$FeCl_3 \cdot 6H_2O$ Catalyzed Disproportionation of Allylic Alcohols and Selective Allylic Reduction of Allylic Alcohols and Their Derivatives with Benzyl Alcohol

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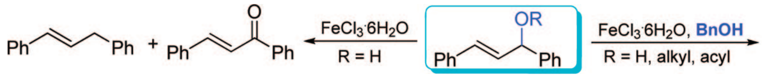

Iron chloride has been found to be an efficient catalyst for the disproportionation of allylic alcohols, which provides a convenient method for selective transformation of allylic alcohols to alkenes and α,*β*-unsaturated ketones. Furthermore, this catalytic system is also effective for highly selective allylic reduction of allylic alcohols, allylic ethers, and allylic acetates with benzyl alcohol under neutral and convenient reaction conditions.

Introduction

Reduction and oxidation of alcohols are useful and important in organic synthesis.[1] Traditionally, such transformations employ stoichiometric quantities of reductants (e.g., Bu_3SnH) or oxidants such as potassium dichromate, and most of them involve a toxic or expensive catalyst.[2] Considerable efforts have been made to devise more acceptable reductants and oxidants such as silanes and O_2, as well as nontoxic and low-cost catalysts.[3] In that scenario, the disproportionation of alcohols represents an efficient, atom-economical, and versatile transformation due to the simultaneous formation of easily separable hydrocarbon and aldehyde/ketone molecules and thus should be of great synthetic potential. There has been a growing effort in the past to develop efficient and selective catalysts for this highly valuable but challenging transformation.[4] Although several catalytic systems have been reported for effecting this reaction, they have some shortcomings such as harsh reaction conditions and the lack of generality.[4d−h] Consequently, further improvements in this area are desirable. In particular, on the industrial scale, the application of environmentally benign and cheap catalysts is essential.

Recently, much attention has been directed toward Lewis acid catalyzed substitution of the hydroxyl groups of allylic alcohols using nucleophilic reagents as a powerful method for the formation of various carbon−carbon and carbon−heteroatom bonds.[5] However, in no case the disproportionation products are observed. Our continuous interest in Lewis acid catalyzed nucleophilic substitution reactions of allylic and propargylic alcohols prompted us to explore this possibility.[6] Herein, we

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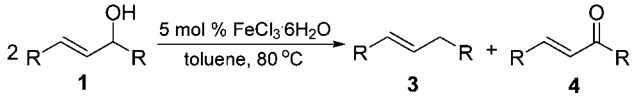
TABLE 1. Iron Catalyzed Disproportionation of Allylic Alcohols[a]



entry	R	catalyst	temp (°C)	solvent	yield (%) 3	yield (%) 4
1[b]	Ph (**1a**)	$FeCl_3 \cdot 6H_2O$	20	toluene	0	0
2	Ph (**1a**)	$FeCl_3 \cdot 6H_2O$	80	toluene	48 (**3a**)	44 (**4a**)
3	Ph (**1a**)	$FeCl_3 \cdot 6H_2O$	reflux	hexane	40 (**3a**)	39 (**4a**)
4[c]	Ph (**1a**)	$FeCl_3 \cdot 6H_2O$	reflux	THF	11 (**3a**)	8 (**4a**)
5[c]	Ph (**1a**)	$FeCl_3 \cdot 6H_2O$	80	CH_3NO_2	20 (**3a**)	17 (**4a**)
6[d]	Ph (**1a**)	$FeCl_3 \cdot 6H_2O$	80	DMF	0	0
7	Ph (**1a**)	$FeCl_3$	80	toluene	48 (**3a**)	45 (**4a**)
8	Ph (**1a**)	$FeCl_2 \cdot 4H_2O$	80	toluene	35 (**3a**)	30 (**4a**)
9	Ph (**1a**)	$Fe(acac)_3$	80	toluene	0	0
10	Ph (**1a**)	$Fe(OAc)_2$	80	toluene	0	0
11	Ph (**1a**)		80	toluene	0	0
12	*p*-MeC_6H_4 (**1b**)	$FeCl_3 \cdot 6H_2O$	80	toluene	47 (**3b**)	45 (**4b**)
13	*p*-$MeOC_6H_4$ (**1d**)	$FeCl_3 \cdot 6H_2O$	80	toluene	46 (**3d**)	44 (**4d**)
14	*p*-ClC_6H_4 (**1e**)	$FeCl_3 \cdot 6H_2O$	80	toluene	46 (**3e**)	43 (**4e**)

[a] Reaction conditions: allylic alcohol (0.5 mmol), solvent (1 mL), and catalyst (5 mol %) for 2 h. [b] Diallyl ether (**2a**) was obtained in 93% yield for 4 h. [c] The main product was diallyl ether (**2a**). [d] Only diallyl ether (**2a**) was obtained in 23% yield.

report the first example of $FeCl_3$ catalyzed disproportionation of allylic alcohols, which allows allylic alcohols to be efficiently transformed into alkenes and unsaturated ketones under neutral and convenient reaction conditions. Significantly, $FeCl_3$ is also capable of catalyzing the selective allylic reduction of allylic alcohols and allylic derivatives with benzyl alcohol, via tandem etherization and disproportionation, to give the corresponding alkenes and benzaldehyde in good to high yields with complete chemoselectivity.

Results and Discussion

I. Disproportionation of Allylic Alcohols. Considering that iron salts are readily available, inexpensive, and environmentally benign,[7] initial disproportionation of **1a** was studied in the presence of various iron catalysts to obtain the optimum reaction conditions. In the presence of 5 mol % iron(III) chloride, different temperatures were tested. Treatment of **1a** with $FeCl_3 \cdot 6H_2O$ in toluene at 20 °C for 4 h afforded only the etherization product **2a** in 93% yield (Table 1, entry 1), while the disproportionation products, 1,3-diphenyl-1-propene (**3a**) and chalcone (**4a**), were obtained with excellent yields when the reaction was carried out at 80 °C (Table 1, entry 2). The disproportionation reaction also proceeded quite smoothly in hexane with a slight decrease of the product yield (Table 1, entry 3). However, the replacement of toluene with polar solvents gave a significantly negative effect to the disproportionation reaction. In THF and CH_3NO_2, **1a** gave both disproportionation and ether formation (Table 1, entries 4 and 5), whereas in DMF the disproportionation did not proceed at all, and only a small amount of ether was obtained (Table 1, entry 6). Other iron salts, such as anhydrous $FeCl_3$ and $FeCl_2 \cdot 4H_2O$, proved also applicable independent of their oxidation states as catalysts (Table 1, entries 7 and 8), but $Fe(acac)_3$ and $Fe(OAc)_2$ were not effective (Table 1, entries 9 and 10). In the absence of ferric chloride, no reaction occurred under the same conditions (Table 1, entry 11). These results demonstrate that the nature of ligands bound to the iron ion might play a key role in the present catalytic disproportionation of allylic alcohols.

Reactions of several allylic alcohols **1** were subsequently investigated. Typical results are shown in Table 1. The reaction was not affected by either electron-withdrawing or electron-donating substituents on the benzene rings (Table 1, entries 12−14). Aromatic C−O (entry 13) and C−Cl (entry 14) bonds survived the catalytic conditions to yield selectively the corresponding methoxyl- and halogen-substituted alkenes. By contrast, in the present catalytic system the disproportionation reaction did not proceed at 80 °C in toluene even for 6 h when benzyl alcohol was used as a substrate. Instead, the Friedel−Crafts reaction of benzyl alcohol with toluene clearly occurred to produce diarylmethanes.[8] Similarly, the reaction of diphenylmethanol in the presence of 5 mol % $FeCl_3 \cdot 6H_2O$ in toluene at 80 °C also gave the Friedel−Crafts products as the major products. This is in sharp contrast with the observations in Pd/C-catalyzed disproportionation of diphenylmethanol[4b] and noncatalytic disproportionation of diphenylmethanol in supercritical water,[4e] which afforded a mixture of diphenylmethane and benzophenone in good yields.

II. Allylic Reduction of Allylic Alcohols Using Benzyl Alcohol. In the field of organic synthesis, highly chemo- and regioselective deoxygenation of hydroxyl groups that are very common and ubiquitous in many organic molecules is often necessary. Since a hydroxyl group is a poor leaving group, it should be generally activated before treating with a reducing reagent. Tosylation,[9] acetylation,[3e,10] mesylation,[11] or thiocarboxylation[12] are generally employed for activation. Direct

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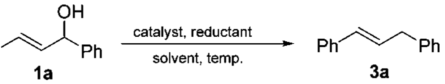
TABLE 2. Screening of Conditions for Reduction of 1a to 3a[a]



entry	catalyst	solvent	reductant	yield (%)
1	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (1 equiv)	55
2	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (2 equiv)	78
3	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (4 equiv)	95
4	$FeCl_3 \cdot 6H_2O$	BnOH		96
5	$FeCl_3 \cdot 6H_2O$	toluene	*p*-$O_2NC_6H_4CH_2OH$ (4 equiv)	96
6	$FeCl_3 \cdot 6H_2O$	toluene	*p*-$MeOC_6H_4CH_2OH$ (4 equiv)	95
7[b]	$FeCl_3 \cdot 6H_2O$	toluene	EtOH (4 equiv)	0
8[c]	$FeCl_3 \cdot 6H_2O$	toluene	2-propanol (4 equiv)	0
9	$FeCl_3 \cdot 6H_2O$	THF	BnOH (4 equiv)	16
10	$FeCl_3 \cdot 6H_2O$	CH_3NO_2	BnOH (4 equiv)	35
11	$FeCl_3 \cdot 6H_2O$	DMF	BnOH (4 equiv)	0
12[d]	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (4 equiv)	0
13[e]	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (4 equiv)	0
14[f]	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (4 equiv)	67
15[g]	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (4 equiv)	94
16[h]	$FeCl_3 \cdot 6H_2O$	toluene	BnOH (4 equiv)	93
17	$FeCl_3$	toluene	BnOH (4 equiv)	94
18	$FeCl_2 \cdot 4H_2O$	toluene	BnOH (4 equiv)	70
19	$Fe(acac)_3$	toluene	BnOH (4 equiv)	0
20	$Fe(OAc)_2$	toluene	BnOH (4 equiv)	0
21	$ZnCl_2$	toluene	BnOH (4 equiv)	5
22	$FeCl_3 \cdot 6H_2O$	toluene	$(TMS)_3SiH$ (4 equiv)	35
23	$FeCl_3 \cdot 6H_2O$	toluene	Et_3SiH (4 equiv)	95

[a] Reaction conditions: **1a** (0.5 mmol), catalyst (5 mol %), reductant, and solvent (1 mL) at 80 °C for 1 h. [b] Allyl ethyl ether was obtained in 96% yield. [c] Allyl isopropyl ether was obtained in 95% yield. [d] The reaction was carried out at 15 °C for 4 h, and allyl benzyl ether was obtained as the sole product. [e] The reaction was carried out at 50 °C for 4 h, and allyl benzyl ether was obtained as the sole product. [f] 1 mol % $FeCl_3 \cdot 6H_2O$. [g] 10 mol % $FeCl_3 \cdot 6H_2O$. [h] 20 mol % $FeCl_3 \cdot 6H_2O$.

reductions of alcohols remain little explored.[3a−d,13] Encouraged by the above results, we were interested in the possibility that other alcohols might serve as the selective hydrogen donor in a Lewis acid catalyzed reduction of allylic alcohols. Indeed, this was shown to be feasible by smooth, quantitative deoxygenation of **1a** to **3a**, with $FeCl_3 \cdot 6H_2O$ in toluene containing 4 equiv of benzyl alcohol at 80 °C (Table 2, entry 3). The yield of **3a** depended on the stoichiometric ratio of **1a** and benzyl alcohol, and the best result was achieved in neat benzyl alcohol (96% yield of **3a**, Table 2, entry 4). *p*-Nitrobenzyl alcohol and *p*-methoxybenzyl alcohol also worked as reducing agents (Table 2, entries 5 and 6), but ethanol and 2-propanol were not effective. For the latter, only ethers were obtained in excellent yields (Table 2, entries 7 and 8).[14] Furthermore, we found that the nature of solvents and the reaction temperature had a significant impact on the reduction of **1a** (Table 2, entries 9−13). Compared to other solvents such as tetrahydrofuran and nitromethane, which afforded **3a** in 16 and 35% yield, respectively, toluene proved superior. Only allyl benzyl ether was obtained when the temperature was decreased to 50 °C (Table 2, entry 13).

A series of catalysts were also examined, and a tendency similar to that seen above was observed in the disproportionation of allylic alcohol **1a**. Other iron salts such as anhydrous $FeCl_3$ and $FeCl_2 \cdot 4H_2O$ also worked as catalysts (Table 2, entries 17 and 18), but $Fe(acac)_3$ and $Fe(OAc)_2$ were ineffective (Table 2, entries 19 and 20). $ZnCl_2$ as a catalyst was also explored for this process and exhibited low activity (Table 2, entry 21). Furthermore, we have investigated the iron catalyzed reactions of **1a** with hydrosilanes under the same reaction conditions. The reactions of **1a** with $(TMS)_3SiH$ and Et_3SiH at 80 °C afforded the corresponding alkene **3a** in 35% and 95% yields, respectively, after isolation (Table 2, entries 22 and 23).[3a−c] Considering that benzyl alcohol is readily available and inexpensive as well as that its oxidized product (benzaldehyde) is an important starting material in organic synthesis, we then consistently used it to explore the scope of this reaction.

These optimized conditions were then applied for the reduction of other substrates. As shown in Table 3, various allylic alcohols were efficiently reduced by benzyl alcohol. The change of a substituent from the para- to ortho-position on the phenyl ring led to a slight decrease of the yield, probably due to the steric effect (Table 3, entries 2 and 3). The presence of strong electron-withdrawing groups such as fluoro, trifluoromethyl, and nitro on the benzene rings decreased slightly the yield of alkenes (Table 3, entries 12−17). For the allylic alcohols bearing different substituents at the 1- and 3-positions, two reduction isomers involving double bond isomerization were observed, and the isomer distributions are controlled by the nature of the substituent on the phenyl ring. The structure of **3b** was confirmed by X-ray diffraction analysis (see Supporting Information). The results clearly indicate that the allylic alcohol is reduced to an alkene. However, monoaryl-substituted allylic alcohols, such as 3-phenyl-2-propen-1-ol and 1-phenyl-2-propen-1-ol, gave a complex mixture.

III. Allylic Reduction of Allylic Ethers Using Benzyl Alcohol.

Examples of selective disproportionation between two

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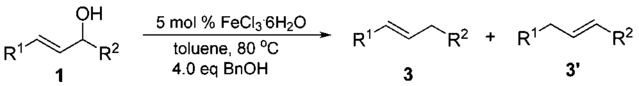
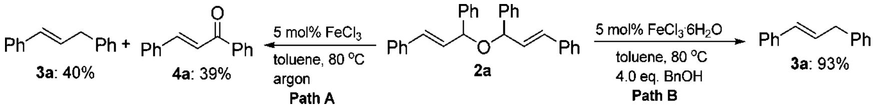
TABLE 3. Reduction of Allylic Alcohols with Benzyl Alcohol Catalyzed by $\mathrm{FeCl_3\cdot 6H_2O}$[a]



entry	R^1	R^2	time (h)	products (yield, %)	**3/3′** [b]
1	C_6H_5	C_6H_5	1	**3a** (95)	
2	*p*-MeC_6H_4	*p*-MeC_6H_4	1	**3b** (93)	
3	*o*-MeC_6H_4	*o*-MeC_6H_4	1	**3c** (80)	
4	*p*-MeOC_6H_4	*p*-MeOC_6H_4	1	**3d** (92)	
5	*p*-ClC_6H_4	*p*-ClC_6H_4	1	**3e** (93)	
6	*p*-ClC_6H_4	C_6H_5	1	**3f/3f′** (90)	55/45
7	*p*-MeC_6H_4	*p*-ClC_6H_4	1	**3g/3g′** (89)	34/66
8	*p*-MeC_6H_4	C_6H_5	1	**3h/3h′** (91)	35/65
9	*o*-MeC_6H_4	C_6H_5	1	**3i/3i′** (91)	50/50
10	*p*-MeOC_6H_4	C_6H_5	1	**3j/3j′** (90)	15/85
11	*o*-MeOC_6H_4	C_6H_5	1	**3k/3k′** (92)	1/99
12	*p*-FC_6H_4	C_6H_5	2	**3l/3l′** (79)	55/45
13[c]	*p*-$CF_3C_6H_4$	C_6H_5	2	**3m/3m′** (83)	
14	*m*-$NO_2C_6H_4$	C_6H_5	2	**3n/3n′** (75)	75/25
15[d]	*p*-$NO_2C_6H_4$	C_6H_5	4	**3o/3o′** (65)	85/15
16	*p*-$NO_2C_6H_4$	*p*-MeOC_6H_4	2	**3p/3p′** (78)	88/12
17	*p*-MeC_6H_4	*p*-$NO_2C_6H_4$	2	**3q/3q′** (80)	15/85
18	C_6H_5	H	2		
19	H	C_6H_5	2		

[a] Reaction conditions: allylic alcohol (0.5 mmol), benzyl alcohol (2.0 mmol), and $\mathrm{FeCl_3\cdot 6H_2O}$ (5 mol %) in toluene (1 mL) at 80 °C. [b] Ratios of isomers based on ^{1}H NMR. [c] Ratio of **3m** and **3m′** cannot be identified by ^{1}H NMR. [d] 20 mol % $\mathrm{FeCl_3\cdot 6H_2O}$ was used.

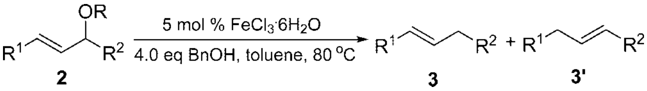
SCHEME 1



different alcohols are very rare.[4d] To elucidate the mechanism of the reduction of allylic alcohols, the following reactions were performed. First, we examined the reaction of diallylic ether (**2a**) with anhydrous $\mathrm{FeCl_3}$ in toluene without an additive under argon. As shown in Scheme 1, the disproportionation of **2a** took place successfully in only the presence of $\mathrm{FeCl_3}$ and toluene, providing **3a** and **4a** (Scheme 1, path A). When the reaction was carried out in the presence of 4 equiv of BnOH, the chalcone **4a** was not observed; instead, **3a** and benzaldehyde were obtained in high yields (Scheme 1, path B).

The reduction of ethers with alcohols remains little explored.[15] Hence, we expanded the scope of the substrates. The results are summarized in Table 4. It was found that a variety of allylic ethers could be selectively reduced by BnOH in the present catalytic system, to give the corresponding alkenes in good to excellent yields. However, for allyl alkyl ethers such as EtOCH(Ph)CH=CHPh, no desired reduction product was observed in the absence of benzyl alcohol (Table 4, entry 1). Furthermore, when dibutyl ether was used as a substrate, the reduction reaction did not take place, even in the presence of excess benzyl alcohol and with a longer time. On considering the obtained results, it becomes clear that the substrates must satisfy certain requirements for the $\mathrm{FeCl_3}$ catalyzed disproportionation of ethers: transition-state-stabilizing allyl or benzyl substituents are necessary, or otherwise different benzyl sources have to be used.

TABLE 4. Reduction of Allylic Ethers with Benzyl Alcohol Catalyzed by $\mathrm{FeCl_3\cdot 6H_2O}$[a]



entry	R^1	R^2	R	time (h)	yield (%)	3/3′ [b]
1[c]	Ph	Ph	Et	2	0	
2	Ph	Ph	Et	2	94 (**3a**)	
3	Ph	Ph	*i*-Pr	2	90 (**3a**)	
4	Ph	Ph	*n*-Bu	2	91 (**3a**)	
5	Ph	*p*-$CH_3C_6H_4$	Et	2	90 (**3h′/3h**)	62/38
6	*p*-$CH_3OC_6H_4$	Ph	Et	2	90 (**3j/3j′**)	16/84
7	*p*-ClC_6H_4	Ph	Et	2	86 (**3f/3f′**)	55/45
8	*p*-$CH_3C_6H_4$	*p*-$NO_2C_6H_4$	Et	3	80 (**3q/3q′**)	17/83

[a] Reaction conditions: allylic ethers (0.5 mmol), benzyl alcohol (2.0 mmol), and $\mathrm{FeCl_3\cdot 6H_2O}$ (5 mol %) in toluene (1 mL) at 80 °C. [b] Ratios of isomers based on ^{1}H NMR. [c] In the absence of BnOH.

IV. Allylic Reduction of Allylic Acetates Using Benzyl Alcohol. Encouraged by above results, we further investigated the deoxygenation of allylic acetates. As shown in Table 5, various allylic acetates were readily reduced by benzyl alcohol in the presence of iron chloride. The reaction gave the reduction products in moderate to high yields for a shorter reaction time. Notably, reduction isomerization involving double bond transposition was also observed for allylic acetates containing two different aryl groups at the 1- and 3-positions of allyl units (Table 5, entries 5−8). Their isomer distributions are similar to those of the reductive products of allylic alcohols and allylic ethers. The presence of a strong electron-withdrawing group such as nitro on the benzene ring led to the decrease of the yields (Table 5, entry 8). However, the expected product was not obtained in the absence of benzyl alcohol (Table 5, entry 1). The deoxygenation of alcohols via acetylation represents an important method for the indirect reduction of this type of compounds. However, to the best of our knowledge, alcohols as hydrogen donors for the reduction of acetates have remained

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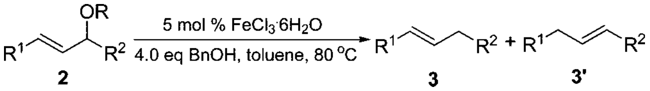
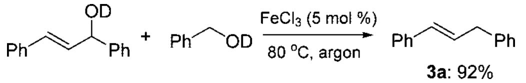
TABLE 5. Reduction of Allylic Acetates with Benzyl Alcohol Catalyzed by $FeCl_3 \cdot 6H_2O$[a]



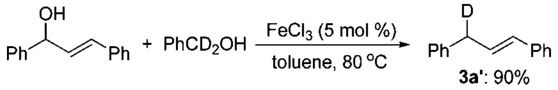
entry	R1	R2	R	time (h)	yield (%)	3/3′ [b]
1[c]	Ph	Ph	Ac	1	0	
2	Ph	Ph	Ac	2	94 (**3a**)	
3	Ph	Ph	PhCO	1	94 (**3a**)	
4	Ph	Ph	$PhCH_2CO$	1	92 (**3a**)	
5	Ph	p-$CH_3C_6H_4$	Ac	1	93 (**3h′**/**3h**)	64/36
6	p-$CH_3OC_6H_4$	Ph	Ac	1	91 (**3j**/**3j′**)	15/85
7	p-ClC_6H_4	Ph	Ac	1	92 (**3f**/**3f′**)	55/45
8	p-$CH_3C_6H_4$	p-$NO_2C_6H_4$	Ac	1	79 (**3q**/**3q′**)	15/85

[a] Reaction conditions: allylic acetates (0.5 mmol), benzyl alcohol (2.0 mmol), and $FeCl_3 \cdot 6H_2O$ (5 mol %) in toluene (1 mL) at 80 °C. [b] Ratios of isomers based on ^1H NMR. [c] In the absence of BnOH.

SCHEME 2



SCHEME 3

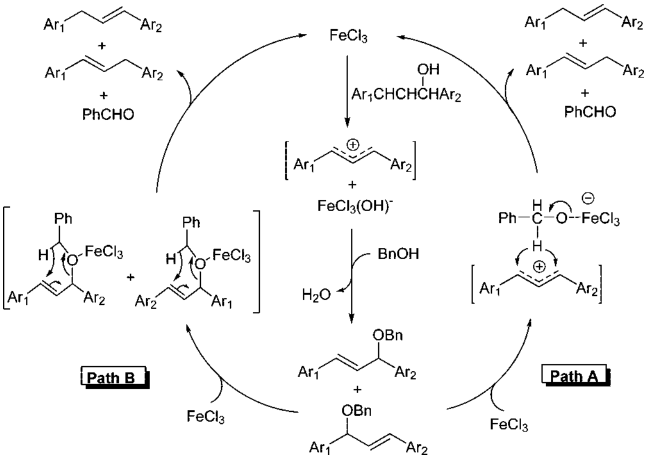


unexplored to date.[16] These results demonstrate that the reduction of allylic acetates with benzyl alcohol also involves an ether intermediate that can undergo the disproportionation.

V. Proposed Mechanism. In order to obtain further insight into the allylic reduction process, we examined the reaction of deuterated 1,3-diphenylprop-2-en-1-ol-d and $PhCH_2OD$ in the presence of anhydrous $FeCl_3$ under argon (Scheme 2). GC-MS analysis and ^1H NMR data indicated that the reduction product **3a** does not contain deuterium. However, treatment of **1a** with α,α-dideuteriobenzyl alcohol under the same conditions gave 3-deuterio-1,3-diphenyl-1-propene (**3a′**) in 90% yield (Scheme 3). These results suggest that the hydrogen at the benzylic position rather than the hydroxyl hydrogen of benzyl alcohol is transferred to allylic alcohols.

Scheme 4 displays the selectivity for the formation of two reduction isomers. It is observable that the double bond trends to transpose from the neighboring site of the electron-rich aryl ring to those adjacent to the aryl ring bearing the electron-withdrawing group and treatment of **5q** and **5q′** with anhydrous ferric chloride in toluene at 80 °C under argon atmosphere gave the reduction products with the similar ratio of isomers (Scheme 4). The structure of benzyl 3-(4-methylphenyl)-1-(4-nitrophenyl)allylic ether (**5q**) was verified by X-ray diffraction analysis (see Supporting Information). These results are clearly in agreement with the involvement of free allylic cations in this process (Scheme 5, path A) and are in contrast with the intramolecular six-membered ring intermediate (Scheme 5, path B). This sequence, identical with that already observed with the nucleophilic substitution of allylic alcohols, could be interpreted as the prevalence of the electronic effects in this transformation.[5,6a,c,17]

SCHEME 5. Plausible Mechanism for $FeCl_3$ Catalyzed Reduction of Allylic Alcohols with Benzyl Alcohol

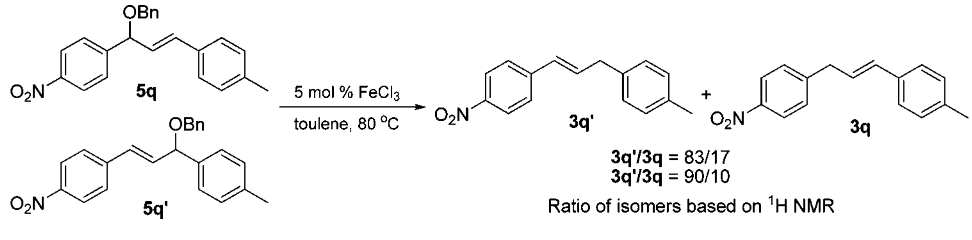


On the basis of the above results, a plausible reaction mechanism for the $FeCl_3$ catalyzed allylic reduction of allylic alcohol with benzyl alcohol is outlined in Scheme 5 (path A). First, the C−OH activation leads to the formation of an allylic cation as a reactive intermediate that may undergo isomerization as observed previously.[5a−d,6a,b,18] Subsequently, the benzyl alcohol attacks the allylic cation, giving allyl benzyl ether. Finally, the disproportionation of allylic benzyl ether through the newly $FeCl_3$ mediated selective cleavage of the C−O bond and sequent hydrogen transfer reaction give the desired products and benzaldehyde.

Conclusion

In conclusion, we have developed the iron catalyzed disproportionation of allylic alcohols leading to the corresponding alkenes and α,β-unsaturated ketones in good to high yields. Furthermore, this catalytic system is also effective for the allylic reduction of allylic alcohols (ethers or acetates) with benzyl alcohol to give the corresponding alkenes in moderate to excellent yields with complete selectivity. The Lewis acid catalyzed allylic reduction of allylic alcohols under mild, neutral, and convenient reaction conditions has until now been an unknown reaction system, in contrast to the recently reported Lewis acid catalyzed hydroxy substitution reactions of allylic alcohols with nucleophiles. The simplicity, economy, high efficiency, and use of environmentally benign reagents render

SCHEME 4



this method useful and competitive to the conventional approaches relying on application of external reducing agents.

Experimental Section

Typical Procedure for the Disproportionation of 1a Using $FeCl_3 \cdot 6H_2O$ as a Catalyst. To a solution of 1,3-diphenylprop-2-en-1-ol **1a** (0.5 mmol) in toluene (1.0 mL) was added 5 mol % $FeCl_3 \cdot 6H_2O$. The reaction mixture was stirred at 80 °C (monitored by TLC). The crude product was purified by silica gel column chromatography to provide the desired product 1,3-diphenyl-1-propene (**3a**) and chalcone (**4a**). **3a**, ^1H NMR (400 MHz, $CDCl_3$): δ 7.16−7.32 (m, 10H), 6.41 (d, $J = 16.04$ Hz, 1H), 6.28−6.35 (m, 1H), 3.50 (d, $J = 6.40$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.4, 137.7, 131.3, 129.5, 128.9, 128.8, 127.4, 126.5, 126.4, 39.6. MS (EI) *m*/*z*: 194 (100) [M^+], 179 (43), 115 (49), 91 (16).

Typical Procedure for the Allylic Reduction of Allylic Alcohol with Benzyl Alcohol. To a mixture of **1a** (105 mg, 0.5 mmol) and benzyl alcohol (0.2 mL, 2.0 mmol) in 1 mL of toluene was added 5 mol % $FeCl_3 \cdot 6H_2O$ (7 mg, 0.025 mmol), and then the reaction mixture was stirred at 80 °C. After completion of the reaction (monitored by TLC), the mixture was quenched with saturated NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over Na_2SO_4. After filtration and removal of solvent in vacuum, the crude product was purified with flash chromatography using petroleum ether/ethyl acetate as the eluent.

Typical Procedure for the Allylic Reduction of Allylic Ethers with Benzyl Alcohol. To a mixture of 1,3-diphenylallyl ethyl ether (119 mg, 0.5 mmol) and benzyl alcohol (0.2 mL, 2.0 mmol) in 1 mL of toluene was added 5 mol % $FeCl_3 \cdot 6H_2O$ (7 mg, 0.025 mmol), and then the reaction mixture was stirred at 80 °C. After completion of the reaction (monitored by TLC), the mixture was quenched with saturated NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over Na_2SO_4. After filtration and removal of solvent in vacuum, the crude product was purified with flash chromatography using petroleum ether/ethyl acetate as the eluent.

Typical Procedure for Allylic Reduction of Allylic Acetates with Benzyl Alcohol. To a mixture of 1,3-diphenylallyl acetate (126 mg, 0.5 mmol) and benzyl alcohol (0.2 mL, 2.0 mmol) in 1 mL of toluene was added 5 mol % $FeCl_3 \cdot 6H_2O$ (7 mg, 0.025 mmol), and then the reaction mixture was stirred at 80 °C. After completion of the reaction (monitored by TLC), the mixture was quenched with saturated NH_4Cl solution, and the aqueous layer was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over Na_2SO_4. After filtration and removal of solvent in vacuum, the crude product was purified with flash chromatography using petroleum ether/ethyl acetate as the eluent.

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Supporting Information Available: Experimental details, spectroscopic characterization data, copies of ^1H and ^{13}C NMR of reduction products, and crystal data of **3b** and **5q**. This material is available free of charge via the Internet at http://pubs.acs.org.

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