이학석사학위논문

Oxidant-free, Iron-catalyzed Acceptorless Alcohol Dehydrogenation

철을 촉매로 한 수소수용체 부재 하의 알코올의 탈수소화 : 산화제를 배제한 산화 반응

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Abstract

Oxidation of alcohols is an essential organic reaction, affording versatile carbonyl groups. To provide a sustainable solution for environmentally harmful traditional oxidation methods, the transition-metal catalyzed oxidant-free dehydrogenation of alcohols has attracted much attention. The widely used catalysts for the dehydrogenation reaction are based on precious metals, which are not economical and environmentally benign catalysts. We developed an operationally simple, economical, and environmentally benign acceptorless Fe-catalyzed dehydrogenation of various secondary benzylic alcohols to afford the corresponding ketones and H_2. A simple *in-situ* mixture of readily available Fe(III) acetylacetonate, 1,10-phenanthroline, and K_2CO_3 was identified as an active catalyst for this transformation.

Keywords

iron catalysis; dehydrogenation; oxidation; alcohol; ketone; H_2 production

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Introduction

Oxidation of alcohols is a fundamental and important organic transformation. Readily available alcohols have been widely used as the precursors for synthetically useful carbonyl compounds.[1] Traditional methods for the oxidation of alcohols require stoichiometric amounts of oxidants such as hypochlorite,[2] Cr salts,[3] Mn salts,[4] oxalyl chloride,[5] hypervalent iodine,[6] oxygen with transition-metal catalysts,[7] and H_2O_2.[8] The traditional methods have several drawbacks in terms of atom economy, economics, and environmental effects as most of the methods generate a huge amount of wastes or undesirable by-products.

The catalytic acceptorless dehydrogenation of alcohols has been considered as an important transformation to overcome these problems. Many catalytic systems have been developed, based on precious metals such as Rh,[9] Ru,[10] Ir,[11] and Os.[12] Although the oxidation method itself is simple and clean, the precious metals used for the catalytic dehydrogenation of alcohols have disadvantages in terms of toxicity and high cost. Therefore, significant recent efforts have been made to develop dehydrogenation catalysts based on earth-abundant metals such as Co[13] and Fe.

Fe is the most abundant, economical, and nontoxic transition metal.[14] Fe has been developed as a catalyst for many organic reactions: (i) chemical reduction processes such as the hydrogenation of C-C multiple bonds or

polar multiple bonds,[15] transfer hydrogenation,[16] and hydrosilylation,[17] and (ii) bond-forming processes such as C-H bond oxidation,[18] and C-N,[19] C-O,[20] and C-C bond formation.[21] The hydrogenation reactions using Fe as the catalyst have been well developed. Chirik and coworkers developed Fe(II) complexes **1** (Figure 1), which can catalyze alkene hydrogenation and hydrosilylation.[22] Casey and coworkers demonstrated that Knölker's Fe complex **2**[23] is an efficient and selective catalyst for the hydrogenation of the polar multiple bonds of carbonyl compounds and imines.[24] Milstein and coworkers reported PNP pincer-type ligand-based Fe complexes **3**, which were active for the hydrogenation of ketones and CO_2, and the dehydrogenation of formic acids.[25]

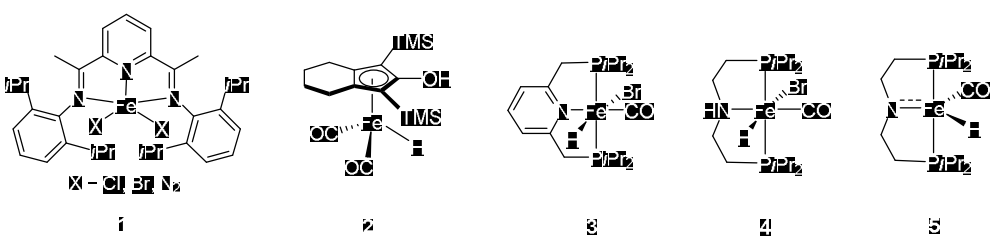


Figure 1. Previously reported Fe complexes

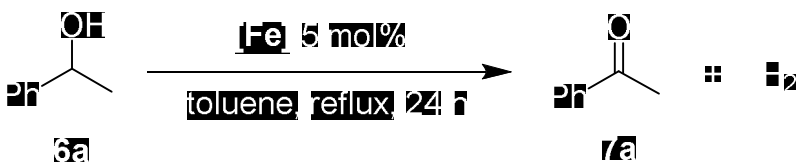
Compared to the actively ongoing development of Fe catalysts for hydrogenation reactions, the development of Fe catalysts for the dehydrogenation process has been limited. . Recently, Jones and coworkers reported a well-defined Fe complex **5** supported by a bis(phosphino)amine pincer ligand for acceptorless dehydrogenation and hydrogenation of

N-heterocycles.[26] For dehydrogenation of alcohols, Beller and coworkers used the dehydrogenation of MeOH for the generation of H_2 catalyzed by Fe-hydride complex **4**.[27] Nakazawa and coworkers just reported the $CpFe(CO)_2Cl$-catalyzed dehydrogenation of alcohols; however, the catalytic reaction only worked for 2-pyridylmethanol derivative because of the crucial chelating role of pyridine for the catalytic activity.[28] Because some Fe complexes can mediate hydrogen-transfer reactions, we envisioned that an operationally simple Fe-based catalytic system is possible for the environmentally benign and atom-economical acceptorless dehydrogenation of alcohols. Herein, we report the Fe-catalyzed dehydrogenation of secondary benzylic alcohols using a simple *in-situ* Fe-catalyst system based on readily available sources.

Results and Discussion

The dehydrogenation of 1-phenylethanol (**6a**) was selected as the model reaction to achieve our goal. First of all, we investigated reactivity of iron sources to alcohol dehydrogenation reaction (Table 1). Various iron sources which were Fe(0), Fe(II), and Fe(III) salts were tested. We expected the Fe(0) sources could be reactive to alcohol dehydrogenation reaction, because it could be considered that mechanism cycle of Fe(0) to Fe(II) is more reasonable. However, all of iron salts had very low reactivity or no reactivity to alcohol dehydrogenation without any additional additives. Relatively, $Fe(acac)_2$ and $Fe(acac)_3$ showed meaningful results (entries 11, 12). It means acetylacetonate ligand is important for the reaction regardless of the oxidation state of iron.

Table 1. Test of iron sources



Entry[a,b]	[Fe]	Yield[b] (%)
1[d]	$Fe_2(CO)_9$	1
2[e]	$Fe_3(CO)_{11}$	2

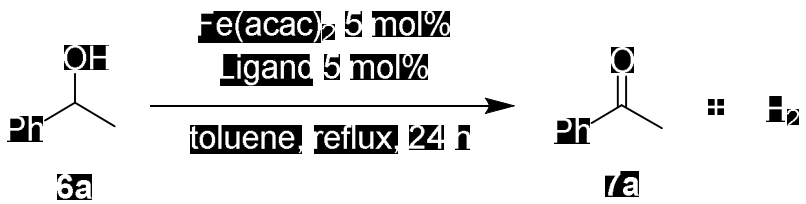
3	FeI_2	3
4	$FeBr_2$	1
5	$FeBr_3$	1
6	FeF_2	2
7	FeF_3	3
8[c]	$FeCl_3$	0
9[c]	$Fe(OAc)_2$	5
10[d]	$Fe(BF_4)_2 \cdot 6H_2O$	2
11[e]	$Fe(acac)_3$	15
12[f]	$Fe(acac)_2$	20

[a]1-Phenylethanol (0.4 mmol). [b]reactions were conducted in 4 mL vial. [c]HPLC yield using anisole as the internal standard. [d]2.5 mol% of $Fe_2(CO)_9$. [e]1.7 mol% of $Fe_3(CO)_{11}$.

To investigate the effect of phosphine ligands with $Fe(acac)_2$, several experiments were conducted (Table 2). There were no improvement with tested monodentate and bidentate phosphine ligands. Some of ligands such as tricyclohexylphosphine, tri(2-methylphenyl)phosphine, and tri(4-methoxyphenyl)phosphine showed relatively good yields (entries 2, 4,

8), however it was not higher than the yield when only iron salt was used for the reaction. And most of bidentate ligands interrupted the reaction, as a reason, it can be thought that the bidentate ligands hinder the effect of acetylacetonate of $Fe(acac)_2$ which is also bidentate ligand.

Table 2. Test of iron and phosphine ligands combinations



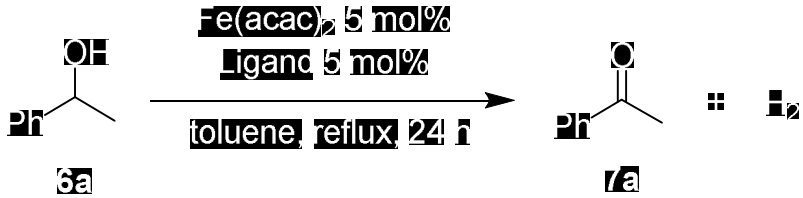
Entry[a, b]	Ligand	Yield[c] (%)
1	PPh_3	8
2	PCy_3	25
3	P(*p*-tolyl)$_3$	4
4	P(*o*-tolyl)$_3$	22
5	trimesitylphosphine	12
6	(*p*-CF_3Ph)$_3$P	6
7	(*p*-CH_3OPh)$_3$P	22
8	dppm	15

9	dppe	7
10	dppp	1
11	dppb	8
12	dpppe	8
13	dcpe	9
14	dppf	17

[a]1-Phenylethanol (0.4 mmol). [b]reactions were conducted in 4 mL vial. [c]HPLC yield using anisole as the internal standard.

We turned to N-ligands, which is widely used as a ligand in organic and organometallic chemistry. Various monodentate and bidentate N-ligands were prepared and used for the reaction (Table 3). Most of prepared N-ligands showed low reactivity except 1,10-phenanthorilne, and TMEDA which have reactivity for the dehydrogenation relatively (entries 6, 12). On the contrary to the case of phosphine ligands, bidentate N-ligands can catalyze the reaction slightly. Based on this fact, it can be thought that the suitability of bidentate N-ligands as a ligand to the dehydrogenation reaction is better than that of bidentate phosphine ligands with iron source.

Table 3. Test of iron and N-ligands combinations



Entry[a,b]	Ligand	Yield[c] (%)
1	pyiridine	3
2	DMAP	3
3	2,2,-bipyridine	16
4	2-(p-tolyl)pyridine	9
5	2,6-diacetylpyridine	8
6	1,10-phenanthroline	20
7	2-ethyl pyridine	5
8	2-phenyl pyridine	5
9	2-formylpyridine	11
10	dNbpy	6
11	pyridazine	4
12	TMEDA	19

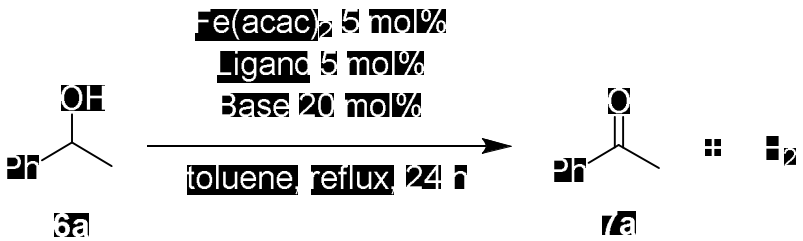
13 ethylene diamine 9

[a]1-Phenylethanol (0.4 mmol). [b]reactions were conducted in 4 mL vial. [c]HPLC yield using anisole as the internal standard.

To improve the yield of product, base was used as an additive (Table 4). When tri(2-methylphenyl)phosphine and TMEDA were used as ligands, there were no improvement despite addition of base (entries 2, 5). However, when tricyclohexylphosphine, tri(4-methxoyphenyl)phosphine, and 1,10-phenanthroline were used as lignads, the yields of product were slightly increased with addition of potassium carbonate as a base (entries 1, 3, 4). It means that base can help activation of *in situ* iron catalyst or alcohol activation by detach of proton from O-H bond.

It was found that reaction vessel is very important. When the reactions were conducted in 25 mL Schlenk tube with reflux condenser, the reactivity to dehydrogenation reaction was highly increased and the case of using 1,10-phenanatholine as a ligand and potassium carbonate as a base led to quantitative yield (entry 8). It can be estimated that hydrogen gas is generated from alcohols, so a bigger free space of reaction vessel can accelerate the hydrogen gas generation reaction.

Table 4. Test of iron, ligand, and base combinations



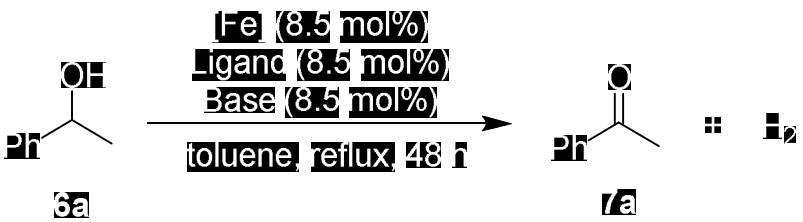
Entry[a]	Ligand	Ligand	Yield[b] (%)
1[c]	PCy_3	K_2CO_3	31
2[c]	P(*o*-tolyl)$_3$	K_2CO_3	20
3[c]	(*p*-$CH_3OPh)_3P$	K_2CO_3	37
4[c]	1,10-phenanthroline	K_2CO_3	34
5[c]	TMEDA	K_2CO_3	20
6[d]	PCy_3	K_2CO_3	32
7[d]	(*p*-$CH_3OPh)_3P$	K_2CO_3	54
8[d]	1,10-phenanthroline	K_2CO_3	>99

[a]1-Phenylethanol (0.4 mmol). [b]HPLC yield using anisole as the internal standard. [c]reactions were conducted in 4 mL vial. [d]reactions were conducted in 25 mL Schlenk tube with reflux condenser.

Finally, we investigated various combinations of Fe sources, ligands, and bases (Table 5). To our delight, the use of $Fe(acac)_2$ or $Fe(acac)_3$ afforded acetophenone (**7a**) in quantitative yields using 1,10-phenanthroline as the ligand and K_2CO_3 as the base (entries 1 and 2). Without Fe, the reaction did not occur (entries 5 and 7). $Fe(acac)_2$ and $Fe(acac)_3$ exhibited identical activity under the reaction conditions investigated (entries 1, 2, 8 and 9), and we selected more economical $Fe(acac)_3$ as the Fe source for further studies. When the base was not used, the product was obtained in 58% yield (entry 3). When 1,10-phenanthroline was not used, the product was obtained in 54% yield (entry 4). A shorter reaction time of 24 h decreased the conversion of alcohol to ketone than 48 h (entries 8 and 9). Other Fe sources were investigated; however, $Fe(acac)_3$ was the best catalyst for this transformation (entries 11–20). The reactions of Fe(0) carbonyl compounds afforded the corresponding ketones in moderate yields (entries 11 and 12). The use of Fe(II) sources such as Fe(II) halides and $Fe(OAc)_2$ usually afforded low yields (entries 13–17), except $FeCl_2$ (73%, entry 16) and $Fe(acac)_2$ (>99%, entry 1). Other Fe(III) species with ligands such as 2,2,6,6-tetramethyl-3,5-heptanedionate (TMHD), hexafluoroacetylacetonate (Hfac), and trifluoroacetylacetonate (Tfac) afforded **7a** in moderate yields (entries 18–20). Other bases instead of K_2CO_3 exhibited reduced activity (entries 21–24). Several *N*,*N*-bidentate ligands were also investigated. The use of bipyridyl ligands afforded the products in moderate yields (entries 25

and 26). The diimine-type ligand, reported by Ritter to facilitate the Fe-catalyzed 1,4-hydroboration of 1,3-dienes,[29] was not effective. Tetramethylethylenediamine (TMEDA) was also investigated; however, it showed a low reactivity (entry 28).

Table 5. Optimization of reaction conditions



Entry [a]	[Fe]	Ligand	Base	Yield [b] (%)
1	$Fe(acac)_2$	1,10-phenanthroline	K_2CO_3	>99
2	$Fe(acac)_3$	1,10-phenanthroline	K_2CO_3	>99
3	$Fe(acac)_3$	1,10-phenanthroline	-	58
4	$Fe(acac)_3$	-	K_2CO_3	54
5	-	1,10-phenanthroline	K_2CO_3	N.R.
6	$Fe(acac)_3$	-	-	29
7	-	1,10-phenanthroline	-	N.R.

8[c]	$Fe(acac)_2$	1,10-phenanthroline	K_2CO_3	80
9[c]	$Fe(acac)_3$	1,10-phenanthroline	K_2CO_3	80
10[d]	$Fe(acac)_3$	1,10-phenanthroline	K_2CO_3	trace
11[e]	$Fe_2(CO)_9$	1,10-phenanthroline	K_2CO_3	38
12[f]	$Fe_3(CO)_{11}$	1,10-phenanthroline	K_2CO_3	60
13	FeI_2	1,10-phenanthroline	K_2CO_3	36
14	$FeBr_2$	1,10-phenanthroline	K_2CO_3	5
15	FeF_2	1,10-phenanthroline	K_2CO_3	5
16	$FeCl_2$	1,10-phenanthroline	K_2CO_3	73
17	$Fe(OAc)_2$	1,10-phenanthroline	K_2CO_3	13
18	$Fe(TMHD)_3$	1,10-phenanthroline	K_2CO_3	59
19	$Fe(Hfac)_3$	1,10-phenanthroline	K_2CO_3	72
20	$Fe(Tfac)_3$	1,10-phenanthroline	K_2CO_3	50
21	$Fe(acac)_3$	1,10-phenanthroline	NaOAc	60
22	$Fe(acac)_3$	1,10-phenanthroline	NaOH	83

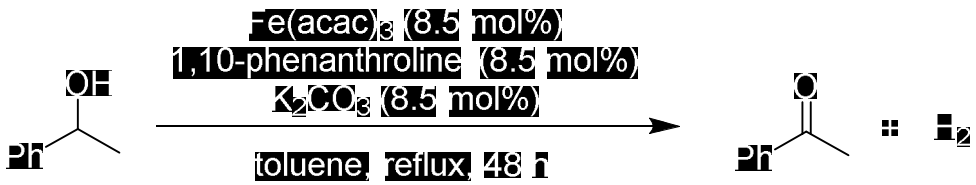
23	$Fe(acac)_3$	1,10-phenanthroline	$NaCO_3$	71
24	$Fe(acac)_3$	1,10-phenanthroline	$NaHCO_3$	77
25	$Fe(acac)_3$	2,2'-bypyridyl	K_2CO_3	43
26	$Fe(acac)_3$	4,4'-dinonyl-2,2'-dipyridyl	K_2CO_3	42
27	$Fe(acac)_3$	(*E*)-2,6-diisopropyl-*N*-(pyridin-2-ylmethylene) aniline	K_2CO_3	29
28	$Fe(acac)_3$	TMEDA	K_2CO_3	34

[a]1-Phenylethanol (0.4 mmol). [b]HPLC yield using anisole as the internal standard. [c]24 h reaction time. [d]room temperature. [e]4.3 mol% of $Fe_2(CO)_9$. [f]2.8 mol% of $Fe_3(CO)_{11}$.

The reaction conditions were investigated to evaluate the stability of the catalytic system in air and the effect of open and closed systems (Table 6). The dehydrogenation reaction in air atmosphere afforded the product in an excellent yield, demonstrating that the *in-situ* Fe catalyst system is quite stable to air (entry 2). When the reaction was conducted in a closed system, the reaction efficiency significantly decreased, indicating that the removal of

H_2 from the reaction mixture is essential for reaction progress, as reported in other dehydrogenative transformations (entry 3).[30]

Table 6. Reactions in open/closed systems



Entry[a]	Open/Closed	Atmosphere	Yield[b] (%)
1	Open	Ar	>99
2	Open	Air	92
3	Closed	Ar	36

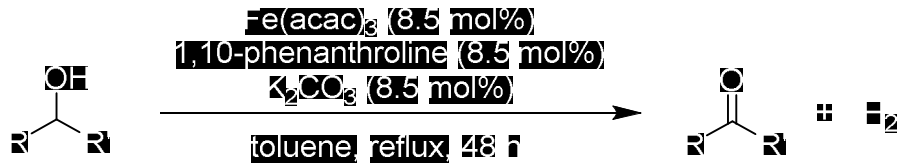
[a]1-Phenylethanol (0.4 mmol) in a 25 mL Schlenk tube. [b]HPLC yield using anisole as the internal standard

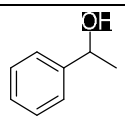
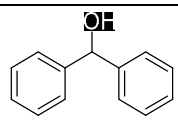
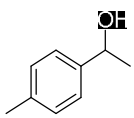
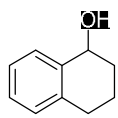
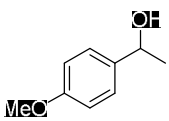
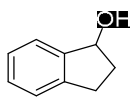
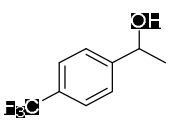
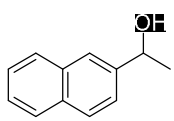
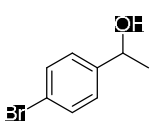
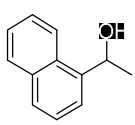
The substrate scope and selectivity of alcohols with various electronic properties and functional groups were investigated using the developed method (Table 7). The reactions of *para*-substituted aryl alcohols afforded the corresponding ketones in excellent yields regardless of the presence of electron-donating or -withdrawing functional groups (entries 2−7). The reactions of *meta*-substituted benzyl alcohols afforded the corresponding products in good yields (entries 8 and 9). Various functional groups

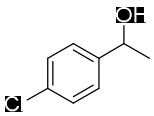
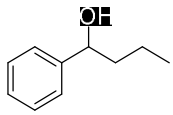
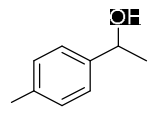
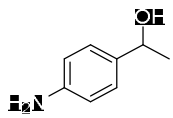
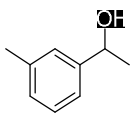
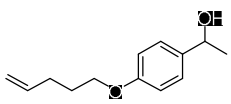
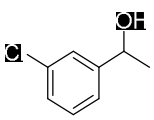
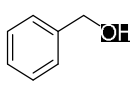
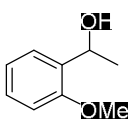
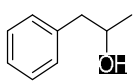
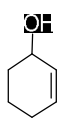
including aryl halides, ethers, amines, olefins, and trifluoromethyl groups were tolerant under the catalytic reaction conditions. The reactions of 2-methoxyphenyl-1-ethanol (**6j**) and diphenylmethanol (**6k**) afforded the corresponding ketones in excellent yields (entries 10 and 11). 1,2,3,4-Tetrahydro-1-naphthalenol (**6l**) was oxidized in a moderate yield, and 1-indanol (**6m**) afforded the corresponding product in 22% yield (entries 12 and 13). The acetylnaphthalene products were obtained in high yields (entries 14 and 15). The reaction of 1-phenylbutanol (**6p**) afforded the corresponding ketone in a moderate yield (entry 16). Amino group was tolerated, even though the yield was slightly reduced (entry 17). The reaction of a secondary alcohol with an intramolecular olefin moiety, 1-(4-(pent-4-en-1-yloxy)phenyl)ethanol (**6r**), was investigated. Unlike in the reported Ru-catalyzed dehydrogenation of olefin-containing alcohols,[10b] where the hydrogenation of olefins occurred, the olefin functional group was not reduced (entry 18); thus, this reaction can be beneficial for the selective dehydrogenation of olefin-containing alcohols.

Unfortunately, primary and aliphatic alcohols were not dehydrogenated under our catalytic reaction conditions. When benzyl alcohol (**6s**) and 2-phenylethanol (**6t**) were used as the substrates, trace amounts of corresponding carbonyl products were obtained with mostly remaining unreacted starting materials (entries 19 and 20). An allyl secondary alcohol (**6u**) also did not react (entry 21).

Table 7. Substrate scope



Entry[a]	Substrates	Yield[b] (%)	Entry[a]	Substrates	Yield[b] (%)
1	 **6a**	>99[c]	11	 **6k**	94
2	 **6b**	>99	12[e]	 **6l**	60
3	 **6c**	>99	13	 **6m**	22
4	 **6d**	>99	14[d]	 **6n**	87
5[d]	 **6e**	>99	15[e]	 **6o**	93

6	 **6f**	>99	16[e]	 **6p**	61
7	 **6g**	94	17	 **6q**	54
8[e]	 **6h**	70	18[e]	 **6r**	80
9	 **6i**	87	19	 **6s**	trace
10[d]	 **6j**	97	20	 **6t**	trace
			21	 **6u**	N.R.

[a]substrate 0.4 mmol. [b]isolated yield. [c]HPLC yield using anisole as the internal standard. [d]15 mol% catalyst loading. [e]10 mol% catalyst loading

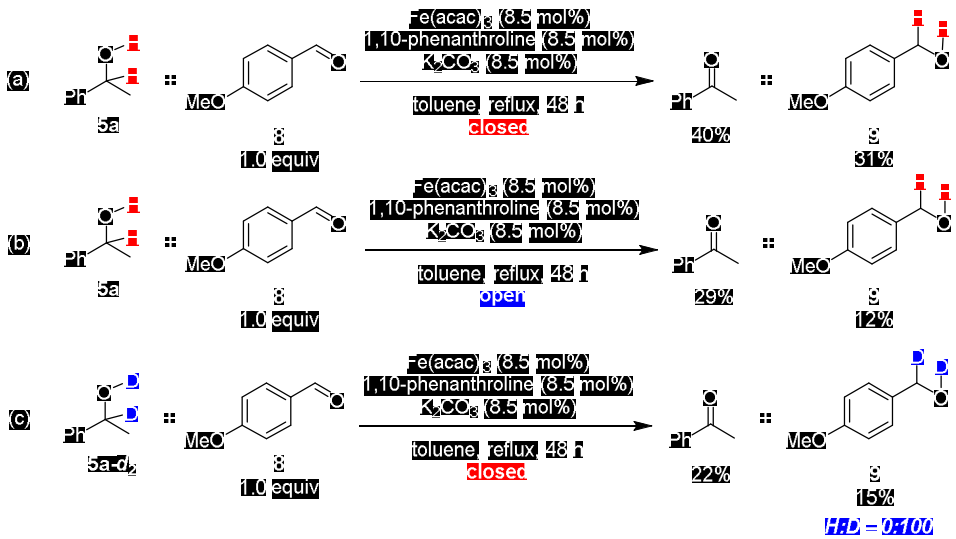
To confirm H_2 evolution in the reactions, intermolecular hydrogen transfer experiments were conducted (Scheme 1). When the

dehydrogenation of **6a** was conducted in the presence of 4-methoxybenzaldehyde (**8**) in a closed system, 1-phenylethanol was dehydrogenated to acetophenone (**7a**) in 40% yield, and **7** was hydrogenated to (4-methoxyphenyl)methanol (**9**) in 31% yield (Scheme 1a). In an open system and Ar atmosphere, the dehydrogenation and hydrogen transfer reactions were relatively retarded (Scheme 1b). The hydrogen transfer efficiency was calculated using a simple equation: [yield of **9**]/[yield of **7a**]; 77 % of hydrogen transfer occurred in a closed system (Scheme 1a). In contrast, in an open system, the yield of the reaction significantly decreased to 41% (Scheme 1b). In addition, we detected H_2 gas evolved during dehydrogenation of **6a** by gas chromatography (GC) analysis (Figure S1). The results conclusively indicate that the catalytic reaction system works in a dehydrogenative manner, producing H_2 similar to other reported precious metal-based catalytic systems. The results indicate that the catalytic reaction system works in a dehydrogenative manner, producing H_2 similar to other reported precious metal-based catalytic systems. A deuterium-labeled study was conducted using **6a-*d*$_2$** to confirm the source of hydrogen of hydrogenated compounds. Only deuterium exchange was observed in **9**, which conclusively proved that the source of H_2 was exclusively from the dehydrogenation of **6a** (Scheme 1c).

With the concern that the reaction could be mediated by precious-metal contamination, the reaction was screened with eight different $Fe(acac)_3$

samples from various sources: two different chemical manufacturers, three different laboratories, and different purity grades (>97%, >99%, and >99.9%). In all the cases, the products of the dehydrogenation of **6a** were obtained in quantitative yields in a consistent manner under the standard catalytic reaction conditions (entry 1, Table 2).

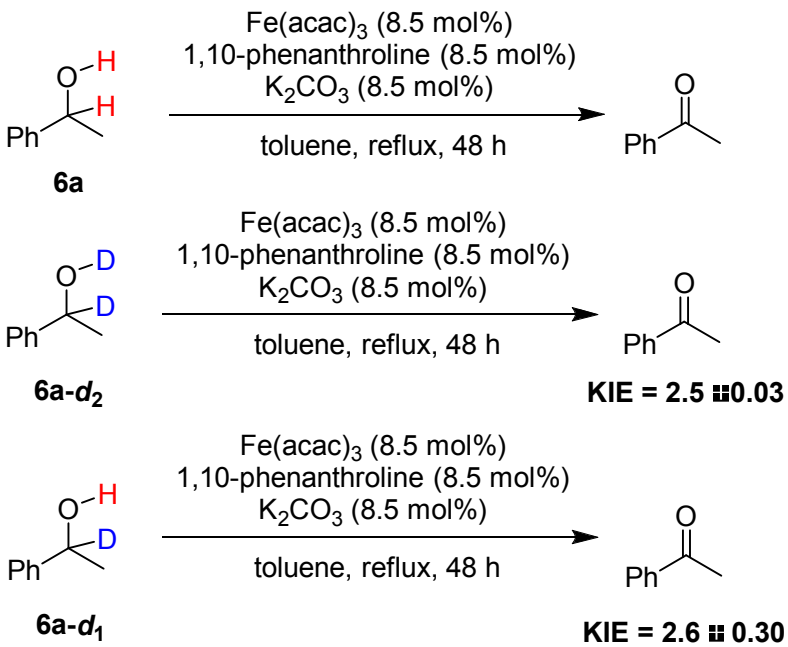
Scheme 1. Intermolecular Hydrogen Transfer Process



Kinetic isotope effect (KIE) was measured to gain insight into the rate-limiting step of the developed Fe-catalyzed dehydrogenation reactions. The initial reaction rates of the three reactions were measured with nondeuterated (**6a**) and deuterated (**6a-d_2** and **6a-d_1**) substrates (Scheme 2 and Figure 2). The KIEs showed a primary isotope effect of ~2.5. Compounds **6a-d_2** and **6a-d_1** exhibited essentially the same reaction rates.

From these results, we concluded that $C_{(\alpha \text{ position of alcohol})}$-H cleavage is the rate-limiting step similar to those in the reported precious transition-metal-based catalytic dehydrogenation reactions.[31]

Scheme 2. Isotope-Labeling Reactions for Measuring Kinetic Isotope Effect



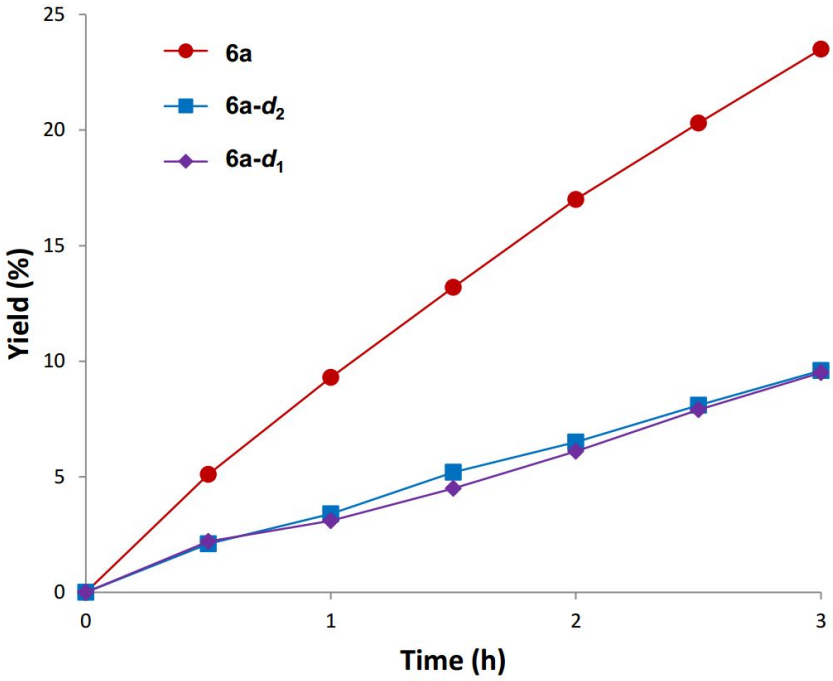


Figure 2. Reaction profile with deuterated 1-phenylethanol for KIE study

Based on these facts, the mechanism could be proposed (Figure 3). First, $Fe(acac)_3$ should be active species with the help of ligand and base, and the active form could be estimated like **A**. When secondary benzylic alcohol react with **A**, carbonyl oxygen of acetylacetonate ligand could absorb hydrogen atom from O-H bond of alcohol like dehydrogenation reaction mechanism of Shvo's catalyst.[32] And the example which was related with this step, the mechanism of acid-promoted dehydrogenation of alcohol was revealed and reported.[10i]

Then iron alkoxide **B** is formed, and β-hydride elimination led to produce the ketone. Iron hydride species could generate hydrogen gas by taking hydrogen atom back from coordinated ligand and active species **A** is regenerated.

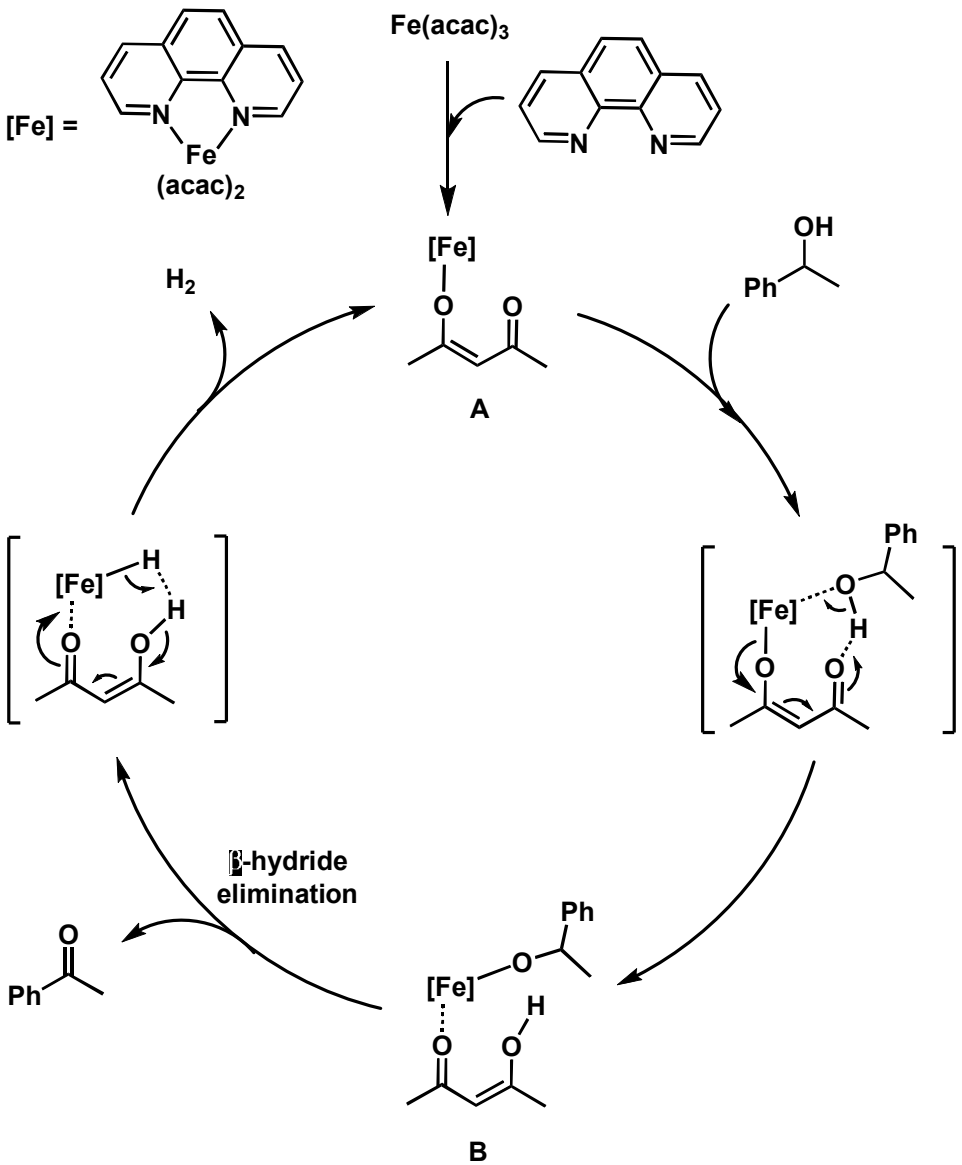


Figure 3. Proposed mechanism

Conclusion

An operationally simple, economical, and environmentally benign acceptorless Fe-catalyzed dehydrogenation of alcohols was developed based on readily available starting materials such as $Fe(acac)_3$, 1,10-phenanthroline, and K_2CO_3. Various types of secondary benzylic alcohols, which were inaccessible to the dehydrogenation reaction with the recently reported Fe-based catalytic systems, could be converted to the corresponding ketones with good functional group tolerance. Based on this catalytic system, further studies are underway to develop well-defined Fe complexes in order to expand the substrate scope of the reaction and understand the precise role of Fe and ligands.

Experimental

General Information Unless otherwise noted, all reactions were carried out using standard Schlenk techniques or in an argon-filled glove box. **6g**,[33] **6j**,[34] **6r**,[35] **6a-*d*$_2$**,[36] and **6a-*d*$_1$**[37] were prepared by modified literature procedures. Other chemicals were purchased from commercial suppliers and used as received without further purification. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25mm thickness). Column chromatography was performed on Merck 60 silica gel (230-400 mesh). ^{1}H NMR spectra were recorded on a Bruker DPX-300 (300 MHz) spectrometer and TMS (tetramethylsilane) was used as a reference. Chemical shifts were reported in ppm. GC analysis was carried out with 7980A GC system from Agilent Technologies, equipped with an HP-5 column and FID detector. HPLC analysis was carried out with 1260 Infinity LC system from Agilent Technologies, equipped with an Eclipse Plus C18 column and DAD detector.

General procedure for dehydrogenation of alcohols $Fe(acac)_3$ (12 mg, 0.034 mmol), 1,10-phenanthroline (6 mg, 0.034 mmol), K_2CO_3 (5 mg, 0.034 mmol), and toluene (0.5 mL) were added to an oven-dried 25 mL Schlenk tube equipped with a reflux condenser under Ar atmosphere using Schlenk techniques. The pre-catalyst mixture was heated to reflux for 30 min. After being cooled down to room temperature, an alcohol substrate (0.4 mmol) was added using micro-syringe under Ar atmosphere. The reaction mixture

was heated again to reflux for 48 h in an open condition before being cooled down to room temperature. All the volatiles were removed under vacuum. Purification of the product was performed by flash chromatography.

^{1}H NMR data for products

1-(4-methylphenyl)ethanone[38] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.90 (d, 2H, Ar-*H*); 7.30 (d, 2H, Ar-*H*); 2.60 (s, 3H,O=CCH_3), 2.44 (s, 3H, Ar-CH_3).

1-(4-methoxyphenyl)ethanone[38] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.95 (d, 2H, Ar-*H*); 6.97 (d, 2H, Ar-*H*); 3.90 (s, 3H, OCH_3); 2.58 (s, 3H, O=CCH_3).

1-(4-trifluoromethylphenyl)ethanone[39] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 8.07 (d, 2H, Ar-*H*); 7.77 (d, 2H, Ar-*H*); 2.67 (s, 3H, O=CCH_3).

1-(4-bromophenyl)ethanone[40] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.83 (d, 2H, Ar-*H*); 7.65 (d, 2H, Ar-*H*); 2.61 (s, 3H, O=CCH_3).

1-(4-chlorophenyl)ethanone[40] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.90 (d, 2H, Ar-*H*); 7.44 (d, 2H, Ar-*H*); 2.61 (s, 3H, O=CCH_3).

1-(4-iodophenyl)ethanone[41] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.84 (d, 2H, Ar-*H*); 7.70 (d, 2H, Ar-*H*); 2.60 (s, 3H, O=CCH_3).

1-(3-methylphenyl)ethanone[42] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.60 (s, 2H, Ar-*H*); 7.39 (s, 2H, Ar-*H*); 2.62 (s, 3H,O=CCH_3), 2.44 (s, 3H, Ar-CH_3).

1-(3-chlorophenyl)ethanone[40] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.95 (s, 1H, Ar-*H*); 7.85 (d, 1H, Ar-*H*); 7.54 (d, 1H, Ar-*H*); 7.43 (d, 1H, Ar-*H*); 2.62 (s, 3H,O=CCH_3).

1-(2-methoxyphenyl)ethanone[42] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.75 (s, 1H, Ar-*H*); 7.48 (s, 1H, Ar-*H*); 7.02 (s, 2H, Ar-*H*); 3.94 (s, 3H, OCH_3); 2.64 (s, 3H,O=CCH_3).

Benzophenone[43] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.82 (d, 4H, Ar-*H*); 7.62 (t, 2H, Ar-*H*); 7.51 (t, 4H, Ar-*H*).

3,4-dihydro-1(2H)-naphthalenone[44] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 8.04 (d, 1H, Ar-*H*); 7.50 (t, 1H, Ar-*H*); 7.33 (t, 1H, Ar-*H*); 7.29 (d, 1H, Ar-*H*); 3.00 (t, 2H, CH_2); 2.69 (t, 2H, CH_2); 2.17 (m, 2H, CH_2).

1-indanone[44] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 8.04 (d, 1H, Ar-*H*); 7.50 (t, 1H, Ar-*H*); 7.33 (t, 1H, Ar-*H*); 7.29 (d, 1H, Ar-*H*); 3.00 (t, 2H, CH_2); 2.69 (t, 2H, CH_2); 2.17 (m, 2H, CH_2).

1-(2-naphthyl)ethanone[40] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 8.50 (s, 1H, Ar-*H*); 8.05 (d, 1H, Ar-*H*); 8.01 (d, 1H, Ar-*H*); 7.94 (d, 1H, Ar-*H*); 7.91 (t, 1H, Ar-*H*); 7.29 (t, 2H, Ar-*H*); 2.76 (s, 3H, CH_3).

1-(1-naphthyl)ethanone[42] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 8.78 (d, 1H, Ar-*H*); 8.04 (d, 1H, Ar-*H*); 7.96 (d, 1H, Ar-*H*); 7.89 (d, 1H, Ar-*H*); 7.56 (m, 3H, Ar-*H*); 2.78 (s, 3H, CH_3).

1-phenyl-1-butanone[42] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.97 (d, 2H, Ar-*H*); 7.58 (t, 1H, Ar-*H*); 7.48 (t, 2H, Ar-*H*); 2.97 (t, 2H, CH_2); 1.81 (m, 2H, CH_2); 1.03 (t, 3H, CH_3).

1-(4-aminophenyl)ethanone[45] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.83 (d, 2H, Ar-*H*); 6.74 (d, 2H, Ar-*H*); 4.61 (br, 2H, NH_2); 2.54 (s, 3H, CH_3).

1-(4-(pent-4-en-1-yloxy)phenyl)ethanone[46] ^{1}H NMR ($CDCl_3$, 25 ºC), δ: 7.95 (d, 2H, Ar-*H*); 6.95 (d, 2H, Ar-*H*); 5.86 (m, 1H, CH_2=C*H*); 5.05 (t, 2H, CH_2=C*H*); 4.06 (t, 2H, OCH_2); 2.58 (s, 3H, CH_3); 2.28 (q, 2H, CHCH_2); 1.93 (m, 2H, CH_2).

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요 약 문

알코올의 산화 반응은 카르보닐기를 생성하는 핵심적인 유기 반응이다. 환경적으로 유해한, 전통적인 방식의 산화 반응에 대하여 지속 가능한 해결법을 제시하기 위하여, 전이 금속을 촉매로 한 알코올의 탈수소화 반응이 큰 주목을 받고 있다. 탈수소화 반응에 널리 쓰이는 촉매들은 주로 귀금속을 바탕으로 하며, 이러한 귀금속은 경제적이지 않으며 독성을 갖기 때문에 환경적인 관점에서 적절하지 않다. 이에 본 연구실에서는 간단하고 경제적이며 친환경적인 철을 촉매로 한 수소수용체 부재 하의 벤질 2 차 알코올의 탈수소화 반응을 개발하였다. 이 반응은 케톤 화합물과 수소 기체를 생성하며, 간단한 Fe(III) acetyl-acetonate, 1,10-phenanthroline, K_2CO_3 의 *in-situ* 혼합물이 활성촉매로서 이용된다.

주요어 : 철촉매, 탈수소화, 산화, 알코올, 케톤, 수소기체생성