OL Organic Letters

Letter

Cite This: *Org. Lett.* XXXX, XXX, XXX−XXX

pubs.acs.org/OrgLett

Iron(II)-Catalyzed Heck-Type Coupling of Vinylarenes with Alkyl Iodides

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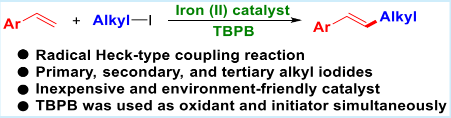
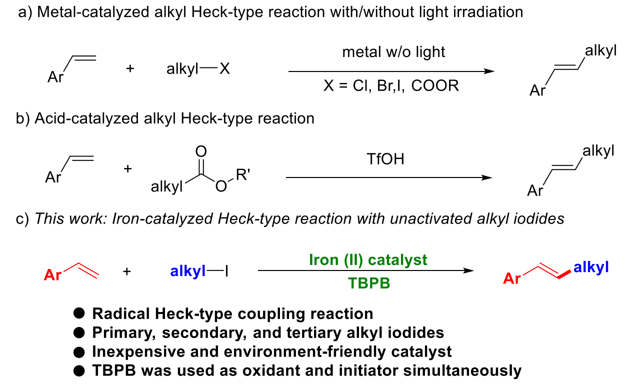
S *Supporting Information*

ABSTRACT: An iron(II)-catalyzed radical alkyl Heck-type reaction of alkyl iodides with vinylarenes under mild conditions has been reported. *t*-Butyl peroxybenzoate (TBPB) behaves simultaneously as a radical relay initiator, a precursor for the generation of alkyl radical from alkyl iodides, and an oxidant to recycle iron(II)/iron(III). Unactivated primary, secondary, and tertiary alkyl iodides are compatible with the reaction conditions. The mechanistic studies suggest that a radical-polar-crossover pathway might be involved in the catalytic cycle.



The Mizoroki-Heck coupling reaction has been confirmed as one of the most significant methods for the construction of carbon−carbon bond in organic synthesis since 1970s.[1] However, compared to the rapid development of coupling of aryl or vinyl halides with alkenes,[2] the coupling of olefins and alkyl halides bearing β-hydrogen(s) has rarely been documented.[3] The reason is that the alkyl-metal species is inclined to undergo β-hydride elimination before insertion of alkene.[4] Additionally, the rate of oxidative addition of alkyl halide to metal-center is slower than that of aryl halide.[5] To overcome the issues mentioned above, radical strategies for alkyl Heck (or Heck-type) reaction have been established.[6] Exploratory studies on radical Heck-type reaction with activated alkyl halides have been reported by Lei, Nishikata, and Thomas, in the presence of nickel salt,[7] ruthenium salt,[8] copper salt,[9] and iron salt[10] as the catalyst, respectively. The generated alkyl radicals are stabilized by the linked electron-withdrawing groups through conjugative effect, thus limiting the substrate scopes. Radical Heck-type reactions of unactivated alkyl halides have been pioneeringly achieved by Oshima with a ligated cobalt catalyst (Scheme 1a).[11] However, a stoichiometric amount of trimethylsilylmethylmagnesium chloride is crucial to smoothly promote the reaction. In recent years, palladium salts were found to be good catalysts for radical alkyl Heck-type reaction through an open-shell pathway.[12,13] Fu[14] and Gevorgyan[15] independently described elegant palladium-catalyzed Heck reactions of unactivated alkyl halides under photoirradiation (Scheme 1a). A range of alkyl halides, especially tertiary alkyl halides bearing β-hydrogen(s), can be involved. However, these reactions need to proceed under light irradiation and to use noble metal as the catalyst.

Scheme 1. Intermolecular Alkyl Heck-type Reaction



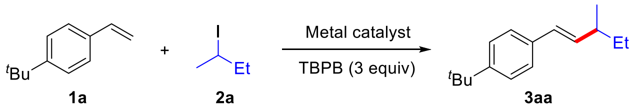
Our group previously described a radical decarboxylative alkyl Heck-type reaction catalyzed by triflic acid (Scheme 1b) and iron catalysts.[16,17] We found that *t*-butyl peroxybenzoate (TBPB) is a good initiator for the iron-catalyzed alkyl Heck-type reactions through a radical relay process.[18,19] Considering that iron is an inexpensive and environmentally benign catalyst,[20] we reported herein a general iron-catalyzed radical alkyl Heck-type reactions with both unactivated and activated alkyl iodides (Scheme 1c).[10]

Received: December 17, 2018

DOI: 10.1021/acs.orglett.8b04024
Org. Lett. XXXX, XXX, XXX−XXX

Initially, 4-*tert*-butylstyrene (**1a**) and alkyl iodide (**2a**) were used as the model substrates to explore the alkyl Heck-type reaction (Table 1). 5 mol % of metal catalysts, such as Pd(OAc)$_2$, NiCl$_2$, CuI, and Fe(OAc)$_2$, were employed to run the reaction. Unfortunately, only a trace amount of alkylated product was detected in these cases when the reaction was performed at 50 °C in THF for 3 h (Entries 1–4). To our delight, 25% yield of the coupling product (**3aa**) was obtained by using Fe(OTs)$_3$ as the catalyst (Entry 5). Inspired by this result, other iron catalysts were tested. While catalyst Fe(OTf)$_3$ afforded product **3aa** in 66% yield, Fe(OTf)$_2$ offered a better yield, as high as 70% (Entries 6 and 7). Then, the solvents were screened, and up to 72% isolated yield of **3aa** could be produced in 1,4-dioxane (Entry 10 vs Entries 8 and 9). When the reaction was performed at a lower temperature (25 °C), only a trace amount of product was detected (Entry 11). A higher temperature could not increase the yield of product (Entry 12).

Table 1. Optimization of the Reaction Conditions[a]



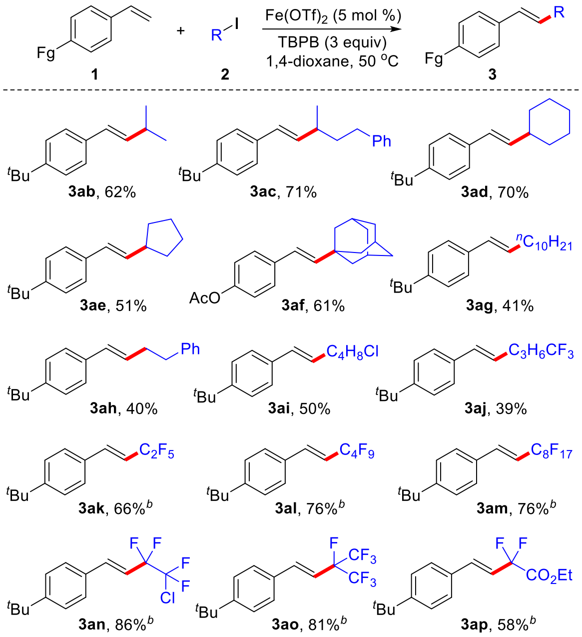
entry	catalyst (mol %)	solvent	temp (°C)	yield (%)[b]
1	Pd(OAc)$_2$ (5)	THF	50	trace
2	NiCl$_2$ (5)	THF	50	trace
3	CuI (5)	THF	50	trace
4	Fe(OAc)$_2$ (5)	THF	50	trace
5	Fe(OTs)$_3$ (5)	THF	50	25
6	Fe(OTf)$_3$ (5)	THF	50	66
7	Fe(OTf)$_2$ (5)	THF	50	70
8	Fe(OTf)$_2$ (5)	CH_3CN	50	9
9	Fe(OTf)$_2$ (5)	DME	50	65
10	Fe(OTf)$_2$ (5)	1,4-dioxane	50	73 (72)[c]
11	Fe(OTf)$_2$ (5)	1,4-dioxane	25	trace
12	Fe(OTf)$_2$ (5)	1,4-dioxane	70	73

[a] Reaction conditions: alkene **1a** (1 mmol, 1 equiv), alkyl iodide **2a** (3 mmol, 3 equiv), TBPB (3 mmol, 3 equiv), solvent (4 mL), 3 h. [b] Yield of product was determined by crude. ^{1}H NMR. [c] Isolated yield in parentheses.

With the optimal reaction conditions in hand, the scope of alkyl iodides was investigated (Scheme 2). Both of the acyclic and cyclic secondary alkyl iodides smoothly couple with 4-*tert*-butylstyrene (**1a**) to deliver the corresponding products (**3ab**–**3ae**) in 51–71% yields. Tertiary alkyl iodide is transformed into product (**3af**) in 61% yield. A variety of primary alkyl coupling products (**3ag**–**3aj**), possessing long-chain alkyl, phenyl, chloride, and trifluoromethyl groups, are obtained in 39–50% yields. Perfluoroalkyl iodides are also compatible with this Heck-type reaction, affording the desired products (**3ak**–**3am**) in moderate to good yields (66–76%). In addition, 1-chloro-2-iodo-tetrafluoroethane is used as a coupling partner, providing the product (**3an**) in 86% yield. 2-Iodo-heptafluoropropane is applicable to the reaction, giving 81% yield of product **3ao**. Difluoroacetylated alkene **3ap** could be attained through this transformation in 58% yield. However, 3-iodooxetane or *tert*-butyl 3-iodoazetidine-1-carboxylate fails to afford the corresponding product.

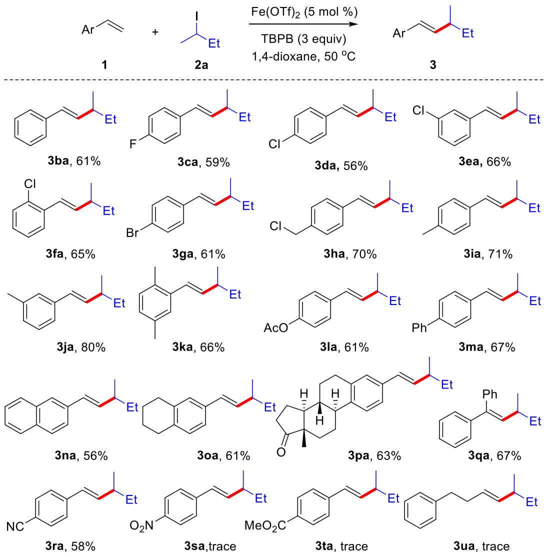
The alkyl Heck-type cross coupling reaction can also be extended to various styrene derivatives (Scheme 3). Styrene **1b** is employed to react with alkyl iodide **2a**, leading to the generation of product **3ba** in 61% yield. The aryl alkenes bearing electron-withdrawing (halides) and electron-donating groups (**3ca**–**3ma**) are tolerated in the reaction with moderate to good efficiency (56–80%). 2-Vinyl naphthalene and 6-vinyl tetrahydronaphthalene afford the alkyl-Heck products (**3na** and **3ma**) in 56% and 61% yields, respectively. Particularly, the estrone derivative containing a C═C double bond is readily converted into the corresponding product (**3pa**, 63% yield).

Scheme 2. Scope of Alkyl Iodides[a]



[a] Reaction conditions: alkene (1 mmol, 1 equiv), alkyl iodide **2** (3 mmol, 3 equiv), Fe(OTf)$_2$ (5 mol %), TBPB (3 mmol, 3 equiv), 1,4-dioxane (4 mL), 50 °C, 3 h. Isolated yields. [b] Alkene (1 mmol, 1 equiv), alkyl iodide **2** (2 mmol, 2 equiv), TBPB (2 mmol, 2 equiv), DME (4 mL), 2 h.

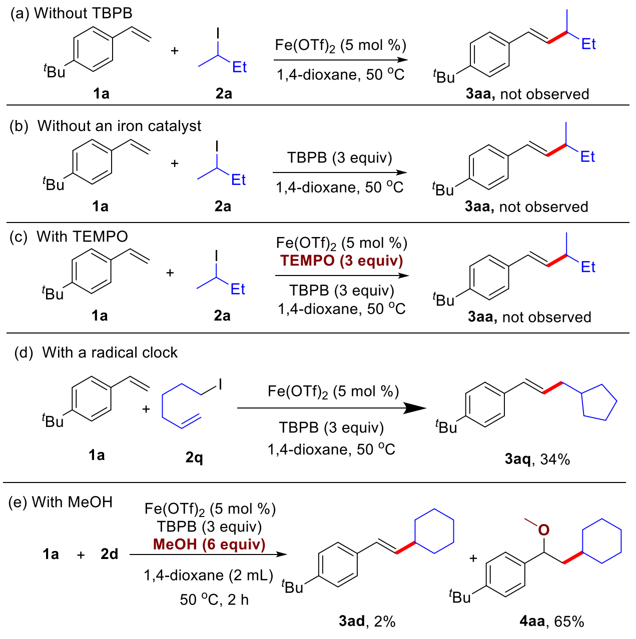
Scheme 3. Scope of Aryl Olefins[a]



[a] Reaction conditions: alkene **1** (1 mmol, 1 equiv), alkyl iodide **2a** (3 mmol, 3 equiv), Fe(OTf)$_2$ (5 mol %), TBPB (3 mmol, 3 equiv), 1,4-dioxane (4 mL), 50 °C, 3 h. Isolated yields.

1,1-Disubstitued alkene is also compatible to the reaction, giving the alkylated alkene (**3qa**) in 67% yield. Notably, 4-vinylbenzonitrile could afford the desired product (**3ra**) in 58% yield, while methyl 4-vinylbenzoate and 1-nitro-4-vinylbenzene are incompatible with the optimized reaction conditions. Moreover, but-3-en-1-ylbenzene as an aliphatic alkene, and benzyl acrylate or pent-1-en-3-one as a conjugated alkene, are also not tolerated the reaction conditions and fail to afford the desired products.

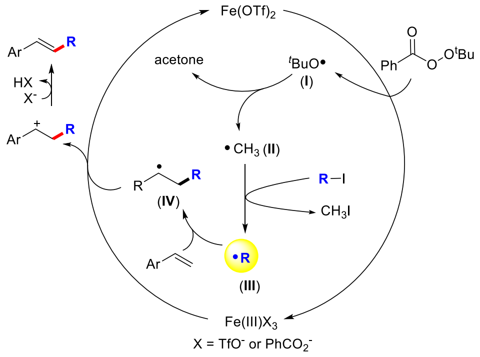
Scheme 4. Preliminary Mechanistic Studies



To insight into the mechanism of this alkyl Heck-type cross coupling reaction, the preliminary experiments were performed (Scheme 4). The control experiments proceeded separately in the absence of TBPB or $Fe(OTf)_2$ under standard reaction conditions, and alkylated product (**3aa**) is not detected by GC-MS in both cases (Scheme 4a,b). These results indicated that both the iron catalyst and the TBPB are crucial for this alkyl Heck-type transformation. Moreover, when 3 equiv of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) is added as a radical inhibitor, the product (**3aa**) cannot be observed as well (Scheme 4c). Moreover, substrate 6-iodohex-1-ene (**2q**) could only afford a cyclized Heck-type product (**3aq**) (Scheme 4d). These results imply that radical species might be involved in the reaction. With methanol as an additive, the selective formation of product **4aa** suggested that a benzylic cation might be involved (Scheme 4e).

Therefore, based on the mechanistic experiments, a possible mechanism for the alkyl Heck-type reaction is proposed (Scheme 5). Fe(II) is oxidized by TBPB, generating Fe(III) and a *tert*-butoxy radical (**I**), followed by the production of a methyl radical (**II**) and acetone. The alkyl radical (**III**) would arise via atom transfer process between methyl radical (**II**) and alkyl iodide. The addition of the alkyl radical (**III**) to aryl alkene leads to the formation of a benzyl radical (**IV**) which could be further oxidized by the Fe(III) species, providing a benzyl cation and the regenerated Fe(II) species. As a consequence of deprotonation of the benzyl cation, the Heck-type product is acquired.

Scheme 5. Possible Mechanism



In summary, a radical relay process for iron(II)-catalyzed Heck-type alkylation of aryl alkenes with alkyl iodides has been established. Activated/unactivated primary, secondary, and tertiary alkyl iodides are compatible in this reaction to afford various alkyl alkenes in moderate to good yields. TBPB is employed as an internal oxidant to oxidize iron(II) species, meanwhile, as an initiator to promote the generation of alkyl radical from alkyl iodides. The mechanistic studies suggest that a radical-polar-crossover pathway might be involved in the catalytic cycle.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b04024.

Experimental procedures, characterization of new compounds, synthetic applications, mechanistic studies, NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

H.B. thanks the National Key R&D Program of China (2017YFA0700103), the NSFC (Grant Nos 21502191, 21672213, and 21871258), the Strategic Priority Research Program of the Chinese Academy of Sciences (Grant No. XDB20000000), and the Haixi Institute of CAS (Grant No. CXZX-2017-P01) for financial support. E.V.dE. acknowledges the support of RUDN University Program 5-100.

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DOI: 10.1021/acs.orglett.8b04024
Org. Lett. XXXX, XXX, XXX−XXX