

# Active-iron-promoted hydrodehalogenation of organic halides

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Dedicated to Prof. Bruno Vuano on the occasion of his 68th birthday.

## Abstract

Under very mild reaction conditions, the active-iron-based reducing system composed of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , an excess of lithium powder and a catalytic amount (5 mol%) of 4,4'-di-*tert*-butylbiphenyl (DTBB) as electron carrier, efficiently performed the hydrodehalogenation of alkyl and aryl halides in tetrahydrofuran at room temperature. The reaction of a series of alkyl and aryl chlorides, bromides, and iodides with this reducing combination led to the formation of the corresponding products resulting from a halogen/hydrogen exchange. Interestingly, the reducing system was efficient in the hydrodehalogenation of aryl fluorides and polychlorinated aromatics. The use of deuterium oxide instead of water in the iron salt allowed the preparation of the corresponding deuterated products. A reaction mechanism has been proposed on the basis of different experiments.

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**Keywords:** Active-iron; Hydrodehalogenation; Organic halides; Polychlorinated aromatics

## 1. Introduction

Organic halides remain important and versatile molecules with many applications in synthetic organic chemistry and in industrial chemical processes. Despite natural organohalogens often possess an astonishing biological activity [1], many of synthetic origin are classified as high priority pollutants due to their adverse impact on the environment with persistent toxic effects (for reviews, see Ref. [2]). Therefore, efficient methods and techniques that allow their complete detoxification or transformation into less noxious chemicals are welcome. Several technologies have been developed in order to solve this environmental problem, i.e., incineration, pyrolysis, chemical [3] and biochemical degradation [4]. However, some of them lead to the formation of other halogenated pollutants or are methodologies not sufficiently developed.

On the other hand, chemical methods (for general methods reviews, see Ref. [5]) have demonstrated to be the most

effective and consequently the most studied ones. Among them, the reductive hydrodehalogenation of organic halides, a fundamental chemical transformation in organic synthesis (for a review on the metal-mediated hydrodehalogenation of organic halides, see Ref. [6(a)]; for a special issue on catalytic dehalogenation, see Ref. [6(b)]), represents an attractive alternative to the more noxious oxidative methods, allowing the conversion of halocompounds into more environmentally friendly and useful chemicals. Thus, catalytic hydrogenation (for a monograph, see Ref. [7(a)]; see also, for instance, Ref. [7(b)]), metal or low-valent metal compounds (for a review, see Ref. [8]), metal hydrides or complex metal hydrides (for monographs and reviews, see Refs. [9,10]), as well as some strong nucleophilic neutral or anionic species (for reviews, see Refs. [11,12]), are some of the general reagents and methods able to accomplish the above mentioned transformation. It is worthy of note that the use of zero-valent transition metals to degrade halogenated contaminants represents an active research area and one of the latest technologies for environmental remediation (see for instance, Ref. [13]). In this field, the use of iron metal prevails over other metals, mainly due to its virtually nil environmental impact, in fact there is no

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exposure limit to humans, as stated by the OSHA (United States Occupational Safety and Health Administration). However, most of the studies carried out involving iron metal deal with a very specific type of substrates, mostly halomethanes, haloethanes, and haloethenes, whereas broader methodological studies covering the reactivity of the carbon–halogen bond (i.e. carbon hybridization or type of halogen) are very seldom [6(a)].

In recent years, we have studied new active-metal-based reducing systems, consisting of a mixture of hydrated chlorides of different transition metals ( $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ), and lithium in the presence of a catalytic amount of an arene. The most studied  $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ -Li-arene(cat.) system showed to be very effective in the reduction of a wide variety of functional groups (for a review, see Ref. [14]). The  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ -Li-arene(cat.) system was successfully applied to the reduction of carbonyl compounds and imines [15], as well as to that of sulfonates [16], whereas the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -Li-arene(cat.) exhibited a remarkable behaviour in the stereoselective reduction of cyclic ketones [17]. With regard to the hydrodehalogenation of organic halides, the active-nickel-based reducing system efficiently performed the reduction of alkyl and aryl halides (chlorides, bromides, and iodides), albeit fluorides remained unaltered [18]. The active-copper-based reducing system, in addition to the behaviour of the nickel-based analogue, showed to be effective in the hydrodehalogenation of both alkyl and aryl fluorides [19], its lower toxicity and commercial availability being additional advantages. Moreover, deuterium labeled compounds could be prepared in both cases when the deuterium oxide containing salts were used instead of the water-containing ones.

Our ongoing interest in the field above described, together with the intrinsic importance of a methodological comparative study about the reactivity of different transition metals, prompted us to explore new synthetic applications of these active-metal-based reducing systems, now focusing on iron, as a possible candidate to be used in the reduction of organic halocompounds.

We want to present herein our results on the study of the hydrodehalogenation of organic halides, under very mild reaction conditions, based on the use of active-iron, generated from commercially available iron(II) chloride tetrahydrate, lithium, and a catalytic amount of an arene (DTBB) as electron carrier.

## 2. Experimental

### 2.1. Materials

All moisture sensitive reactions were carried out under a nitrogen atmosphere. Anhydrous tetrahydrofuran was freshly distilled from sodium/benzophenone ketyl. Other solvents used were treated prior to use by standard methods [20]. All starting materials were of the best available grade (Acros, Aldrich, Fluka, Merck) and were used without further purification. Commercially available iron(II) chloride tetrahydrate was used in the hydrodehalogenation reactions; its deuterated derivative  $\text{FeCl}_2 \cdot 2\text{D}_2\text{O}$  was prepared by treating anhydrous iron(II)

chloride with an excess of deuterium oxide and then by heating in vacuo (*ca.* 0.5 Torr) at 80 °C in the short path for 1 h. Column chromatography was performed with Merck silica gel 60 (0.040–0.063  $\mu\text{m}$ , 240–400 mesh). Thin layer chromatography (TLC) was performed on pre-coated silica gel plates (Merck 60, F254, 0.25 mm).

### 2.2. Instrumentation and analysis

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker ARX-300 spectrophotometer using  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as internal reference. Mass spectra (EI) were obtained at 70 eV on a Hewlett Packard HP-5890 GC/MS instrument equipped with a HP-5972 selective mass detector. Infrared (FT-IR) spectra were obtained on a Nicolet-Nexus spectrophotometer. The purity of volatile compounds and the chromatographic analyses (GC) were determined with a Shimadzu GC-9A instrument equipped with a flame-ionisation detector and a 2 m column (1.5% OV17 9<sub>A</sub> SUS Chrom 103 80/1000), using nitrogen as carrier gas.

### 2.3. Reduction of halogenated compounds using the $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -Li-DTBB combination: general procedure

A solution of the halogenated compound (1.0 mmol) in THF (5 mL) was added to a mixture of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (198 mg, 1 mmol) or its deuterated salt (166 mg, 1 mmol), lithium powder (56 mg, 8.0 mmol) and DTBB (27 mg, 0.1 mmol) in THF (5 mL) at room temperature under a nitrogen atmosphere. The reduction of 1-chloronaphthalene (Table 2, entry 4) was performed in the absence of an external arene as electron carrier, the substrate itself acting as an arene. The reaction mixture, which was initially dark green, changed to black, thus indicating the formation of activated iron(0). After total conversion of the starting material (GLC), the resulting suspension was diluted with diethyl ether (20 mL). Then, 10% HCl (20 mL) was added and the mixture stirred until transparency. The organic layer was washed with water (20 mL), dried over anhydrous sodium sulfate, and evaporated (15 Torr). The resulting residue was purified by column chromatography (silica gel; hexane/ethyl acetate). For volatile products, the dried organic layer was analysed by GLC using toluene as an internal standard. The hydrodehalogenated products were fully characterised by comparison of their chromatographic and spectral data with those of the corresponding commercially available pure samples (*n*-nonane, *n*-dodecane, ethylbenzene, *tert*-butylbenzene, *iso*-butylbenzene, anisole, naphthalene, benzene, toluene, phenol, and biphenyl). *p*-Menthane [21], 4-deuteriotoluene [22], and 1-deuteriododecane [23] were characterised by comparison of their chromatographic and spectral data with those described in the literature.

## 3. Results and discussion

The hydrodehalogenation of a series of organic halides was successfully carried out using a mixture of commercially available iron(II) chloride tetrahydrate (1.0 mmol), an excess of

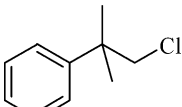
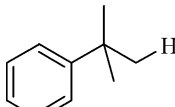
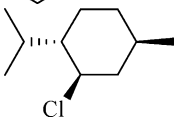
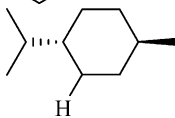
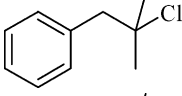
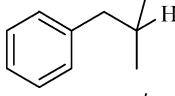
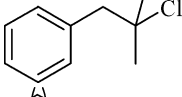
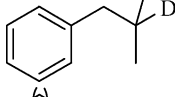






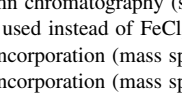

lithium powder (1:8 molar ratio, referred to the iron salt) and a catalytic amount of DTBB (0.1 mmol per mmol of iron salt, 5.0 mol%) in tetrahydrofuran at room temperature. The presence of the hydrated iron salt was demonstrated to be essential for the success of the reaction by carrying out a series of blank experiments. Thus, in the absence of the hydrated salt or using the corresponding anhydrous one, yields were much lower due to the formation of by-products, mainly derived from homocoupling or elimination reactions of the starting materials [24].

This active-iron-based reducing system showed to be effective in the reduction of a variety of alkyl halides under mild reaction conditions. Primary, secondary, and tertiary alkyl chlorides (Table 1, entries 1, 2, and 3, respectively), were easily transformed into the corresponding hydrodehalogenated products, as well as a primary alkyl bromide (Table 1, entry 5), and primary alkyl iodides (Table 1, entries 7 and 8). Due to the strength of the C–F bond, organic fluorides are rather resistant to reduction (for reviews on carbon–fluorine bond activation, see Ref. [25]). In fact, alkyl fluorides remained unaltered even after long reaction times, higher reaction temperature, or using an excess of the reducing system. In this sense, this new active-iron reducing system showed a similar

chemical reactivity to that of its nickel-based analogous one previously reported by us [18].

Concerning alkyl iodides, the reaction temperature demonstrated to play a significant role in driving the reaction toward the formation of the hydrodehalogenated or homocoupling products. A series of experiments were carried out at different temperatures ranging from  $-78\text{ }^{\circ}\text{C}$  to THF reflux, the results showing that the lower the temperature, the higher the yield in homocoupling products. For instance, the reduction of 1-iodononane or phenethyl iodide either at  $-78$  to  $25\text{ }^{\circ}\text{C}$  (overnight) or at  $-20\text{ }^{\circ}\text{C}$  (6 h) gave the same *ca.* 1:3 ratio of *n*-nonane/*n*-octadecane and ethylbenzene/1,4-diphenylbutane, respectively. However, at room or higher temperature a *ca.* 2:1 ratio of the same products was obtained, room temperature ( $25\text{ }^{\circ}\text{C}$ ) being, therefore, the best choice in order to drive the reaction toward the hydrodehalogenated products. It should be pointed out that an opposite temperature-dependent reactivity was observed in the reduction of alkyl iodides with the analogous copper-based reducing system [19]. In this case, the lower the temperature, the lower the yield in homocoupling products.

Table 1  
Reduction of alkyl halides

Entry	Starting material	Reaction conditions <sup>a</sup>		Product <sup>b</sup>	
		FeCl <sub>2</sub> ·4H <sub>2</sub> O (equiv.)	<i>t</i> (h)	Structure	Yield <sup>c</sup> (%)
1		1.0	4		80
2		1.0	4		90 <sup>d</sup>
3		1.0	5		91
4		1.0 <sup>e</sup>	5		74 <sup>d,f</sup>
5		1.0	3		72 <sup>d</sup>
6		1.0 <sup>e</sup>	3		70 <sup>d,g</sup>
7		1.0	3		66 <sup>h</sup>
8		1.0	3		62 <sup>i</sup>

<sup>a</sup> Alkyl halide (1 mmol), Li (8 mmol), DTBB (0.1 mmol), THF (10 mL),  $25\text{ }^{\circ}\text{C}$ .

<sup>b</sup> All isolated products were >95% pure (GLC).

<sup>c</sup> GLC yield based on the starting halogenated compound.

<sup>d</sup> Purified by column chromatography (silica gel, hexane/ethyl acetate).

<sup>e</sup> FeCl<sub>2</sub>·2D<sub>2</sub>O was used instead of FeCl<sub>2</sub>·4H<sub>2</sub>O.

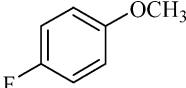
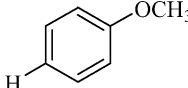
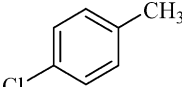
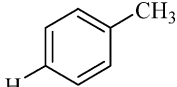
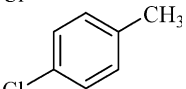
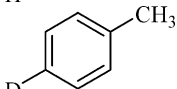
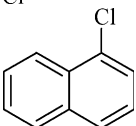
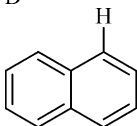
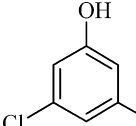
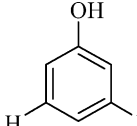
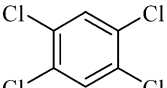
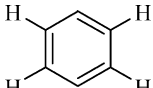
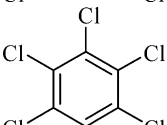
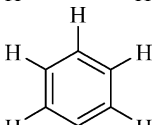
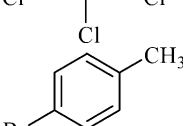
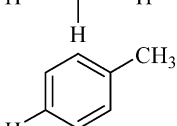
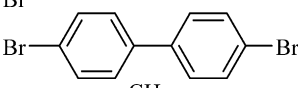
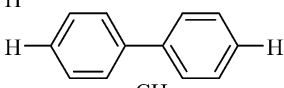
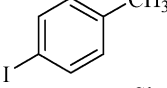
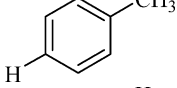
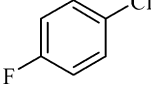
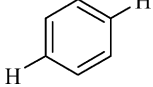
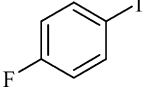
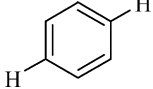
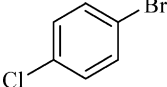
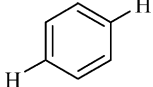
<sup>f</sup> 70% deuterium incorporation (mass spectrometry, 300 MHz <sup>1</sup>H NMR).

<sup>g</sup> 73% deuterium incorporation (mass spectrometry, 300 MHz <sup>1</sup>H NMR).

<sup>h</sup> 30% of *n*-octadecane was obtained as by-product.

<sup>i</sup> 33% of 1,4-diphenylbutane was obtained as by-product.

Table 2  
Reduction of aryl halides

Entry	Starting material	Reaction conditions <sup>a</sup>		Product <sup>b</sup>	
		FeCl <sub>2</sub> ·4H <sub>2</sub> O (equiv.)	t (h)	Structure	Yield <sup>c</sup> (%)
1		1.0	3		72 <sup>d</sup>
2		1.0	2		83
3		1.0 <sup>e</sup>	2		90 <sup>d,f</sup>
4		1.0	2 <sup>g</sup>		93 <sup>d</sup>
5		2.5	3		90 <sup>d</sup>
6		5.0	5		89
7		7.0	5		85
8		1.0	2		70
9		2.5	3		85 <sup>d</sup>
10		1.0	2		75
11		2.0	4		84
12		2.0	4		80
13		2.0	4		81

<sup>a</sup> Alkyl halide (1 mmol), Li (8 mmol), DTBB (0.1 mmol), THF (10 mL), 25 °C.

<sup>b</sup> All isolated products were >95% pure (GLC).

<sup>c</sup> GLC yield based on the starting halogenated compound.

<sup>d</sup> Purified by column chromatography (silica gel, hexane/ethyl acetate).

<sup>e</sup> FeCl<sub>2</sub>·2D<sub>2</sub>O was used instead of FeCl<sub>2</sub>·4H<sub>2</sub>O.

<sup>f</sup> 60% deuterium incorporation (mass spectrometry, 300 MHz <sup>1</sup>H NMR).

<sup>g</sup> Reaction performed in the absence of the external electron carrier DTBB.

As an additional advantage of this methodology, the use of the deuterated iron salt,  $\text{FeCl}_2 \cdot 2\text{D}_2\text{O}$ , easily prepared from anhydrous  $\text{FeCl}_2$  and  $\text{D}_2\text{O}$ , followed by thermal treatment under vacuum (see experimental), led to the corresponding deuterium labeled products in a simple and economic way (Table 1, entries 4 and 6).

With regard to the hydrodehalogenation of aromatic halides, a more important subject from the environmental point of view, this iron-based reducing combination demonstrated to be very efficient in their complete reduction, even in the case of polyhalogenated aromatic compounds.

In contrast with the inertness exhibited by the alkyl C–F bond toward the iron-based reducing combination, aromatic fluorides could be hydrodehalogenated in good yields under the same reaction conditions. For instance, *p*-fluoroanisole was transformed into anisole in good yield (Table 2, entry 1). This behaviour allowed the selective reduction of an aromatic fluoride, such as *p*-fluoroanisole (100% conversion), in the presence of an alkyl fluoride, such as 1-fluorononane (Scheme 1). By comparing this reactivity of fluorides with that shown by its nickel- and copper-based counterparts, it can be said that these three reducing systems are complementary to each other in synthetic applications, making possible to reduce chlorides, bromides, or iodides in the presence of any kind of fluorides when using nickel, to completely reduce alkyl and aryl fluorides when using copper, or to reduce aryl fluorides in the presence of alkyl ones when using iron.

Monochlorinated aromatics such as *p*-chlorotoluene or 1-chloronaphthalene (Table 2, entries 2 and 4, respectively), were also efficiently hydrodehalogenated to give the corresponding arene products in good yields. Deuterated aromatic hydrocarbons were obtained when  $\text{FeCl}_2 \cdot 2\text{D}_2\text{O}$  was used instead of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in the reducing system (Table 2, entry 3). On the other hand, the hydrodehalogenation of polychlorinated aromatics is a subject of continuous interest for many research groups [26–28] due to their toxic effects and persistence in the environment. For instance, 3,5-dichlorophenol has been classified as a reproductive effector, whereas 1,2,4,5-tetrachlorobenzene, a fungicide and electrical insulator, is considered as a tumorigen agent. Moreover, hexachlorobenzene, an agricultural chemical and pesticide with many other applications, has been defined as a carcinogenic of category 2, toxic and dangerous for the environment, as well as a tumorigen, mutagen, and reproductive effector agent. In particular, the detoxification of the two latter by incineration requires high temperatures and/or pressures due to their thermal stability, whereas other methods, such as the reductive dechlorination in sediment under sulfate reducing conditions, are rather low [29]. In this sense, the  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ -Li-arene system was able to completely hydrodehalogenate 3,5-dichlorophenol at room temperature in only 3 h and with

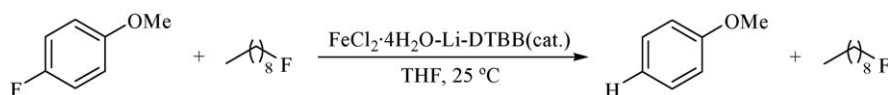
excellent yield (Table 2, entry 5). It is noteworthy that by using an excess of the reducing system under the same mild reaction conditions, 1,2,4,5-tetrachlorobenzene and hexachlorobenzene were completely reduced to benzene in 5 h (100% conversion), without any trace of chlorinated by-products (Table 2, entries 6 and 7, respectively).

This methodology was equally efficient in the reduction of aryl bromides and iodides. Thus, by applying the same standard reductive conditions, *p*-bromotoluene and *p*-iodotoluene were reduced to toluene (Table 2, entries 8 and 10), whereas 4,4'-dibromobiphenyl (a PBB congener) was completely debrominated and converted into biphenyl in high yield (Table 2, entry 9). It is worthy of note that in contrast with the reduction of alkyl iodides, none homocoupling by-product was observed in the hydrodehalogenation of aryl iodides, even at lower ( $-50\text{ }^\circ\text{C}$ ) or at higher (THF reflux) reaction temperatures.

In order to study the possible halogen chemoselectivity of this iron-based reducing system, the hydrodehalogenation of dihalogenated aromatic compounds bearing two different halogens was tested. We chose *p*-chlorofluorobenzene, *p*-fluoroiodobenzene, and *p*-bromochlorobenzene (Table 2, entries 11–13) as representative substrates. Unfortunately, no selectivity was observed for any of the dihalogenated substrates tested using 1.0 equiv. of the reducing system (referred to the starting material), even at low temperatures ( $-20$  to  $-78\text{ }^\circ\text{C}$ ) or shorter reaction times [30]. The use of 2.0 equiv. of the reducing system yielded benzene as the only reaction product in all the experiments.

From a mechanistic point of view, the reaction pathways of the reductions involving zero-valent iron in the presence of water are not well elucidated, though generally, a two-electron transfer occurs either directly at the iron surface (by absorption of the organic halide) or through some intermediary. In a different mechanistic context, numerous studies have shown that dissociative adsorption of water takes place at clean iron metal surfaces, resulting in surface-bound hydroxyl, atomic oxygen, and atomic hydrogen (“nascent hydrogen”). The latter species can combine with itself, accounting for the formation of molecular hydrogen, or react with other compounds in the system, resulting in their hydrogenation. A third possibility would be the reduction by iron(II), resulting from corrosion of the metal. A debate over the relative importance of these mechanisms has gone on for many years, but the electron transfer model is generally preferred [6(a)].

A variety of experiments were carried out with 1-bromodecane as a model compound in order to disclose the reaction mechanism of the above hydrodehalogenations. Experiment A: reaction with Li-DTBB(cat.) furnished unreacted starting material (68%), tetracosane (18%), and dodecane (13%); the addition of  $\text{D}_2\text{O}$  at the end led to 0% D incorporation in dodecane. Experiment B: reaction with anhydrous  $\text{FeCl}_2$ -Li-DTBB(cat.)



Scheme 1.

furnished unreacted starting material (63%), tetracosane (10%), and dodecane (23%); the addition of D<sub>2</sub>O at the end led to 15% D incorporation in dodecane. Experiment C: reaction with FeCl<sub>2</sub>·4H<sub>2</sub>O-Li-DTBB(cat.) and addition of D<sub>2</sub>O at the end furnished 70% dodecane with 0% D incorporation. Experiment D: 1-bromododecane added to preformed active-iron [from FeCl<sub>2</sub>·4H<sub>2</sub>O-Li-DTBB(cat.)], using the exact amount of lithium to reduce the iron salt led to 55% dodecane; the addition of D<sub>2</sub>O at the end led to 0% D incorporation in dodecane. Experiment E: the generation of active-iron [from FeCl<sub>2</sub>·4H<sub>2</sub>O-Li-DTBB(cat.)] was followed by intended elimination of any H<sub>2</sub> under vacuum and addition of 1-bromododecane giving 95% starting material. Experiment F: the generation of active-iron [from FeCl<sub>2</sub>·2D<sub>2</sub>O-Li-DTBB(cat.)] was followed by intended elimination of any D<sub>2</sub> under vacuum and addition of 1-bromododecane giving 85% starting material and 15% dodecane with 50% D incorporation. Experiment G: 1-bromododecane was added to preformed active-iron [from FeCl<sub>2</sub>-Li-DTBB(cat.)] under a H<sub>2</sub> atmosphere, giving 70% dodecane.

From the results above it can be inferred that: (a) both the iron salt and the hydration water are indispensable to obtain the reduced product in good yield but metal lithium seemingly could account for a 10–15% of the reduced product (experiments A and B). The low or nil incorporation of deuterium in these experiments suggests that protonation of the corresponding intermediate mainly occurs in the reaction medium (e.g., from THF); (b) experiments C and D reveal that all the hydrogen incorporation takes place during the reaction course. The lower yield obtained when the substrate was added to the preformed active-iron (15% lower) could be attributed to the fact that some molecular hydrogen is lost while being generated in situ in the absence of the substrate; (c) experiments E and F point to the in situ generation of molecular hydrogen; (d) experiment G reveals that molecular hydrogen present in the reaction medium (either formed in situ from the iron hydrated salt or added to the active-iron obtained from the corresponding anhydrous salt) is the main hydrogen source for the hydrodehalogenation reaction. Therefore, the most plausible reaction mechanism must involve the reduction of Fe(II) to Fe(0) by the lithium-arene(cat.) pair and the in situ formation of molecular hydrogen by reaction of the excess of lithium with the hydration water of the iron salt. This molecular hydrogen would be activated on the surface of Fe(0) to hydrodehalogenate the substrate. As a side reaction, metal lithium could generate the corresponding organolithium compound, which as a strong base, could deprotonate the solvent. This fact would explain the incomplete incorporation of deuterium in all the products when using FeCl<sub>2</sub>·2D<sub>2</sub>O.

#### 4. Conclusions

In conclusion, we have found that the FeCl<sub>2</sub>·4H<sub>2</sub>O-Li-arene(cat.) combination is an interesting and useful alternative for hydrodehalogenation reactions under very mild reaction conditions. This active-iron-based reducing system demonstrated to be very efficient to reduce alkyl and aryl chlorides, bromides and iodides, as well as aryl fluorides in short reaction

times ( $\leq 5$  h). From the environmental point of view, this new reducing combination completely reduced some hazardous polyhalogenated aromatics such as 3,5-dichlorophenol, 1,2,4,5-tetrachlorobenzene, hexachlorobenzene, and 4,4'-dibromobiphenyl (a PBB congener). An additional advantage of this methodology is the simple and economic preparation of deuterium labeled alkyl and aromatic hydrocarbons by using the deuterated iron salt. The main reaction pathway involves the in situ generation of both active-iron and molecular hydrogen.

By comparing the three different metal-based reducing systems (nickel-, copper-, and iron-based) tested so far, we can conclude that, in general, all of them can be applied to the reduction of varied alkyl and aryl halides. For some halogenated substrates, however, the nature of the transition metal used is crucial to direct the reaction pathway towards the desired products. The nickel-based reducing system worked well at low or room temperature with alkyl and aryl chlorides, bromides, and iodides, without the formation of any homocoupling by-products, fluorides remaining unaltered. The copper-based analogous one reduced all alkyl and aryl halides, including fluorides, but low temperatures were required for the reduction of aryl iodides in order to prevent the formation of homocoupling by-products. This new iron-based reducing system was efficient in the reduction of alkyl and aryl halides, with the exception of alkyl fluorides. In the case of alkyl iodides, room or higher temperature were required to minimize the formation of homocoupling by-products.

Finally, the commercial availability and low toxicity of the iron salt (much lower than that of the analogous nickel or copper salts previously studied) makes it a potential alternative to other reducing agents. Thus, the method that we have developed represents a mild, efficient, environmentally friendly and economical procedure that can prove useful in both organic synthesis and in the detoxification of noxious halogenated compounds.

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