

Article

Iron-Catalyzed Conjugate Addition of Aryl Iodides onto Activated Alkenes under Air in Water

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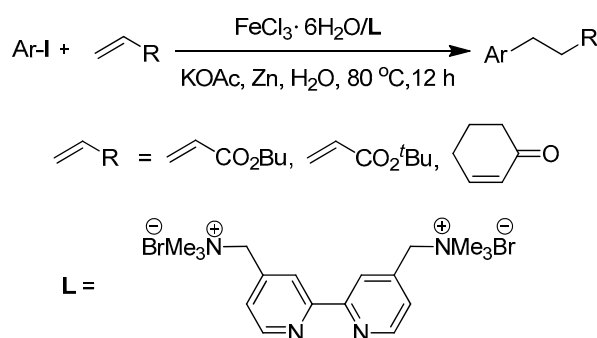
Abstract: The combination of commercially available $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a water-soluble cationic 2,2'-bipyridyl catalytic system was found to enable the direct conjugate addition of aryl iodides onto activated alkenes, such as an α,β -unsaturated ester and a ketone, in a weakly acidic aqueous solution. This operationally simple protocol was carried out at 80 °C under air atmosphere in a potassium acetate-buffered aqueous solution for 12 h in the presence of Zn dust as a reductant to provide the desired 1,4-adducts in good yields.

Keywords: iron catalyst; water; conjugate addition; aryl iodide; activated alkene

1. Introduction

Transition-metal-catalyzed conjugate addition onto α,β -unsaturated carbonyl compounds for the formation of C–C bonds is one of the most promising and powerful methods in organic synthesis [1]. Conventionally, pre-formed stoichiometric organometallic compounds, such as organoboron, organotin, organozinc, and organosilicon (which are usually prepared from alkyl/aryl halides), are required as the nucleophilic reagents to couple with activated olefins under Co [2], Ni [3–7], Cu [8–10], Ru [11], Rh [12–40], Pd [41–63], and Ir [64,65] catalysis. Recently, Pd-based [66–69] and first transition series catalysts, such as Co [70–77], Ni [77–80], In/Cu [81], and Cu [82–86], for the conjugate addition of organic halides, triflates, or tosylates onto activated alkenes have been well-documented. The advantage of this protocol is that the pre-formed stoichiometric organometallic nucleophile is not required prior to the conjugate addition [87]. Typically, the transition-metal-catalyzed conjugate addition of organic halides onto activated olefins is conducted in hydrous organic solvents, where H_2O is used to facilitate the protonolysis of the carbon–metal bond to afford the 1,4-adducts. There are only a few reports of these reactions performing in aqueous media [81–86]. Hence, the challenge remains to develop efficient conjugate addition reactions conducted in aqueous solutions to reduce the waste of organic solvents.

Based on the environmental and economic concerns, the use of iron—which is nontoxic and the cheapest transition metal—to catalyze 1,4-addition is highly desirable. Lipshutz reported that an Fe(II) salt can catalyze the reductive coupling of alkyl halides with either vinyl aromatics or heteroaromatics in an aqueous solution in the presence of a surfactant [88]. However, the iron-catalyzed conjugate addition of aryl halides onto activated olefins in water has not yet been explored. We previously found that the combination of commercially available $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ with a water-soluble cationic 2,2'-bipyridyl ligand, **L**, as a catalytic system is able to catalyze the Sonogashira coupling of aryl iodides with terminal alkynes in water in the presence of excess Zn dust as a reductant [89]. Herein, we report that this iron catalytic system is capable of catalyzing the conjugate addition of aryl iodides onto activated alkenes in water under an air atmosphere by an operationally simple procedure (Scheme 1).



Scheme 1. Iron-catalyzed conjugate addition of aryl iodides onto activated alkenes.

2. Results and Discussion

To examine our initial idea for iron-catalyzed conjugate addition, iodobenzene **1a** (1 mmol) and *n*-butyl acrylate **2a** (4 mmol) were added into an $\text{FeCl}_3 \cdot 6\text{H}_2\text{O/L}$ aqueous solution (10 mol% in 3 mL H_2O) in the presence of Zn dust (3 mmol) as a reductant at 80 °C for 12 h; this produced butyl 3-phenylpropanoate, **3a**, with a yield of only 22% (Table 1, Entry 1). We found that the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O/L}$ aqueous solution was very acidic with a pH value of 1.8; hence, Zn may have reacted with the acid prior to reducing Fe(III). The addition of various amounts of potassium acetate (KOAc) to the aqueous phase led to the formation of a buffer solution with pH values between 5.0 and 5.8, which further increased the 1,4-adduct yields (Table 1, Entries 2–4). A more effective outcome was achieved when 2 mmol KOAc was added to the aqueous solution (Table 1, Entry 3). Other, stronger inorganic bases were also screened, but these basic aqueous solutions produced low yields of **3a**, presumably due to the high hydroxide concentration that retarded the protonolysis of the C–Fe bond. This observation suggested that the pH control for this conjugate addition could be crucial (Table 1, Entries 5–7). Organic bases, such as Bu_3N and $i\text{Pr}_2\text{NEt}$, are known to promote the Pd-catalyzed conjugate addition of aryl iodides onto α,β -unsaturated carbonyl compounds [66–68]; in our system, however, only a 47% yield of **3a** was achieved when Bu_3N was used (Table 1, Entry 8). A higher concentration of *n*-butyl acrylate, **2a**, was necessary to provide higher product yields (Table 1, Entries 3, 9, and 10), which was also reported for the Ni-catalyzed reaction [78]. For the loading amount of Zn, we observed that 3 equivalents of Zn against **1a** resulted in the highest product yield of **3a** (Table 1, Entries 3 and 11–13). In addition, 99.99% pure FeCl_3 was used to verify that this conjugate addition reaction was catalyzed by iron (Table 1, Entry 14) [90]. Without the addition of **L**, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ could not catalyze this conjugate addition, leading to the recovery of 86% of **1a** (Table 1, Entry 15). Furthermore, the replacement of **L** by neutral 2,2'-bipyridine gave rise to an inferior yield of **3a** (Table 1, Entry 16). These results revealed that the water-soluble ligand in the reaction was indispensable. Similarly, no **3a** was formed when the catalytic system was left out of the reaction (Table 1, Entry 17). Finally, a scaled-up reaction was performed employing 5 mmol of **1a** to give **3a** in 75% yield (Table 1, Entry 18). Unfortunately, an aryl bromide, such as bromobenzene, did not participate in this 1,4 addition; hence, bromobenzene remained intact (Table 1, Entry 19).

Since the reaction conditions had been optimized, a variety of aryl iodides (**1**) were further employed to evaluate the conjugate addition with **2a** under the conditions listed in Table 1, Entry 3, and the results are described in Table 2. A weakly electron-donating methyl group at the para position underwent a smooth reaction to produce **3b** with a 74% yield (Table 2, Entry 1). However, this conjugate addition reaction did not proceed efficiently when a strong electron-donating group was added (Table 2, Entry 2). The low yield of **3c** could be attributed to the methoxy group at the para position that decelerated the oxidative addition rate. Sterically congested aryl iodides, such as **1d** and **1e**, only slightly affected the reaction, producing 70% and 72% yields of **3d** and **3e**, respectively (Table 2, Entries 3 and 4). 3-Substituted aryl and 1-naphthyl iodides, **1f–1i**, can also participate in this reaction, which produced the corresponding 1,4-adducts with yields between 75% and 79% (Table 2,

Entries 5–8). For the electron-withdrawing groups **1j** and **1k**, moderate product yields were recorded (Table 2, Entries 9 and 10). Because Zn was prone to insertion into the carbon–iodine bond in the presence of aryl iodides bearing an electron-withdrawing group at the para position, the formation of ArZnI was dominant when **1j** and **1k** were applied. Though arylzinc iodides could be temporarily stabilized by a certain surfactant in water [91], in our cases with **1j** and **1k**, the swift protonolysis of the moisture-sensitive arylzinc iodides in weakly-acidic hot water resulted in the formation of the deiodinated by-products acetophenone and chlorobenzene, respectively [72,89]. The fast hydrolysis of ArZnX was further demonstrated using 3,5-dimethylphenylzinc chloride instead of using the iodide analogue, which gave rise to only *m*-xylene under the reaction conditions of Entry 7 in Table 2. The heteroaromatic 2-iodothiophene, **1l**, failed to provide the desired conjugate adduct, resulting in the recovery of **1l** (Table 2, Entry 11). A similar outcome was also observed in the Pd nanoparticle-catalyzed 1,4-addition reaction [68].

To further expand the substrate scope, other α,β -unsaturated carbonyl compounds, **2b** and **2c**, were added to this reaction (Table 3). The conjugate addition of aryl iodides onto alkenes proceeded smoothly, producing the desired products in yields of 70–84% (Table 3, Entries 1, 2, 4–11, and 13–18), except for the use of 4-iodoanisole **1c** (Table 3, Entries 3 and 12). In contrast to 2-substituted aryl iodides, the steric hindrance on activated olefins inhibited the application of **2d** and **2e** in the conjugate addition reactions (Table 3, Entries 19 and 20).

Table 1. Iron-catalyzed conjugate addition of iodobenzene (**1a**) onto *n*-butyl acrylate (**2a**)^a.

Entry	2a (mmol)	Zn (mmol)	Base (mmol)	pH	Yield (%) ^b
1	4	3	–	1.8	22
2	4	3	KOAc (1)	5.0	74
3	4	3	KOAc (2)	5.5	85
4	4	3	KOAc (3)	5.8	80
5	4	3	K ₂ CO ₃ (2)	11.5	40
6	4	3	K ₃ PO ₄ (2)	13.5	35
7	4	3	KOH (2)	15.4	23
8	4	3	Bu ₃ N (2)	6.8	47
9	3	3	KOAc (2)		77
10	2	3	KOAc (2)		52
11	4	2.5	KOAc (2)		74
12	4	2	KOAc (2)		61
13	4	0	KOAc (2)		0
14 ^c	4	3	KOAc (2)		86
15 ^d	4	3	KOAc (2)		0
16 ^e	4	3	KOAc (2)		12
17 ^f	4	3	KOAc (2)		0
18 ^g	20	15	KOAc (10)		75
19 ^h	4	3	KOAc (2)		0

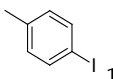
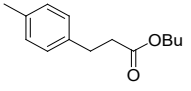
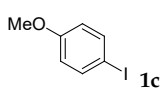
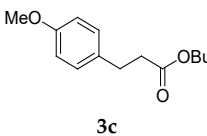

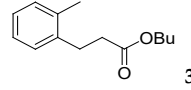
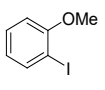
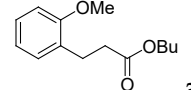
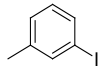
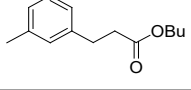
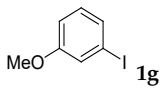
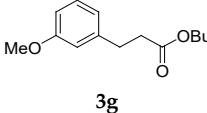
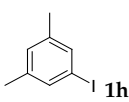
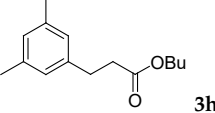
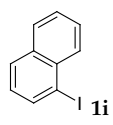
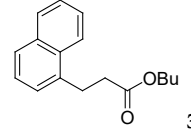
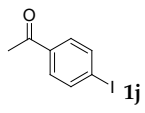
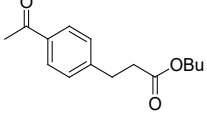
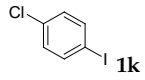
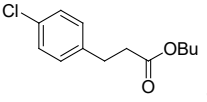
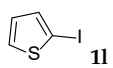
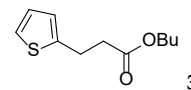
^a Reaction conditions: **1a** (1 mmol), **2a**, Zn, base, FeCl₃·6H₂O/L (10 mol%), and H₂O (3 mL) at 80 °C for 12 h.

^b Isolated yields. ^c 99.99% pure FeCl₃ was used. ^d In the absence of ligand L. ^e Neutral 2,2'-bipyridine was used as the ligand. ^f In the absence of FeCl₃·6H₂O/L. ^g 5 mmol of **1a** was used. ^h Iodobenzene **1a** was replaced by bromobenzene.

To elucidate the reaction mechanism, the reaction conditions listed in Table 1, Entry 3 were performed in the presence of a 1 mmol radical scavenger, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl—TEMPO. We found that the presence of TEMPO in the reaction did not suppress the conjugate addition, which still produced **3a** in an identical yield to that in Table 1, Entry 3; the radical pathway for this conjugate addition is therefore unlikely. In addition, >98% deuterium at the α -carbon to the product was observed when the reaction was conducted in D₂O (see the Supporting Information for the ¹H and ¹³C NMR spectra). This result implied that the C_{sp}³–Fe bond was hydrolyzed by H₂O to release the final product in the reaction. Following the above results, although the radical pathway cannot be completely ruled out, a similar mechanism to those in first-series transition-metal-catalyzed conjugate

additions of aryl/alkyl halides onto α,β -unsaturated carbonyl compounds has been proposed [71,72,78]. As shown in Scheme 2, Fe(III) was first reduced by Zn dust, followed by the oxidative addition of an aryl iodide, to deliver aryl iron(III) intermediate **A**. The coordination of an activated olefin to the Fe(III) center and a subsequent migratory insertion provided intermediate **B**. The protonolysis of **B** by water afforded the conjugated addition product along with Fe(III). Then, reduction of Fe(III) by Zn regenerated Fe(I) for the next catalytic cycle.

Table 2. Iron-catalyzed conjugate addition of aryl iodides (**1**) onto *n*-butyl acrylate (**2a**)^a.

Entry	Aryl Iodide	Product	Yield (%) ^b
1	 1b	 3b	74
2	 1c	 3c	44
3	 1d	 3d	70
4	 1e	 3e	72
5	 1f	 3f	75
6	 1g	 3g	79
7	 1h	 3h	78
8	 1i	 3i	75
9	 1j	 3j	40
10	 1k	 3k	52
11	 1l	 3l	0

^a Reaction conditions: **1** (1 mmol), **2a** (4 mmol), Zn (3 mmol), KOAc (2 mmol), FeCl₃·6H₂O/L (10 mol%), and H₂O (3 mL) at 80 °C for 12 h. ^b Isolated yields.

Table 3. Iron-catalyzed conjugate addition of aryl iodides (**1**) onto activated alkenes (**2**) ^a.

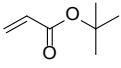
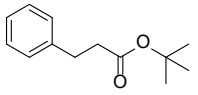
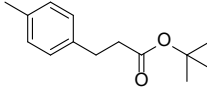
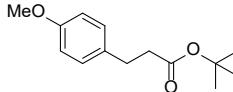
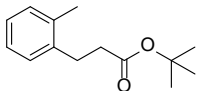
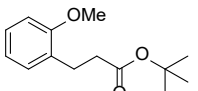
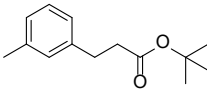
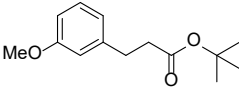
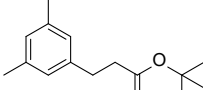
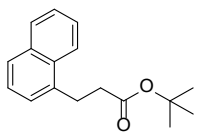
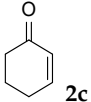
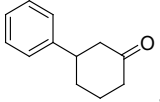
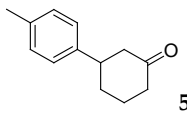
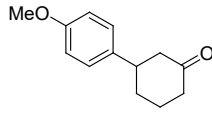
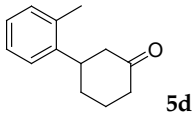
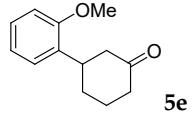
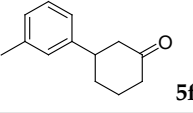
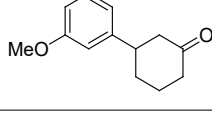
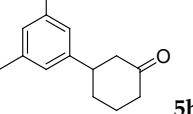
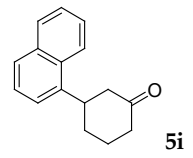
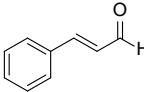
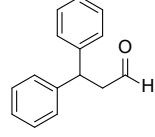
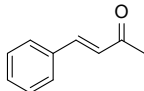
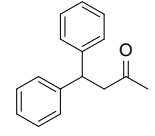
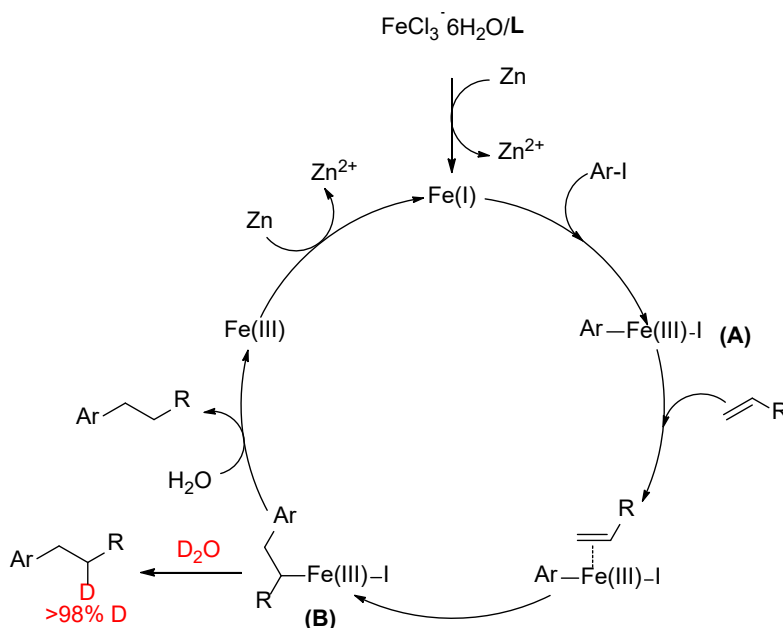
Entry	Aryl Iodide	Alkene	Product	Yield (%) ^b
1	1a	 2b	 4a	82
2	1b	2b	 4b	81
3	1c	2b	 4c	43
4	1d	2b	 4d	84
5	1e	2b	 4e	74
6	1f	2b	 4f	77
7	1g	2b	 4g	73
8	1h	2b	 4h	77
9	1i	2b	 4i	80
10	1a	 2c	 5a	77
11	1b	2c	 5b	75

Table 3. Cont.

Entry	Aryl Iodide	Alkene	Product	Yield (%) ^b
12	1c	2c	 5c	55
13	1d	2c	 5d	73
14	1e	2c	 5e	74
15	1f	2c	 5f	70
16	1g	2c	 5g	72
17	1h	2c	 5h	81
18	1i	2c	 5i	78
19	1a	 2d	 6a	0
20	1a	 2e	 7a	0

^a Reaction conditions: **1** (1 mmol), **2** (4 mmol), Zn (3 mmol), KOAc (2 mmol), FeCl₃·6H₂O/L (10 mol%), and H₂O (3 mL) at 80 °C for 12 h. ^b Isolated yields.



Scheme 2. Proposed mechanism for the conjugated addition.

3. Materials and Methods

3.1. General Methods

Aryl iodides, butyl acrylates, 2-cyclohexen-1-one, Bu_3N , D_2O , and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were acquired from Acros Organics. KOAc, K_2CO_3 , K_3PO_4 , and KOH were purchased from SHOWA Chemical Co. Ltd (Tokyo, Japan). The cationic 2,2'-bipyridyl ligand (**L**) was prepared according to the known procedure [92,93]. NMR spectra were recorded in CDCl_3 on a Bruker Biospin AG 300 NMR spectrometer (Bruker Co., Faellanden, Switzerland) at 25 °C, where the chemical shifts (δ in ppm) were established with respect to CHCl_3 , which was used as a reference (^1H NMR: CHCl_3 at 7.24; ^{13}C NMR: CDCl_3 at 77.0). High-resolution mass spectrometry (HRMS) was performed on a JEOL AccuTOF GCx-plus and SHIMADZU QP2020 at the Instrument Center Service, Ministry of Science and Technology of Taiwan. The spectral data of all conjugate adducts can be found in the Supporting Information.

3.2. Typical Procedure for the Conjugate Addition of Aryl Iodides onto Activated Olefins

A 20 mL cylinder reactor was charged with $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.1 mmol) and cationic 2,2'-bipyridyl ligand **L** (0.1 mmol in 3 mL of H_2O). After stirring this solution at room temperature for 30 min, KOAc (2.0 mmol) was then added to the wine-red solution, which stirred for an additional 5 min. Aryl iodide (1.0 mmol), activated alkene (4.0 mmol), and Zn dust (3.0 mmol) were added in sequence, and the reaction mixture was then stirred at 80 °C under air atmosphere for 12 h. After cooling the reaction to room temperature, 3 N HCl (2 mL) was added into the aqueous solution and extracted with ethyl acetate (3×5 mL); the combined organic phase was then dried over MgSO_4 . The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to give the desired product.

4. Conclusions

In conclusion, we developed an environmentally friendly method for the conjugate addition of aryl iodides onto activated alkenes catalyzed by a green catalytic system in water under an air atmosphere. Several activated olefins, such as an α,β -unsaturated ester and a ketone, can be applied to form 1,4-adducts in good-to-high yields. Nontoxic and cheap iron is used as the catalyst, and neither organometallic reagents nor organic solvents are required in this reaction, rendering this procedure

sustainable. Further development of this green catalytic system for other reactions in water under ambient conditions is now underway in our laboratory.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4344/10/11/1320/s1>: the spectral data and copies of ^1H - and ^{13}C -NMR spectra of all conjugate addition products.

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