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$FeCl_3 \cdot 6H_2O$-catalyzed selective reduction of allylic halides to alkenes with concomitant oxidation of benzylic alcohols to aldehydes

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Iron-catalyzed direct reduction of allylic halides with benzylic alcohol was achieved, providing a new, simple, and efficient method for conducting highly regioselective hydrodehalogenation. This method not only features a readily available reductant, an inexpensive catalyst, simple manipulation, and good tolerance of functional groups including nitriles, nitro, esters, and methoxyl groups, it also has mild reaction conditions and shows complete regioselectivity in that only halides sited at the allylic position are reduced. Alternatively, this method can be applied in the selective transformation of benzylic alcohols to aromatic aldehydes without overoxidation to carboxylic acids.

selective reduction, allylic halides, Fe-based catalysts, hydrodehalogenations, benzyl alcohols

1 Introduction

The selective reduction of organic halides to hydrocarbons is an important reaction in organic synthesis [1] and environmental remediation [2]. Reduction of halide groups has also proven to be an important and efficient strategy for regulating the biological activity of natural and designed products for their final utility as potential pharmaceuticals [3]. Halides have also been applied as protecting and directing groups in organic synthesis [4], wherein a removal of halide functionalities is often needed after fulfilling their obligations [5]. Consequently, many methods have been developed for transformation of organic halides to the corresponding hydrocarbon compounds [6–8]. Metal-catalyzed reductive hydrodehalogenation of organic halides holds great promise because of many effective metals and numerous usable hydrogen sources that are available [7].

Although the application of Fe-based catalysts has yielded excellent results, these hydrodehalogenations are typically conducted in the presence of strong reductants such as $LiAiH_4$, alkylmagnesium halides, lithium [9], or by using expensive biomimetic complexes that are difficult to obtain (e.g. hematin, coenzyme F430) as catalysts [10]. These obstacles limit the scope of their applications. For example, the use of $LiAlH_4$ restricts the functional group tolerance of these reactions. In addition, the carbonyl groups that are very common and ubiquitous in many organic molecules have also been found to be cleavable upon treatment with $LiAlH_4$ [11].

Few existing methods allow halide substituents with apparently similar reactivities to be distinguished in dehalogenation processes [12]. Therefore, the development of reductant systems that permit the selective manipulation of different halide groups in reductive dehalogenation is highly desirable. On the industrial scale in particular, the application of cheap, readily available and environmentally benign reductants and catalysts in combination with a catalytic

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cycle designed to form minimal waste and to operate with maximum simplicity is essential.

Several methods for catalytic hydrodehalogenation of organic halides, using alcohols as a hydrogen source, have been developed [13]. These systems can still be improved, however, because most of them require the use of an expensive catalyst, stoichiometric metal-containing reductant, or base. Allylic halides remain important and versatile molecules with many applications in synthetic organic chemistry and in industrial chemical processes [14]. Therefore, efficient methods and techniques for their hydrodehalogenations are desirable. During studies on $FeCl_3$-catalyzed nucleophilic substitution reactions of allylic and propargylic alcohols [15], we found that allylic alcohols, allylic ethers, and allylic acetates could be selectively reduced by benzyl alcohol in the presence of $FeCl_3$. As a part of our continuing research on making use of benzyl alcohols as practical and versatile reductants, we were interested in the possibility of reducing allylic chlorides. We now report the catalytic reduction of allylic halides to alkenes with the concomitant oxidation of benzylic alcohol to aromatic aldehyde using $FeCl_3·6H_2O$ as catalyst, without any additives. This method shows good tolerance of functional groups and complete regioselectivity in that only halides sited at the allylic position are reduced.

2 Experimental

2.1 Materials and methods

Aldehydes, ketones and alcohols were purchased from Sigma-Aldrich. Catelysts were purchased from Alfa Aesar. Unless otherwise noted, all manipulations were performed in air. NMR spectra were recorded at 400 MHz for ^{1}H NMR and ^{13}C NMR using $CDCl_3$ as the solvent with TMS as the internal standard. Column chromatography was performed on silica gel. All iron salts were commercially produced and purity was A.R.

2.2 Synthesis

Allylic chlorides and allylic bromides were prepared according to the literature [16]. Allylic reduction of allylic chloride with benzyl alcohol was carried out according to the typical procedure: To a mixture of 1,3-diphenylallyl chloride (114 mg, 0.5 mmol) and benzyl alcohol (0.2 mL, 2.0 mmol) in 1 mL toluene was added 5 mol% $FeCl_3·6H_2O$ (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 the solvent by vacuum, the crude product was purified with flash chromatography using petroleum ether/ethyl acetate (100/1 to 50/1) as the eluent.

2.3 Characterizations

2a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.40 (m, 10H), 6.50 (d, J = 16.0 Hz, 1H), 6.37–6.43 (m, 1H), 3.58 (d, J = 6 Hz, 2H).

2b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22–7.24 (d, J = 8.4 Hz, 2H), 7.06–7.13 (m, 6H), 6.40 (d, J = 15.6 Hz, 1H), 6.23–6.31 (m, 1H), 3.47 (d, J = 6.4 Hz, 2H), 2.31 (s, 3H), 2.30 (s, 3H).

2c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 6.8 Hz, 4H), 7.14 (d, J = 8.4 Hz, 4H), 6.83–6.85 (m, 4H), 6.37 (d, J = 16.4 Hz, 1H), 6.15–6.22 (m, 1H), 3.78 (s, 6H), 3.45 (d, J = 6.8 Hz, 2H).

2d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.40 (m, 1H), 7.11–7.21 (m, 7H), 6.58 (d, J = 15.6 Hz, 1H), 6.15–6.21 (m, 1H), 3.54 (d, J = 6.4 Hz, 2H), 2.34 (s, 3H), 2.29 (s, 3H).

2e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.29 (m, 6H), 7.15 (d, J = 8.0 Hz, 2H), 6.38 (d, J = 16.0 Hz, 1H), 6.24–6.32 (m, 1H), 3.50 (d, J = 6.4 Hz, 2H).

2f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.35 (m, 9H), 6.31–6.44 (m, 2H), 3.52 (d, J = 5.6 Hz, 1.1H), 3.46 (d, J = 6.8 Hz, 0.9H).

2g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08–7.35 (m, 9H), 6.23–6.43 (m, 2H), 3.52 (d, J = 6.8 Hz, 0.7H), 3.50 (d, J = 6.4 Hz, 1.3H), 2.31–2.32 (m, 3H).

2h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03–7.33 (m, 9H), 6.57 (d, J = 15.6 Hz, 0.5H), 6.10–6.26 (m, 1.5H), 3.48 (d, J = 6.4 Hz, 1.2H), 3.43 (d, J = 4.4 Hz, 0.8H), 2.24 (s, 1.7H), 2.24 (s, 1.3H).

2i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14–7.36 (m, 7H), 6.82–6.86 (m, 2H), 6.19–6.44 (m, 2H), 3.78 (s, 3H), 3.52 (d, J = 6.8 Hz, 0.5H), 3.48 (d, J = 6.8 Hz, 1.5H).

2j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.27 (m, 8H), 6.22–6.42 (m, 2H), 3.49 (d, J = 6.0 Hz, 2H), 2.33 (s, 1.8H), 2.32 (s, 1.2H).

2k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.54 (m, 2H), 7.28–7.37 (m, 7H), 6.30–6.48 (m, 2H), 3.60 (d, J = 6.8 Hz, 0.8H), 3.57 (d, J = 4.4 Hz, 1.2H).

2**l:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12–8.18 (m, 2H), 7.21–7.47 (m, 7H), 6.47–6.61 (m, 1.6H), 6.27–6.34 (m, 0.4H), 3.64 (d, J = 6.8 Hz, 0.6H), 3.59 (d, J = 6.4 Hz, 1.4H).

2m: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–8.19 (m, 2H), 7.33–7.64 (m, 7H), 6.30–6.56 (m, 2H), 3.65 (d, J = 6.4 Hz, 1H), 3.58 (d, J = 5.2 Hz, 1H).

2n: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 6.44–6.57 (m, 2H), 3.79 (s, 3H), 3.62 (d, J = 5.6 Hz, 0.9H), 3.53 (d, J = 6.4 Hz, 1.1H).

2o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13–8.17 (m, 2H), 7.40–7.46 (m, 2H), 7.11–7.16 (m, 4H), 6.44–6.59 (m, 2H), 3.63 (d, J = 6.8 Hz, 0.6H), 3.55 (d, J = 6.4 Hz, 1.4H), 2.33 (s, 3H).

2p: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.60 (m, 2H), 7.22–7.42 (m, 7H), 6.25–6.53 (m, 2H), 3.57–3.61 (m, 2H).

2q: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–8.00 (m, 2H), 7.22–7.40 (m, 7H), 6.30–6.48 (m, 2H), 4.35 (q, J = 6.8, 2H), 3.57–3.60 (m, 2H), 1.38 (t, J = 6.8, 3H).

2r: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.35 (m, 9H), 6.29–6.48 (m, 2H), 3.51–3.55 (m, 2H), 2.57 (m, 2H), 1.59 (m, 2H), 1.27–1.32 (m, 4H), 0.88 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.9, 140.4, 137.6, 137.4, 135.5, 131.0, 130.9, 129.6, 128.7, 128.6, 128.3, 127.1, 126.2, 126.1, 38.8, 35.4, 31.5, 29.8, 22.4, 14.1.

5a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.64 (m, 3H), 7.68–7.88 (m, 2H), 10.01 (s, 1H).

5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.31–7.32 (m, 2H), 7.75–7.77 (m, 2H), 9.95 (s, 1H).

5c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.51 (m, 2H), 7.80–7.82 (m, 2H), 9.97 (s, 1H).

5d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, 1H), 7.56–7.58 (m, 2H), 7.41–7.46 (m, 4H), 6.70–6.76 (m, 1H).

6a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.58 (s, 2H), 5.01 (d, 1H), 6.31–6.36 (m, 1H), 6.62 (d, 1H), 7.22–7.43 (m, 15H).

3 Results and discussion

3.1 Hydrodechlorination of allylic chlorides using benzyl alcohol

In our initial experiments, the reaction of allylic chloride **1a** with benzyl alcohol was chosen as a model reaction and carried out in the presence of various Lewis acids under different reaction conditions, in order to develop the optimum reaction conditions (Table 1). Only a trace amount of hydrodechlorination product **2a** was obtained when a mixture of **1a** and $PhCH_2OH$ (4 equiv.) was treated using 5 mol% $FeCl_3{\cdot}6H_2O$ in toluene at room temperature (Table 1, entry 1). Elevating the reaction temperature was favorable to the reaction (entries 2 and 3); when the reaction was performed in toluene at 80 °C, **2a** was afforded in the highest yield (Table 1, entry 3). Inferior results were observed when the reaction was performed with strong coordinating solvents such as THF and nitromethane (entries 5–6). Significantly, in the absence of a solvent the reaction could also give **2a** at 85% yield (Table 1, entry 7). Isopropanol did not work as a reducing agent (Table 1, entry 8). The stoichiometric ratio of **1a** and benzyl alcohol did not observably affect the yield (Table 1, entries 3 *vs*. 4). To further improve the yields in this transformation, the effect of metal sources was systematically examined. It was discovered that use of $Fe(acac)_3$ as a replacement was ineffective (Table 1, entry 12). Moreover, treatment of a mixture of **1a** and $PhCH_2OH$ with $InCl_3$, $BiCl_3$, $ZnCl_2$, $CuCl_2$, or $PdCl_2$ in toluene gave **2a** only at low yield (Table 1, entries 13–17). Other metals showed no activity for the reduction (Table 1, entries 18 and 19). Further investigation results indicated that no desired product could be formed in the absence of a catalyst (Table 1, entry 20). Replacement of $FeCl_3{\cdot}6H_2O$ with anhydrous $FeCl_3$ led to a slight increase of the yield (Table 1, entry 21). Taking into account the price of anhydrous $FeCl_3$, the reactions were carried out only with $FeCl_3{\cdot}6H_2O$ thereafter.

These optimized conditions were then applied to the reduction of other substrates. As shown in Table 2, various allylic chlorides were efficiently reduced by benzyl alcohol. The change of substituent from the *para*- to the *ortho*- position on the phenyl ring led to a slight decrease of the yield, probably due to the steric effect (Table 2, entries 2 and 4). To our delight, various electron-rich, electron-neutral, and electron-deficient substituents were well tolerated. The presence of strong electron-withdrawing groups such as trifluoromethyl and nitro on the benzene rings slightly decreased the yields of alkenes (Table 2, entries 10–16). Significantly, when aryl-substituted allylic chlorides **1e** and **1f**, which have a chloride substituent at the *para*-position in the benzene ring, were used as substrates, only the chloride at the allylic position was reduced, even with an elevated reaction temperature and a higher catalyst loading (Table 2, entries 5 and 6). For the allylic chlorides bearing different substituents at the 1- and 3- positions, two reduction isomers involving double-bond isomerization were observed, and the isomer distributions were controlled by the nature of the substituent on the phenyl ring (Table 2, entries 6–18). It was noted that nitro, ethoxycarbonyl, acetyl, and cyano substituents on the phenyl ring, which are incompatible in other Fe-based catalytic systems using $LiAiH_4$ and alkylmagnesium halides as reductants [17], were efficient in this transformation (entries 12–17).

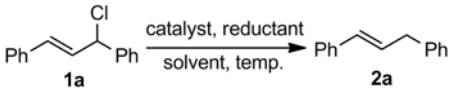
3.2 Hydrodebromination of allylic bromides using benzyl alcohol

It was found that a variety of allylic bromides could also be selectively reduced by BnOH in the present catalytic system, to give the corresponding alkenes in moderate to excellent yields (Table 3). We carried out a series of experiments to illustrate the chemoselectivity of the present reductive system. Mixtures of benzylic halides and allylic halides were prepared and treated with $PhCH_2OH$-$FeCl_3{\cdot}6H_2O$. In all cases, no reduction products arising from benzylic halides were observed, while allylic halides were smoothly reduced.

3.3 Oxidization of allylic alcohols using 1a

The selective oxidation of benzylic alcohols to aromatic aldehydes is one of the most significant and widely used methods in organic syntheses at the industrial level [18]. Oxidation methods based on non-[O]-containing oxidants remain little explored [19], although they are of potential academic and industrial significance, particularly for the oxidation of substrates with oxygen sensitive functionalities. Considering that $FeCl_3{\cdot}6H_2O$ and allylic chlorides are

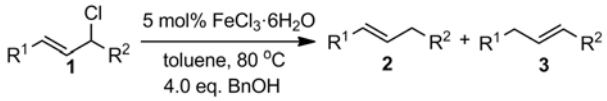
Table 1 Screening conditions for reduction of **1a** to **2a** [a]



Entry	Catalyst	Reductant	Solvent	T (°C)	Yield [b] (%)
1	$FeCl_3·6H_2O$	BnOH	Toluene	r.t.	trace
2	$FeCl_3·6H_2O$	BnOH	Toluene	55	50
3	$FeCl_3·6H_2O$	BnOH	Toluene	80	88
4 [c]	$FeCl_3·6H_2O$	BnOH	Toluene	80	89
5	$FeCl_3·6H_2O$	BnOH	THF	80	25
6	$FeCl_3·6H_2O$	BnOH	CH_2NO_2	80	40
7	$FeCl_3·6H_2O$	BnOH	–	80	85
8	$FeCl_3·6H_2O$	^{i}PrOH	Toluene	80	0
9	$FeCl_3·6H_2O$ [d]	BnOH	Toluene	80	80
10	$FeCl_3·6H_2O$ [e]	BnOH	Toluene	80	60
11	$FeCl_3·6H_2O$ [f]	BnOH	Toluene	80	86
12	$Fe(acac)_3$	BnOH	Toluene	80	0
13	$InCl_3$	BnOH	Toluene	80	15
14	$BiCl_3$	BnOH	Toluene	80	21
15	$ZnCl_2$	BnOH	Toluene	80	34
16	$CuCl_2$	BnOH	Toluene	80	30
17	$PdCl_2$	BnOH	Toluene	80	45
18	$NiCl_2·6H_2O$	BnOH	Toluene	80	trace
19	YCl_3	BnOH	Toluene	80	0
20	–	BnOH	Toluene	80	0
21	$FeCl_3$	BnOH	Toluene	80	90

a) Reaction conditions: allylic chloride (0.1 mmol), benzyl alcohol (0.4 mmol), $FeCl_3·6H_2O$ (5 mol%) in toluene for 1 h; b) yield determined by GC-MS; c) 0.8 mmol BuOH; d) 20 mol% $FeCl_3·6H_2O$; e) reaction time: 0.5 h; f) reaction time: 2 h.

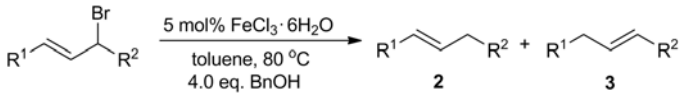
Table 2 Reduction of allylic chlorides with benzyl alcohol catalyzed by $FeCl_3·6H_2O$ [a]



Entry	R^1	R^2	Time (h)	Product (yield, %) [b]	**2/3**
1	C_6H_5	C_6H_5	1	**2a** (88)	
2	*p*-MeC_6H_4	*p*-MeC_6H_4	1	**2b** (85)	
3	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	1	**2c** (80)	
4	*o*-MeC_6H_4	*o*-MeC_6H_4	1	**2d** (75)	
5	*p*-ClC_6H_4	*p*-ClC_6H_4	1	**2e** (70)	
6	*p*-ClC_6H_4	C_6H_5	1	**2f/3f** (75) [c]	55/45
7	*p*-MeC_6H_4	C_6H_5	1	**2g/3g** (82) [c]	35/65
8	*o*-MeC_6H_4	C_6H_5	1	**2h/3h** (78) [c]	40/60
9	*p*-$MeOC_6H_4$	C_6H_5	1	**2i/3i** (78) [c]	25/75
10	*p*-ClC_6H_4	*p*-MeC_6H_4	1	**2j/3j** (75) [c]	52/48
11	*p*-$CF_3C_6H_4$	C_6H_5	2	**2k/3k** (60) [c]	65/35
12	*p*-$O_2NC_6H_4$	C_6H_5	4	**2l/3l** (70) [c]	70/30
13	*m*-$O_2NC_6H_4$	C_6H_5	4	**2m/3m** (60) [c]	55/45
14	*p*-$O_2NC_6H_4$	*p*-$MeOC_6H_4$	4	**2n/3n** (68) [c]	55/45
15	*p*-MeC_6H_4	*p*-$NO_2C_6H_4$	4	**2o/3o** (67) [c]	30/70
16	*p*-NCC_6H_4	C_6H_5	4	**2p/3p**(61) [c]	65/35
17	*p*-$EtOCOC_6H_4$	C_6H_5	4	**2q/3q** (73) [c]	55/45
18	*p*-$C_5H_{11}C_6H_4$	C_6H_5	2	**2r/3r** (71) [c]	–

a) Reaction conditions: allylic chloride (0.5 mmol), benzyl alcohol (2.0 mmol), $FeCl_3·6H_2O$ (5 mol%) in toluene (1 mL) at 80 °C; b) isolated yield; c) obtained as a mixture of double bond transposed isomers; d) ratios of isomers based on ^{1}H NMR.

Table 3 Reduction of allylic bromides with benzyl alcohol catalyzed by $FeCl_3·6H_2O$ [a]



Entry	R^1	R^2	Time (h)	Product(yield, %) [b]	**2/3** [d]
1	C_6H_5	C_6H_5	1	**2a** (89)	
2	*p*-MeC_6H_4	*p*-MeC_6H_4	1	**2b** (90)	
3	*p*-ClC_6H_4	*p*-ClC_6H_4	1	**2e** (81)	
4	*p*-ClC_6H_4	C_6H_5	1	**2f/3f** (83) [c]	51/49
5	*p*-MeC_6H_4	C_6H_5	1	**2g/3g** (88) [c]	31/69
6	C_6H_5	*p*-MeC_6H_4	1	**2g/3g**(85) [c]	39/61
7	*p*-$MeOC_6H_4$	C_6H_5	1	**2i/3i** (91) [c]	26/74
8	*p*-NCC_6H_4	C_6H_5	4	**2p/3p** (62) [c]	75/25

a) Reaction conditions: allylic bromide (0.5 mmol), benzyl alcohol (2.0 mmol), $FeCl_3·6H_2O$ (5 mol%) in toluene (1 mL) at 80 °C; b) yield determined by GC-MS; c) obtained as a mixture of double-bond-transposed isomers; d) ratios of isomers based on ^{1}H NMR.

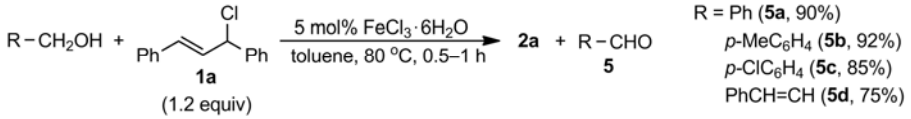
readily available and inexpensive, and that the reduced products (alkenes) are important starting materials in organic synthesis and that no base or other additive is required in the above reaction process, we expanded the utility of this reaction in the selective oxidation of other alcohols to the corresponding aldehydes. As illustrated in Scheme 1, a series of benzylic alcohols $RC_6H_4CH_2OH$ (R = H (**4a**), Me (**4b**), Cl (**4c**), $PhCH{=}CH_2$ (**4d**)) were investigated by oxidation with **1a** in the presence of 5 mol% of $FeCl_3·6H_2O$. In general, the electronic effect of substituents on benzene rings has significant impact on the yield. For example, the reaction of **1a** with benzylic alcohols with an electron-donating methyl (**4b**) gave excellent results (Scheme 1), whereas benzylic alcohols bearing electron-withdrawing groups such as chloro gave the corresponding product at 85% yield. 3- Phenylprop-2-en-1-ol could also be oxidized by **1a** under these conditions, giving the corresponding 3-phenylacrylal- dehyde **5d** at 75% isolated yield.

3.4 Proposed mechanism for the Fe-catalyzed hydrodehalogenation of allylic halides using benzyl alcohol

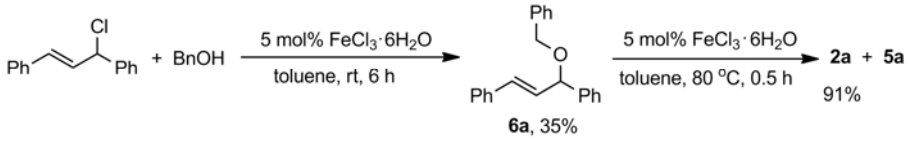
To elucidate the mechanism of the reduction of allylic halides, the following reactions were performed. First, we examined the reaction of allylic chloride (**1a**) with benzyl alcohol in the presence of 5 mol% of $FeCl_3·6H_2O$ in toluene at room temperature. As shown in Scheme 2, when the reaction was carried out at 20 °C for 6 h, the allylic benzyl ether **6a** was isolated at 35% yield. The disproportionation of **6a** took place successfully in only the presence of $FeCl_3·6H_2O$ and toluene, providing **2a** and **5a** in high yields. Furthermore, GC-MS analysis and ^{1}H NMR data indicated that the reduction product **2a**, which resulted from the reaction of **1a** with deuterated $PhCH_2OD$ in the presence of anhydrous $FeCl_3$, does not contain deuterium. These results suggest that the hydrogen at the benzylic position rather than the hydroxyl hydrogen of benzyl alcohol is transferred to allylic halides.

In addition, treatment of **5q** and **5q′** with $PhCH_2OH$ under the same conditions gave the reduction products with similar ratios of isomers (Scheme 3). These results are clearly in agreement with the involvement of free allylic cations in this process.

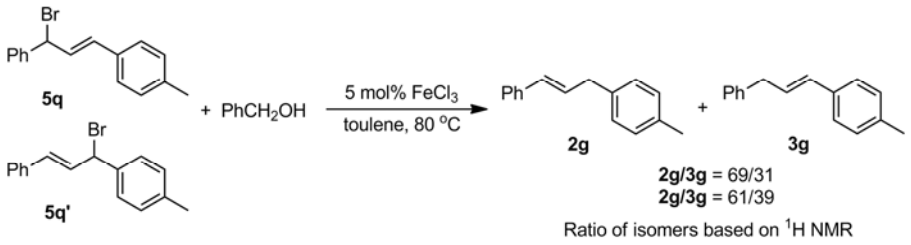
On the basis of the above results, a plausible reaction mechanism for the $FeCl_3$-catalyzed reduction of allylic halides with benzyl alcohol is outlined in Scheme 4. First, the nucleophilic substitution of allylic halide with benzyl alcohol leads to the formation of an allylic benzyl ether as a reactive intermediate (**6**). Subsequently, the disproportionation of allylic benzyl ether through $FeCl_3$-mediated selective



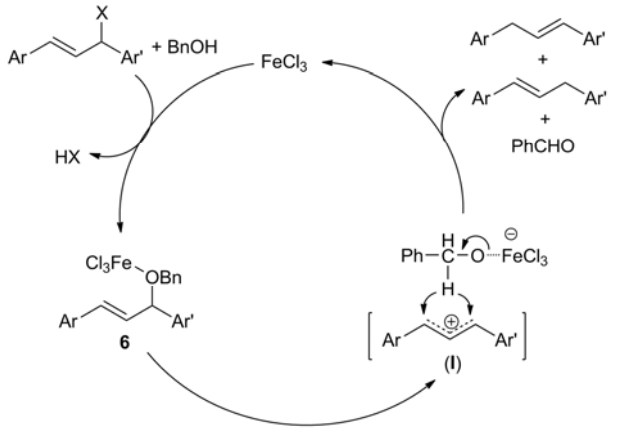
Scheme 1 Oxidization of allylic alcohols with **1a** catalyzed by $FeCl_3·6H_2O$.



Scheme 2 Elucidating the mechanism of the reduction of allylic halides.



Scheme 3 Selectivity for the formation of two reduction isomers.



Scheme 4 A plausible mechanism for the $FeCl_3$-catalyzed reduction of allylic halides with benzyl alcohol.

cleavage of the C–O bond and the subsequent hydrogen transfer reaction gives the desired reduction products and benzaldehyde, as previously observed [15e].

4 Conclusions

In summary, the direct reduction of allylic halides to alkenes using benzyl alcohol as a reductant has been established. The reduction system is selective for the reduction of only halides sited at the allylic position. The advantages of reductive dehalogenation are the ability to utilize commercially available and cheap reductants and catalysts, ease of handling, good tolerance of functional groups, and mild reaction conditions without the requirement of any additives. Moreover, the oxidation product (benzyl aldehyde) is easily isolated as a common bulk chemical, making this transformation an attractive addition to the portfolio of reductions. Alternatively, the reaction also provides an economical, efficient, and functional group-friendly method for the selective oxidation of benzylic alcohols without overoxidation to carboxylic acids.

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