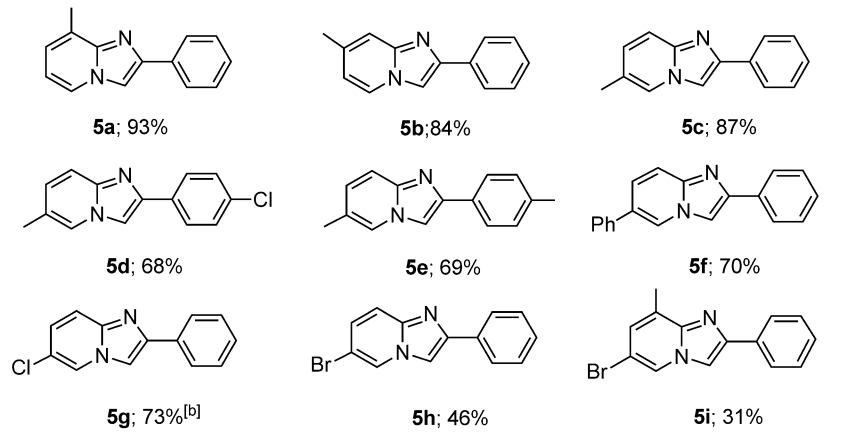




[a] *Reaction conditions;* **1a** (5 mmol), **2** (10 mmol), DMF (2 mL), in an oil bath under O_2 (balloon) 24 h, isolated yield unless otherwise stated.
[b] 15 mmol of **2** were used.

Table 3. Reaction of substituted 2-aminopyridines with various ketones.[a]





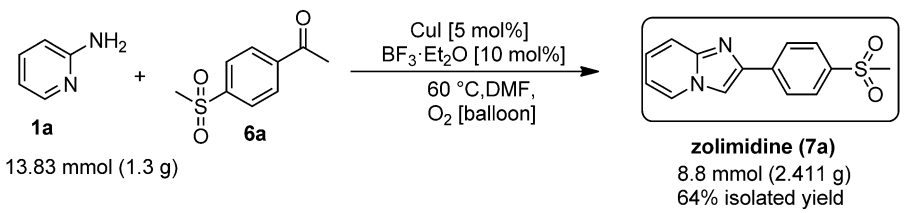
[a] *Reaction conditions*: **4** (5 mmol), **2** (10 mmol), CuI (0.25 mmol), $BF_3{\cdot}Et_2O$ (0.5 mmol), DMF (2 mL), in an oil bath under O_2 (balloon) 24 h, isolated yields.

[b] 15 mmol of **2** were used.

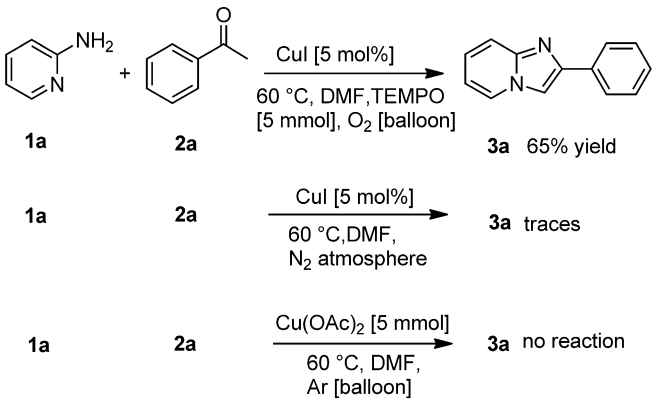
electron-withdrawing groups in the acetophenone moieties at either the (*o/p*) position could be tolerated and afforded the desired IPs in 68–89% yields (**3b–3j**). Electronic effects associated with electron-donating/electron-withdrawing substituents and steric factors on the ketone do not affect the efficiency of the process, as substantiated by the presence of two *ortho* methoxy groups in acetophenone to afford the desired product **3e** in high yield (89%). The present catalytic system is also applicable to heterocyclic and bicyclic methyl ketones which smoothly reacted under typical conditions, affording the desired products **3k–3n** in 59–78% yields. Interestingly, the α,β-unsaturated methyl ketone (*E*)-4-phenylbut-3-en-2-one also resulted in a moderate yield (56%) of **3o**.[19] Aliphatic ketones, for instance, acetone and *tert*-butyl methyl ketone, were also subjected to this reaction, and successfully provided alkyl-substituted IPs **3p** and **3q** in 51% and 67% yields, respectively. However, a mixture of unknown products resulted instead of **3r** when **1a** was reacted with ethyl 3-oxo-3-phenylpropanoate.

Finally, we demonstrated the feasibility of the present catalytic system for the synthesis of IPs by the reaction of various methyl ketones **2** with substituted 2-aminopyridines **4** under the optimum conditions (Table 3). Thus, the domino syntheses of **5a–5f** were obtained in good to excellent yields (68–93%). While comparing the reactions of **4**, it is evident that electron-donating substituents seem to have no influence on the product yield, whereas electron-withdrawing substituents led to lower yields (**5g–5i**). This observation may be due to the low nucleophilicity of acceptor substituted aminopyridines.

The results of Table 2 and Table 3 indicate that, the dehydrogenative annulation of various methyl ketones with 2-aminopyridines in the presence of CuI/$BF_3{\cdot}Et_2O$ is an efficient process to afford IP derivatives in moderate to excellent yields. Next we attempted the synthesis of zolimidine through this novel strategy (Scheme 2). This drug has been synthesized on a gram scale (2.411 g) successfully. It is noteworthy to mention that zolimidine (**7a**) is usually syn-



Scheme 2. Synthesis of zolimidine.

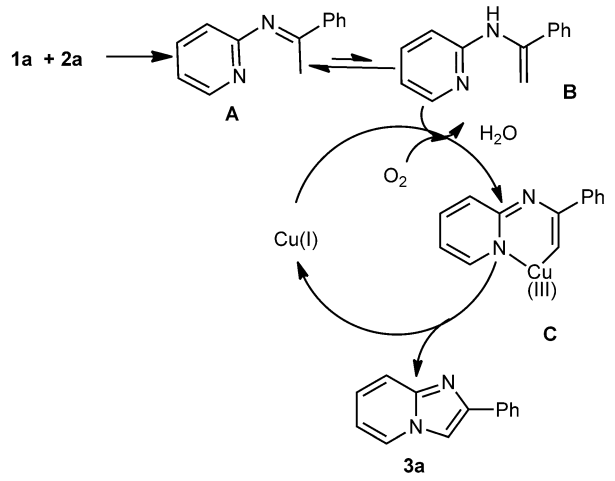


Scheme 3. Mechanistic experiments.

thesized in a multistep procedure.[14f] This is the first report of a single-step synthesis of zolimidine.

To gain insight into the reaction mechanism, additional experiments were performed under the optimised conditions (Scheme 3). Initially, the reaction of **1a** and **2a** was performed with a stoichiometric amount of a radical scavenger (TEMPO), 65% of **3a** was isolated, ruling out the radical reaction pathway.[20] When the same reaction was performed under a nitrogen atmosphere only traces of **3a** were observed. Furthermore, the reaction was attempted using a Cu(II) salt under a nitrogen atmosphere, no reaction occurred.[18] These studies reveal the crucial role of oxygen and Cu(I) for an efficient transformation. Thus, a plausible mechanism is proposed in Scheme 4.

Initially, 2-aminopyridine **1a** reacts with methyl ketone **2a** to form imine **A**, which is in equilibrium with enamine **B**.[21] The oxidative addition of copper iodide in the presence of oxygen forms the copper-(III) complex **C**.[22] Reductive elimination of **C** provides the desired product **3a** with the regeneration of the Cu(I) catalyst to continue the catalytic cycle.



Scheme 4. Plausible mechanism.

We have developed a copper-catalysed aerobic oxidative annulation of 2-aminopyridines with methyl ketones to access imidazo[1,2-*a*]pyridines under mild conditions. The process allows the quick and facile synthesis of IPs including zolimidine from readily and commercially available substrates. The mechanistic studies indicate the essential role of CuI and O_2 for the present investigation.

Experimental Section

Typical Procedure for the Synthesis of 2-Phenylimidazo[1,2-*a*]pyridine (3a)

470 mg (5.0 mmol) of 2-aminopyridine **1a**, 1200 mg (10 mmol) of acetophenone, CuI 5 mol% (47 mg; 0.25 mmol), $BF_3{\cdot}Et_2O$ (45–50% purity); 10 mol%, 0.5 mmol) and DMF (2 mL) were placed in a 25-mL double-necked round-bottomed flask. The mixture was heated in an oil bath at 60 °C for 24 h under an oxygen atmosphere (balloon). After completion of the reaction, it was allowed to attain to room temperature and then the mixture was poured into 20 mL of sodium carbonate solution. The product was extracted with DCM (50 mL × 3) and dried with anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a residue that was purified through column chromatography using silica gel (30% EtOAc/hexane) to afford **3a**; yield: 0.799 g (82%).

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