Manganese(III) Acetate Catalyzed Aerobic Dehydrogenation of Tertiary Indolines, Tetrahydroquinolines and an *N*-Unsubstituted Indoline

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Abstract: A $Mn(OAc)_3 \cdot 2H_2O$ -catalyzed aerobic dehydrogenation of five and six-membered *N*-heterocycles for the synthesis of *N*-heteroarenes is reported. Of note, this protocol can be applied to the dehydrogenation of tertiary indolines with various electron-deficient *N*-substituents. Preliminary mechanistic investigations support that a single-electron transfer pathway might be involved.

Keywords: Manganese; dehydrogenation; tertiary indolines; NH-heterocycles; single-electron transfer

The dehydrogenation from saturated *N*-heterocycles, *e.g.*, indolines and 1,2,3,4-tetrahydroquinolines, to produce their corresponding unsaturated *N*-heterocyclic aromatic compounds is a fundamental yet powerful transformation that has applications across synthetic organic chemistry, material science and medicinal chemistry.^[1] As a consequence, the development of efficient synthetic methods enabling such a transformation has attracted continuous research interests in the past four decades. Conventional methods often require stoichiometric reagents or oxidants such as DDQ, iodates, peroxides, and metal-based oxidants.^[2] However, the use of stoichiometric oxidants or reagents is undesirable from both environmental and economical points of view.

In recent years, significant developments in the direction of catalytic dehydrogenation of *N*-heterocycles have been achieved using homogeneous or heterogeneous metal catalysts^[3] and metal-free catalysts.^[4] Notably, examples of electrocatalysis^[5], photocatalysis^[6] and biocatalysis^[7] have also been developed very recently. Among the methodologies established, transition metal-catalyzed acceptorless dehydrogenations of N-heterocycles are more promising since no stoichiometric oxidants are required, and in addition, only H₂ byproduct is produced during the process (Scheme 1–1a). Important contributions have been made in this field using heterogeneous^[8] or welldefined homogeneous metal catalysts consisting of iridium,^[9] ruthenium,^[10] cobalt,^[11] nickel,^[12] iron,^[13] and osmium compounds as well.^[14] More recently, an acceptorless dehydrogenation of N-heterocycles using a well-defined Mn-PNP complex under basic conditions was also reported.^[15] Despite these remarkable achievements made, the introduction of multi-step synthesized ligands, noble metal complexes, tedious catalysts preparation or harsh reaction conditions are major concerns, thus restricting their potential applications.

Alternatively, transition metal-catalyzed dehydrogenations can also be achieved with the assistance of sacrificial hydrogen acceptors (Scheme 1–1b).^[16] Among them, oxidative dehydrogenation using O_2 as the hydrogen acceptor represents a more compelling route in terms of atom economy and environmental concerns (Scheme 1–1c). Although many elegant catalytic systems have been explored under relatively milder conditions, most of these methods are based on the use of noble metals.^[3d,17] Meanwhile, the use of more abundant, inexpensive and less toxic transition metal catalysts has emerged as attractive alternatives at present.^[18–19] In this context, the use of Mn-based catalysts is of great interest due to the redox properties of different oxidation states of Mn.^[20] Along this line, a handful of Mn-based catalytic materials have been

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2a, 99% (88%^[b])

t-Bu *t-*Bu

2e, 86%



t-Bu

FtO

2d, 51%

2h, 91%

20, R²=SMe, 25%

2t 72%

ÒEt

ď

2c. 48%

2g, 92%

Me

2s. 23%





Scheme 1. State-of-the-art and current transition-metal-catalyzed dehydrogenation of indolines.

R

R

prepared and exhibited good catalytic activities in aerobic dehydrogenation of *N*-heterocycles (Scheme 1–2, top),^[19] thanks to an initial aerobic dehydrogenation using mesoporous manganese oxide catalyst developed by Suib in 2015.^[19a] Regardless of these advances, reported protocols are limited to heterogeneous Mn-based catalysts whose cumbersome preparation methods are normally required. In addition. these documented aerobic dehydrogenations are largely limited to NH-heterocycles, and methods applicable for N-substituted heterocycles, by contrast, are far less developed.[17,19e]

Considering the fact that $Mn(OAc)_3 \cdot 2H_2O^{[21]}$ is a well-known single-electron transfer (SET) reagent, we reasoned that $Mn(OAc)_3 \cdot 2H_2O$ might be used as a catalyst in aerobic dehydrogenation of indolines. The dehydrogenation is supposed to initiate from SET from nitrogen to Mn³⁺. Then the formed aminium radical cation intermediate underwent a direct C-H abstraction to afford the imine cation intermediate, followed by deprotonation and aromatization to afford indole product (Scheme 1-2, bottom). Herein, we describe a



key feature of the current $Mn(OAc)_3 \cdot 2H_2O/O_2$ cata-

Mn(OAc)3^{•2}H₂O (20 mol%) AcOH, air, 80 °C, 12-24 h

OMe

0

2b. 52%

2f, 86%

lytic system. We initially chose N,N-dimethylindoline-1-carboxamide 1 a as the model substrate to investigate the aerobic dehydrogenation process. After extensive screening,^[22] we found that heating 1a in acetic acid (AcOH) at 80 °C under 1 atm of O_2 , in the presence of 20 mol% of Mn(OAc)₃·2H₂O, provided the desired indole product 2a in quantitative yield after 12h (Table 1, entry 1). Besides $Mn(OAc)_3 \cdot 2H_2O$, other manganese salts, such as MnO₂, Mn(OAc)₂, Mn(acac)₃, MnF₂, and MnCl₂, could also effectively catalyze the dehydrogenation reaction to furnish 2a in relatively lower yields (Table 1, entries 2-6). The use of protic solvents other than AcOH, such as 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) or 2,2,2-trifluoroethanol (TFE), clearly gave worse results (Table 1, entries 7 and 8). Only lower conversion or no reaction was observed when using MeOH, toluene or THF as the solvent (Table 1, entries 9–11). Alternative oxidants,

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Table 1. Optimization of Reaction Conditions.^[a]

1a	$ \begin{array}{c} & Mn(OAc)_{3} \cdot 2H_{2}O (20 \text{ mol}\%) \\ & AcOH, O_{2}, 80 ^{\circ}C, 12 \text{ h} \end{array} $	2a N
Entry	Variations from above conditions	Yield [%] ^[b]
1	None	>99
2	MnO_2 instead of $Mn(OAc)_3 \cdot 2H_2O$	81
3	$Mn(OAc)_2$ instead of $Mn(OAc)_3 \cdot 2H_2O$	37
4	$Mn(acac)_3$ instead of $Mn(OAc)_3 \cdot 2H_2O$	82
5	MnF_2 instead of $Mn(OAc)_3 \cdot 2H_2O$	68
6	$MnCl_2$ instead of $Mn(OAc)_3 \cdot 2H_2O$	64
7	HFIP as solvent	85
8	TFE as solvent	44
9	MeOH as solvent	trace
10	Toluene as solvent	trace
11	THF as solvent	8
12	$K_2S_2O_8$ (2.0 equiv.) as oxidant, N_2	83
13	TBHP (2.0 equiv.) as oxidant, N_2	63
14	Under N ₂	20
15	Performed at 60 °C	65
16	Performed at 30 °C	26
17	Using 10 mol% of $Mn(OAc)_3 \cdot 2H_2O$	78
18	Under air	>99

^[a] Conditions: **1a** (0.2 mmol), catalyst (20 mol%), oxidant, solvent (2.0 mL), atmosphere (1 atm), 12 h.

^{[b] 1}H NMR yield by using 1,3,5-trimethoxybenzene as an internal standard.

such as $K_2S_2O_8$ or TBHP, led to diminished yields of **2a** (Table 1, entries 12 and 13). In contrast, only 20% yield of **2a** was obtained when the reaction was performed in the absence of an oxidant, suggesting that the oxidant is vital for the successful catalytic cycle of this transformation (Table 1, entry 14). Carrying out the reaction at lower temperatures (Table 1, entries 15 and 16) or in the presence of a decreased amount of $Mn(OAc)_3 \cdot 2H_2O$ (Table 1, entry 17) had negative effect on the efficiency of the reaction. Finally, we were pleased to find that the reaction could be conducted under ambient air without any loss of reactivity (Table 1, entry 18).

With the optimized reaction conditions in hand, we then turned our attention to the scope of the reaction. The scope of the reaction with respect to indolines with different electron-withdrawing or easily removable *N*-substitutions was first studied and the results are summarized in Scheme 2. The indole product **2a** was readily isolated in 99% yield under the optimal reaction conditions (20 mol% of $Mn(OAc)_3 \cdot 2H_2O$, AcOH, 80 °C, air, 12 h). The reaction also proceeded satisfyingly on a 25-fold (5 mmol) scale, giving rise to **2a** in 88% yield. Diversified other *N*-substituents in the indoline scaffold were also tolerated. Methyl 1*H*indoline-1-carboxylate **1b** or *N*-pivaloyl-substituted indoline 1c were all suitable substrates. Moreover, phosphonate or phosphoryl-protected indoline 1d or 1 e could be compatible with the aerobic dehydrogenation reaction, smoothly affording 2d and 2e in moderate to high yields. N-heteroaryl substituted indoline 1 f or 1 g could smoothly transform to generate 2 f and 2g in 86% and 92% yields, respectively. In addition, phenyl group on the N atom was also tolerated well, delivering the desired product 2h in 91% yield. Next, an investigation into different substituted N-C(O)NMe₂ indolines showed that a number of functional groups could be introduced into the phenyl ring of indoline at different positions to give the corresponding products in good to excellent yields. For examples, indolines bearing methyl or methoxyl groups at different positions of the phenyl ring underwent facile dehydrogenation, affording the corresponding products 2i, 2j, 2l, 2q, and 2r in good to excellent yields. The halogen-containing indolines possessing chloro or bromo substituents delivered 2k and 2m in 75 and 66% yields, respectively. The present catalytic system also proved to be tolerant of indoles with valuable electrophilic ester groups. This tolerance of electron-withdrawing functional groups provides a possibility to use this process in combination with further conventional cross-coupling transformations. However, a substituent at the 3-position of the indoline strongly diminished the efficiency of the reaction (2s), which may be due to steric inhibition during the reaction. In addition, we were pleased to find that the dehydrogenation of **1t** bearing a phenyl group at the C-7 position was also carried out smoothly to produce **2t** in 72% yield.

Encouraged by these results obtained, we then investigated the compatibility of indolines with N-alkyl substituents (Scheme 3). We first explored the reactivity of 1 u under standard Mn(OAc)₃·2H₂O/AcOH/ air conditions. However, decomposition of 1 u leading to benzaldehyde and N-acetyl indole was observed. Gratifyingly, this undesired decomposition could be avoided upon a simple solvent replacement. After a quick reoptimization,^[22] we found that the use of MeOH-TFE (2,2,2-trifluoromethane) mixed solvent and a lower catalyst loading (5 mol%) could allow the formation of 2 u in good yield. Of note, the reaction could be extended to indolines bearing other simple or ester-, alkoxyl-, or siloxy-functionalized N-alkyl groups, affording their corresponding indoles 2v-v in moderate to very good yields. Importantly, indolines bearing N-3-bromopropyl (1z), N-ethanol (1a'), and Nallyl (1 b') were also tolerated and furnished the desired indole products, albeit in lower yields. Furthermore, we found that cyclin-dependent kinase 4 (CDK4) selective inhibitor **2 aa**^[23] or indole-indolinyl compound 2 ab could be prepared from diindoline 1 aa via dehydrogenation under slightly different reaction conditions, and dehydrogenation of 2 ab proceeded

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Scheme 3. Scope of tertiary indolines with alkyl *N*-substitutions.^[a,b] ^[a] Conditions: **1** (0.2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (5 mol%), TFE/MeOH ($\nu/\nu = 1:1, 2.0 \text{ mL}$), under air (1 atm), 80 °C, 10 h. ^[b] Yields are given for isolated yields. ^[e] **1 aa**, (0.2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (40 mol%). ^[d] **1 aa**, (0.2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (10 mol%). ^[e] **2 ab**, (0.1 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (10 mol%).

smoothly to furnish **2 aa** in 78% yield under similar conditions.

Impressively, we found that our current Mn- $(OAc)_3 \cdot 2H_2O/O_2$ system was amenable for dehydrogenation of NH-heterocycles (Scheme 4). For instance, the dehydrogenation of 1,2,3,4-tetrahydroquinoline **3 a** proceeded well upon the Mn(OAc)_3 \cdot 2H_2O/air/TFE-MeOH system to furnish quinoline **4 a** in 64% yield. The reaction is also compatible with tetrahydroquino-



Scheme 4. Scope of NH-heterocycles. Conditions: 3 (0.2 mmol), $Mn(OAc)_3 \cdot 2H_2O$ (30 mol%), TFE/MeOH (v/v = 1:1, 2.0 mL), under air (1 atm), 100 °C, 48 h. Yields are given for isolated yields.

lines bearing an alkyl or an aryl group at the C-2 position, affording corresponding 2-substituted quinolines in moderate to good yields. Moreover, NHindolines, *e.g.*, 5-methoxyindoline **3d**, also participated in this transformation. Although only moderate to good catalytic efficiency was shown for the dehydrogenation of NH-heterocycles tested, the current $Mn(OAc)_3 \cdot 2H_2O/air$ system stands as one of the few effective catalytic systems which are applicable for aerobic dehydrogenation of both *N*-substituted and *N*unsubstituted heterocycles.^[17,19e]

To gain some mechanistic insights into this aerobic dehydrogenation process, we first carried out several radical inhibition experiments under standard reaction conditions (Scheme 5). When butylated hydroxytoluene (BHT), 1,1-diphenylethylene, or an electron transfer (ET) scavenger 1,4-dinitrobenz-ene^[24] was added in the dehydrogenation of 1a, significant decreases in the yields of **2b** highlighted that a radical process via SET was possibly involved in the catalytic cycle. Surprisingly, when radical trapping reagent TEMPO was subjected into the dehydrogenation, a yield of 57% was still obtained (Scheme 5a). In addition, a comparative yield of 2b was achieved even performing the reaction under N_2 (Scheme 5b). These interesting results together with a recent elegant report on iron-catalyzed^[25] dehydrogenation of N-Heterocycles in the presence of TEMPO drive us to explore the potential multiple effects of TEMPO in this transformation, and thereby two more control experiments were then conducted. Interestingly, we found that TEMPO, which has been successfully used as a catalyst for the electro-chemical acceptorless dehydrogenation of N-heterocycles,^[5a] could be used as an effective promoter for the current thermodynamic dehydrogenation under air or even N₂ atmosphere (Scheme 5b). Subsequently, experiments employing 1,2,3,4-tetrahydroquinoline-type substrates were conducted. As expected, no dehydrogenation product was detected when using 2,2,4,7-tetramethyl-1,2,3,4-tetrahydroquinoline **3e** (Scheme 5c) or 1-(pyrimidin-2-yl)-1,2,3,4-tetrahydroquinoline 3f (Scheme 5d) as the substrate, highlighting the importance of the α C–H proton and the N-H motif in 1,2,3,4-tetrahydroquinoline-type substrate for the successful dehydrogenation. These results are consistent with other research studies,^[18c,19b-e] which suggest that a similar reaction mechanism via a SET initiated dehydrogenation to form an imine intermediate, tautomeric cyclic imine, and second dehydrogenation process might be involved for the aerobic dehydrogenation of 1,2,3,4-tetrahydroquinolines under current $Mn(OAc)_3 \cdot 2H_2O/O_2$ catalytic system.

Subsequently, in order to get some information about possible reaction intermediates, we followed the oxidative dehydrogenation of 1a by TLC. Indeed, several unknown products were observed at the early

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Scheme 5. Mechanistic considerations.

stage of the reaction. After several trials, we were pleased to isolate one of the possible intermediate 1 a''(Scheme 5e). In addition, when 1a'' was used as the substrate, a high isolated yield of 2a was obtained even at a lower temperature (60°C). These results clearly support that 1 a'' might be present as a reaction intermediate involved in this dehydrogenation. Furthermore, under ${}^{18}O_2$ atmosphere, ${}^{18}O$ -labeled product 1 a"

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isolated

detected by HRMS

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was detected by HRMS^[22]. The ¹⁸O-labeled experiment indicates the incorporation of oxygen from molecular oxygen.

Though the mechanism for the present transformation is as yet unclear according to these preliminary mechanistic studies and previous results^[4e,18c,19b,26], a plausible reaction mechanism has been postulated (Scheme 5f, path a). The dehydrogenation is supposed to initiate from SET from nitrogen to Mn³⁺ along with the generation of superoxide radical anion $O_2^{\bullet-}$. Then the formed aminium radical cation intermediate I react with $O_2^{\bullet-}$ to give intermediate III and a peroxide radical. The reaction between the peroxide radical and III results in the formation of IV (confirmed by HRMS)^[22], followed by reduction or homolysis to afford V. Finally, the expected product 2 a is obtained by elimination of a water molecule. However, a mechanism involving the formation of an iminium cation intermediate II could not be ruled out at this stage.

summary, we have established a In Mn- $(OAc)_3 \cdot 2H_2O/O_2$ catalytic system for the oxidative dehydrogenation of N-heterocycles under mild reaction conditions. The generality of this protocol was demonstrated on a broad range of N-alkyl, aryl, acyl, and removable protecting groups substituted indolines, and its applicability was further explored with dehydrogenation of N-unsubstituted 1,2,3,4-tetrahydroquinolines and an NH-indoline. Further applications of this Mn- $(OAc)_3 \cdot 2H_2O/O_2$ catalytic system in oxidative transformations are currently underway in our laboratory.

Experimental Section

General procedure for the synthesis of aerobic dehydrogenation products 2 a-t (Scheme 2). Indoline (0.2 mmol, 1 equiv.), Mn(OAc)₃·2H₂O (0.2 equiv.) and anhydrous acetic acid (2 mL) was added to an oven-dried 25 mL J-Young tube under air atmosphere. The reaction mixture was stirred at 80 °C for 12 h or 24 h. Upon completion, it was cooled to room temperature and extracted with EtOAc and H₂O. The combined organic phases were dried over anhydrous Na2SO4, filtered and evaporated in vacuo. The crude residue was purified by flash column chromatography on silica gel using EtOAc-petroleum ether mixture as an eluent to afford the desired compound.

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Manganese(III) Acetate Catalyzed Aerobic Dehydrogenation of Tertiary Indolines, Tetrahydroquinolines and an *N*-Unsubstituted Indoline

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