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Iron-Catalyzed Aerobic Oxidation of Allylic Alcohols: The Issue of C=C Bond Isomerization

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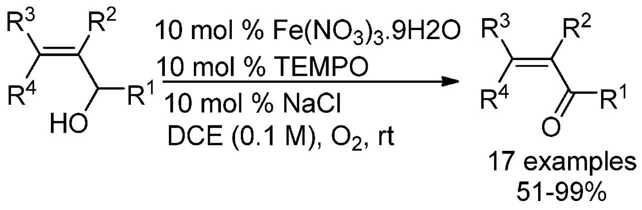
ABSTRACT



An aerobic oxidation of allylic alcohols using $Fe(NO_3)_3 \cdot 9H_2O$/TEMPO/NaCl as catalysts under atmospheric pressure of oxygen at room temperature was developed. This eco-friendly and mild protocol provides a convenient pathway to the synthesis of stereodefined α,β-unsaturated enals or enones with the retention of the C−C double-bond configuration.

α,β-Unsaturated aldehydes/ketones are important intermediates in many organic reactions, such as (hetero)Diels–Alder reactions,[1] Michael addition,[2] (aza) Morita–Baylis–Hillman reaction,[3] Aldol condensation,[4] Heck coupling,[5] cyclization,[6] etc.[7] There are numerous reports for the synthesis of such compounds.[8] Oxidation of the corresponding allylic alcohols is the most convenient method for this transformation. Traditionally, a stoichiometric amount of oxidants such as chromium oxides,[9] MnO_2,[10] DMSO,[11] or hypervalent iodine compounds[12] is needed, which would produce almost the same amount of waste and cause serious environmental problems. In addition, the *Z*/*E*-isomerization of α,β-unsaturated carbonyl compounds was observed during the oxidation of the corresponding allylic alcohols.[13−16]

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On the other hand, molecular oxygen is a natural, cheap, and eco-friendly oxidant, which was applied in the oxidation of allylic alcohols as terminal oxidant with transition-metal catalysts such as Pd,[17] Pt,[18] Au,[19] Ru,[20] Pt–Bi,[21] Os–Cu,[22] V,[23] Cu,[24] Fe,[25] or even without a metallic catalyst.[26] It is worth noting that *Z*/*E*-isomerization has also been observed under aerobic oxidation conditions. For example, Christmann and co-workers have reported a copper-catalyzed aerobic oxidation/isomerization protocol of *Z*-allylic alcohols affording the completely isomerized products *E*-α,β-unsaturated aldehydes under mild conditions in 2012.[27] Therefore, a clean and mild oxidation method toward allylic alcohols without isomerization is highly desirable for both academic preparation and industrial scale production. We have focused on the aerobic oxidation of alcohols and established a general protocol for the aerobic oxidation of a wide range of alcohols under mild conditions using $Fe(NO_3)_3\cdot 9H_2O$/TEMPO/NaCl as catalysts, yielding the corresponding aldehydes or ketones in good to excellent yields.[28] Herein, we report our efforts in the iron-catalyzed aerobic oxidation of allylic alcohols with retention of the C–C double-bond configuration.

We initially tried this oxidation toward geraniol (*E*-**1a**) using 5 mol % $Fe(NO_3)_3\cdot 9H_2O$, 3 mol % TEMPO, and 5 mol % NaCl as catalysts in 1,2-dichloethane (Table1, entry 1). It is interesting to observe that the issue of isomerization is concentration dependent: when the substrate concentration was reduced to 0.1 mol/L, no isomerization was observed (Table 1, entries 6–9). At a higher concentration, serious *E* to *Z* isomerization was observed (Table 1, entries 1–5). For considering conversion and extent of *E*/*Z*-isomerization, we have defined 10 mol % each of $Fe(NO_3)_3\cdot 9H_2O$, TEMPO, and NaCl in DCE (0.1 mol/L of substrate) as standard reaction conditions (Table 1, entry 9).

Changing the loading of NaCl does not affect the *E*/*Z* ratio of the product (Table 2, entries 2–5). As a comparsion, when the reaction was conducted in the absence of NaCl, only 49% of *E*-**2a** was obtained with 25% recovery of *E*-**1a** even with a prolonged reaction time of 24 h (Table 2, entry 1). The exact role of NaCl is still not clear; however, as noted in the previous report,[28a] we believe that it may be acting as a ligand to iron.

Allylic alcohols without such an issue could also be oxidized to the corresponding aldehydes/ketones in moderate to good yield (Table 3, entries 8–10). Farnesol (2*E*,6*E*-**1k**, *E*/*Z* = 90:10), an acyclic sesquiterpene alcohol

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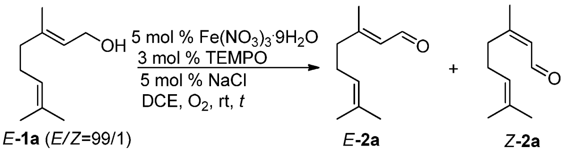
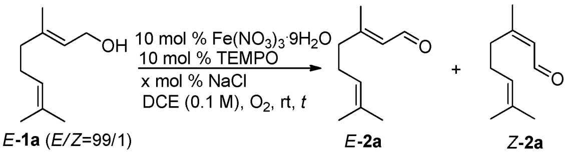
Table 1. Optimization of the Reaction Conditions[a]



entry	conc (mol/L)	time (h)	yield of **2a**[b] (%)	*E*/*Z*
1	5.0	12	98 (0)	80/20
2	2.0	12	98 (0)	89/11
3	1.0	12	68 (32)	90/10
4	0.5	12	33 (51)	91/9
5	0.2	12	22 (59)	93/7
6	0.1	12	22 (66)	97/3
7	0.05	12	19 (72)	97/3
8[c]	0.1	24	44 (50)	97/3
9[d]	**0.1**	**3**	**95 (0)**	**97/3**

[a] The reaction was conducted using 10 mmol of *E*-**1a**, 5 mol % $Fe(NO_3)_3 \cdot 9H_2O$, 3 mol % TEMPO, and 5 mol % NaCl in DCE; [b] ^1H NMR yield of **2a** with recovery of the alcohol in the parentheses; [c] The reaction was conducted using 1 mmol of *E*-**1a**, 5 mol % $Fe(NO_3)_3 \cdot 9H_2O$, 5 mol % TEMPO, and 10 mol % NaCl in DCE; [d] The reaction was conducted using 1 mmol of *E*-**1a**, 10 mol % $Fe(NO_3)_3 \cdot 9H_2O$, 10 mol % TEMPO, and 10 mol % NaCl in DCE.

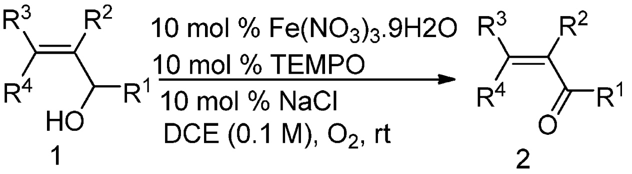
Table 2. Effect of NaCl in the Oxidation of *E*-**1a**[a]

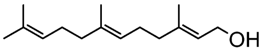
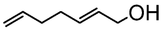
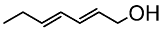
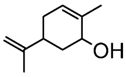
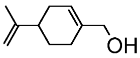


entry	*x*	time (h)	yield of **2a**[b] (%)	*E*/*Z*
1	0	24	49 (25)	97/3
2	5	4	95 (0)	97/3
3	**10**	**3**	**95 (0)**	**97/3**
4	15	3	95 (0)	97/3
5	20	3	95 (0)	97/3

[a] The reaction was conducted using 1 mmol of *E*-**1a**, 10 mol % $Fe(NO_3)_3 \cdot 9H_2O$, 10 mol % TEMPO, and *x* mol % NaCl in DCE; [b] ^1H NMR yield of **2a** with recovery of the alcohol in the parentheses.

Table 3. Substrate Scope of $Fe(NO_3)_3 \cdot 9H_2O$/TEMPO/NaCl-Catalyzed Room Temperature Aerobic Oxidation of Allylic Alcohols



entry	R^1; R^2; R^3; R^4	*t* (h)	yield of **2** (*E*/*Z*)(%)
1	H;H;$Me_2C{=}CH(CH_2)_3$; CH_3 **(1a)**[a]	3	91 (97:3) (**2a**)
2	H;H;*n*-C_4H_9;H **(1b)**	5	83 (>99/1) (**2b**)
3	H; H; *n*-C_8H_{17}; H **(1c)**	2	98 (>99/1) (**2c**)
4	H; H; *p*-$NO_2C_6H_4$; H **(1d)**	2	99 (>99/1) (**2d**)
5	CH_3; H; *n*-C_4H_9; H **(1e)**	2	92 (>99/1) (**2e**)
6	C_2H_5; CH_3; C_2H_5; H **(1f)**	3	60 (>99/1) (**2f**)
7	Cy; H; CH_3; H **(1g)**[b]	9	75 (97:3) (**2g**)
8	Ph; CH_3; H; H **(1h)**	6	75 (**2h**)
9[c]	*n*-C_5H_{11}; H; H; H **(1i)**	13	76 (**2i**)
10[c]	*n*-C_6H_{13}; H; H; H **(1j)**	12.5	86 (**2j**)
11	 (2*E*,6*E*-**1k**/2*Z*,6*E*-**1k** = 90/10)	47	66 (2*E*,6*E*-**2k**/2*Z*,6*E*-**2k** = 89/11)
12	 (*E*-**1l**, *E*/*Z* = 87/13)	9	72 (*E*-**2l**, *E*/*Z* = 88/12)
13	 (2*E*,4*E*-**1m**/2*E*,4*Z*-**1m** = 94/6)	4	70 (2*E*,4*E*-**2m**/2*E*,4*Z*-**2m** = 95/5)
14	 (**1n**)	12	67 (**2n**)
15	 (**1o**)	9	90 (**2o**)

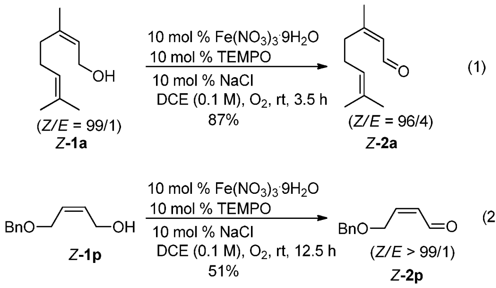
[a] *E*/*Z* = 99/1. [b] *E*/*Z* = 95/5. [c] The reaction was conducted using 5 mol % $Fe(NO_3)_3 \cdot 9H_2O$, 5 mol % TEMPO, 5 mol % NaCl, 0.25 M in 1,2-dichloroethane.

that was extracted from many essential oils, could be oxidized under these conditions to afford the corresponding product with 66% yield with retention of the C=C bond configuration (Table 3, entry 11); allylic alcohols with conjugated as well as unconjugated diene moieties *E*-**1l** and 2*E*,4*E*-**1m** could also be oxidized to the corresponding aldehydes with good yield without changing the *E*/*Z* ratio (Table 3, entries 12 and 13). In addition, as expected, cyclic allylic alcohol **1n** and primary alcohols with two C=C bonds **1o** could also be oxidized to the corresponding ketone **2n** and aldehyde **2o** in moderate to good yields (Table 3, entries 14 and 15).

Interestingly, when *Z*-allylic alcohols *Z*-**1a** and *Z*-**1n** were oxidized under this set of standard conditions, the corresponding *Z*-aldehydes *Z*-**2a** and *Z*-**2p** were obtained in moderate to good yields (Scheme 1).

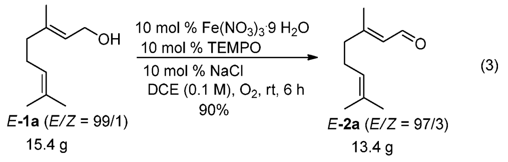
To further show the practicality and efficiency of this catalytic system, a 0.1 mol reaction of *E*-**1a** was conducted under the optimized conditions to give *E*-**2a** in 90% isolated yield in 6 h without changing the *E*/*Z* ratio (Scheme 2) .

Scheme 1. Iron-Catalyzed Aerobic Oxidation of Acyclic *Z*-Allylic Alcohols



In conclusion, we have developed a mild and eco-friendly protocol for the aerobic oxidation of allylic

Scheme 2. 0.1 mol Scale Oxidation of *E*-**1a**



E-**1a** (*E*/*Z* = 99/1)
15.4 g

E-**2a** (*E*/*Z* = 97/3)
13.4 g

alcohols using $Fe(NO_3)_3 \cdot 9H_2O$/TEMPO/NaCl as catalyst in DCE to synthesize α,*β*-unsaturated enals or enones with retention of the C–C double bond configuration. Further studies including the synthesis application are being pursued in our laboratory.

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Supporting Information Available. Experimental procedure and spectroscopic data for products. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.