OL Organic Letters
Letter
Cite This: Org. Lett. XXXX, XXX, XXX−XXX
pubs.acs.org/OrgLett

Iron-Catalyzed Decarboxylative Olefination of Unstrained Carbon−Carbon Bonds Relying on Alkoxyl Radical Induced Cascade

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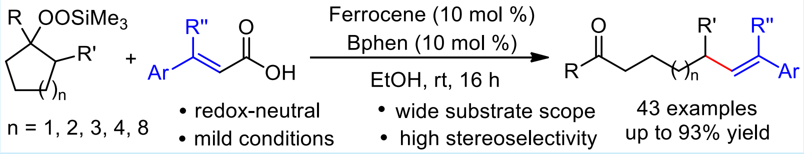
Supporting Information



ABSTRACT: An iron-catalyzed decarboxylative olefination of unstrained carbon−carbon bonds via alkoxyl radical induced C−C bond cleavage is presented. This protocol features mild conditions (room temperature, redox-neutral), good substrate scope and functional group compatibility, as well as excellent stereoselectivity, thus providing a facile access to the distal alkenyl ketones.

Catalytic C−C bond activation of cyclic systems has drawn the attention of chemists in recent years and has provided an attractive strategy for the synthesis of functionalized linear molecules.[1] Over the past few years, significant advances have been made in this field, especially in the unstrained C−C bond cleavage.[2] Among them, the alkoxyl radical triggered C−C bond cleavage has emerged as a powerful tool to obtain diverse functionalized ketones, carboxylic acids, and so on.[3,4] Cycloalkanols and their derivatives have been thoroughly explored as efficient alkoxyl radical precursors. Recently, Knowles, Zuo, Zhu, and others have described hydrogenation, amination, and bromination of unstrained carbon−carbon bonds via oxidative C−C bond cleavage of cycloalkanols.[5] The group of Maruoka and Sakamoto as well as our group reported the amidation, alkynylation, silylation, and borylation of unstrained carbon−carbon bonds via reductive unstrained C−C bond cleavage of cycloalkyl silyl peroxides.[6] In these transformations, a carbonyl group and a new chemical bond have been constructed simultaneously, providing a series of functionalized long-chain ketones. Nevertheless, to the best of our knowledge, the decarboxylative olefination of unstrained carbon−carbon bonds via alkoxyl radical induced C−C bond cleavage remains unexplored. Thus, further exploring the application of alkoxyl radical induced C−C bond cleavage is still desirable.

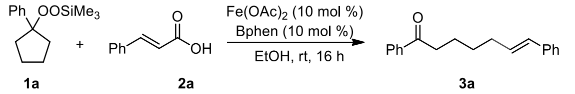
Carboxylic acids as one of the most abundant and inexpensive basic chemicals are widely used in biological and chemical synthesis. The decarboxylation of α,β-unsaturated carboxylic acids is an important and useful process in organic synthesis. In addition to classical transition-metal catalysis,[7] radical-mediated decarboxylative coupling has been established as a reliable protocol for the formation of C−C and C−heteroatom bonds.[8] For example, a number of radical-induced decarboxylative alkylations of α,β-unsaturated carboxylic acids have been presented by different research groups.[9] Although much progress have been gained, most of the above decarboxylative reactions suffer from some drawbacks such as the use of precious late transition-metal catalysts or high reaction temperature, which would limit their further large-scale application. Therefore, development of a low-cost metal-catalyzed and mild decarboxylative strategy is still highly desirable. Iron, as a cheap, readily accessible, environmentally benign metal, has already shown its unique catalytic utility in some transformations.[10] As part of our continuing interest in C−C cleavage reactions,[4i,j,9h] we herein report a mild, redox-neutral iron-catalyzed decarboxylative ketoalkylation of α,β-unsaturated carboxylic acids through alkoxyl radical-triggered unstrained C−C bond cleavage, which provides a facile access to a variety of distally alkenyl ketones.

At the outset, we examined the reaction of cyclopentyl silyl peroxide **1a** with cinnamic acid **2a** under the cheap iron catalysis. To our delight, the reaction occurred and gave the desired δ-alkenyl ketone **3a** in 65% yield in the presence of $Fe(OAc)_2$ (10 mol %) and Bphen (10 mol %) in EtOH at room temperature for 16 h (Table 1, entry 1). Control experiments revealed that the ligand plays an essential role in this transformation (entry 2). Thus, a variety of ligands were evaluated, and Bphen was found to be superior to others (for details, see the SI). Screening of solvents disclosed that EtOH was the most suitable solvent (entries 3−5). Different iron catalysts including $FeCl_2$, ferrocene, $FeSO_4{\cdot}7H_2O$, $FeCl_3$, and Fe powder were then tested (entries 6−10). The results showed that ferrocene gave the best yield of **3a**, while Fe powder did not display any catalytic activity. Reducing the loading of catalyst and ligand to 5 mol % diminished the yield of **3a** to 74%. Other catalysts such as $Cu(OAc)_2$, $Co(OAc)_2{\cdot}$

Received: July 30, 2019

DOI: 10.1021/acs.orglett.9b02675
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization of the Reaction Conditions[a]



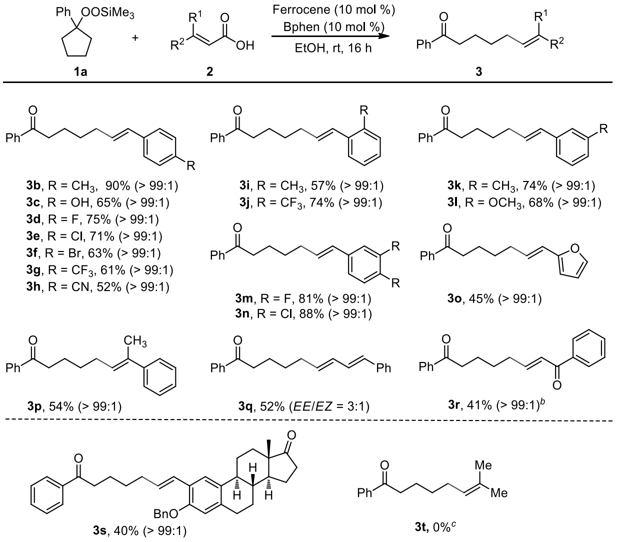
entry	variations from the standard conditions	yield[a] (%)
1	none	65
2	without ligand	trace
3	MeCN as the solvent	50
4	toluene as the solvent	37
5	DCM as the solvent	48
6	$FeCl_2$ as the catalyst	51
7	ferrocene as the catalyst	83 (74)[b]
8	$FeSO_4 \cdot 7H_2O$ as the catalyst	50
9	$FeCl_3$ as the catalyst	46
10	Fe powder as the catalyst	trace
11	$Cu(OAc)_2$ as the catalyst	17
12	$Co(OAc)_2 \cdot 4H_2O$ as the catalyst	6
13	$Pd(OAc)_2$ as the catalyst	trace
14	$Ni(OAc)_2 \cdot 4H_2O$ as the catalyst	trace
15	without catalyst	0

[a] Reaction conditions: catalyst (10 mol %), 4,7-diphenyl-1,10-phenanthroline (Bphen) (10 mol %), **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv) in solvent (2.0 mL) at room temperature for 16 h under N_2. Yields of isolated product. [b] Ferrocene (5 mol %) and Bphen (5 mol %) were used.

$4H_2O$, and $Pd(OAc)_2$ resulted in an inferior yield of **3a** (entries 11−14). Finally, no desired product **3a** could be observed without iron catalyst (entry 15).

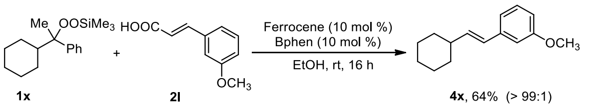
With the optimized conditions in hand, the scope of *α,β*-unsaturated carboxylic acids was tested with peroxide **1a** (Scheme 1). Cinnamic acids bearing either electron-donating or electron-withdrawing groups were engaged efficiently in this transformation, affording the *δ*-alkenyl ketones **3b**−**3n** in moderate to good yields. A variety of functional groups including hydroxy (**3c**), methoxy (**3l**), halogen (**3d**−**3f**, **3m**, **3n**), trifluoromethyl (**3g**, **3j**), and cyano (**3h**) groups were compatible with the reaction conditions. 2-Furylacrylic acid also proves to be efficient, delivering the desired product **3o** in moderate yield. *β*-Methyl cinnamic acid was also suitable, giving the product **3p** in 54% yield. Besides the cinnamic acids, other acrylic acids were also applicable for this transformation. Dienoic acid **2q** afforded the expected product **3q** in 52% yield with excellent regioselectivity. 3-Benzoylacrylic acid **2r** delivered the desired product **3r** in 41% yield by using $Fe(OAc)_2$ as the catalyst. Remarkably, the substrate with steric hindrance, such as estrone-derived acrylic acid **2s**, reacted smoothly to provide the desired product **3s** in 40% yield. However, 3,3-dimethylacrylic acid failed to undergo this transformation, and only phenyl butyl ketone was isolated in 41% yield as a byproduct. When *α,β*-unsaturated carboxylic acids with a phenyl group at the *α*-position were used as substrates under the standard conditions, no desired decarboxylation product was observed, and only some of the other unidentified byproducts were detected in this case. Finally, it is noteworthy that this decarboxylative alkenylation reaction proceeded with excellent stereoselectivity, and only *E*-isomers were obtained in almost all cases.

Scheme 1. Evaluation of Various *α,β*-Unsaturated Carboxylic Acids[a]



[a] Reaction conditions: ferrocene (10 mol %), Bphen (10 mol %), **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv) in EtOH (2.0 mL) at room temperature for 16 h under N_2. Isolated yields. The *E*/*Z* ratio was determined by ^1H NMR analysis, and the data are given in parentheses. [b] The reaction was performed in MeCN at 120 °C for 12 h with $Fe(OAc)_2$ (5 mol %) as the catalyst. [c] Phenyl butyl ketone was isolated in 41% yield.

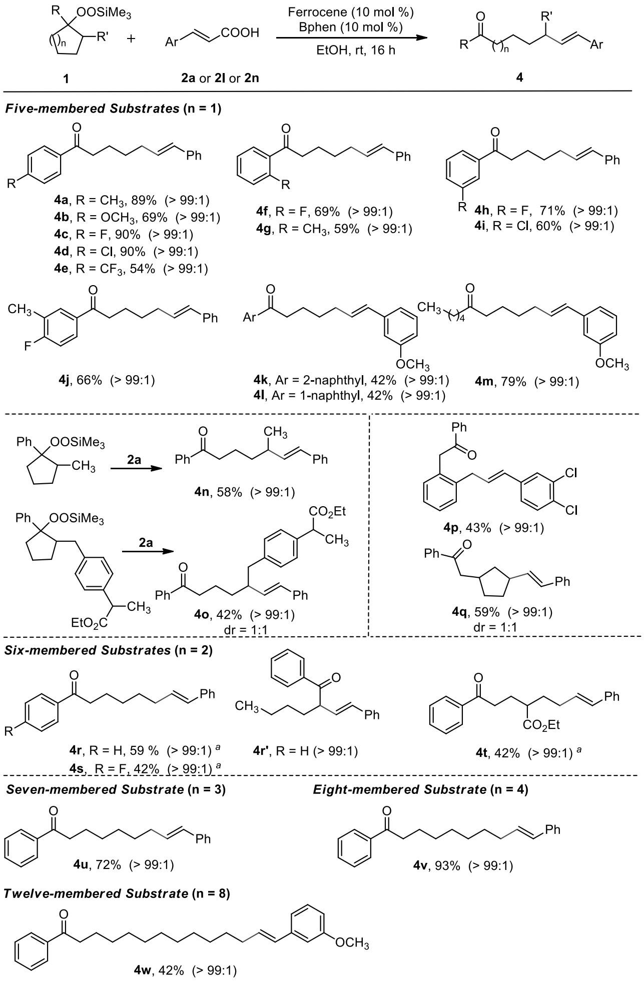
Then the generality and limitations of cycloalkylsilyl peroxides **1** were evaluated (Scheme 2). An array of 1-arylcyclopentyl silyl peroxides **1** reacted well to deliver the corresponding *δ*-alkenyl ketones **4a**−**4j** in good yields. The *α* and *β*-naphthyl substrates **1k** and **1l** gave the corresponding products **4k** and **4l** in moderate yields. The 1-alkylcyclopentyl silyl peroxide **1m** also afforded the desired product **4m** in 79% yield. 1,2-Disubstituted cyclopentyl silyl peroxides **1n** and **1o** (derived from loxoprofen) underwent C−C bond cleavage regioselectively, furnishing **4n** and **4o** in 58% and 42% yields, respectively. Peroxides derived from 2-indanone and norcamphor also resulted in the expected products **4p** and **4q** in 43% and 59% yields. Interestingly, when 1-phenylcyclohexyl silyl peroxide **1r** was subjected to the standard conditions, the *ε*-alkenyl ketone **4r** was obtained along with a small amount of *α*-alkenyl ketone **4r′** as byproduct. The formation of **4r′** involves a C−C bond cleavage/1,5-HAT/decarboxylative C−C(sp^2) bond formation cascade. Luckily, it could be inhibited by using an increased concentration (1.0 M) of reaction system. Other cyclohexyl substrates gave the corresponding *ε*-alkenyl ketones **4s** and **4t** in moderate yields under slightly modified conditions. Satisfactorily, the peroxides with large-sized rings including seven-, eight- and even 12-membered ring also successfully produced the expected products **4u**−**4w** in 42−93% yields. Additionally, the acyclic alkylsilyl peroxide **1x** underwent the C−C bond cleavage/decarboxylative coupling process to give the alkene **4x** in 64% yield with perfect *E*-selectivity (eq 1).



(1)

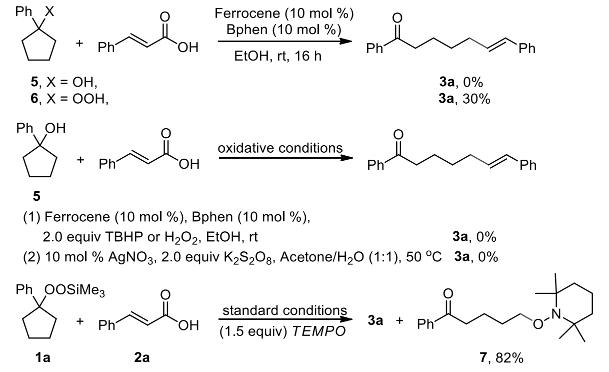
To shed light on this transformation, some control experiments were conducted (Scheme 3). The use of cyclopentyl hydroperoxide **6** instead of silyl peroxide **1a**

Scheme 2. Evaluation of Cycloalkylsilyl Peroxides[a]



[a]The reaction run at 1.0 M concentration.

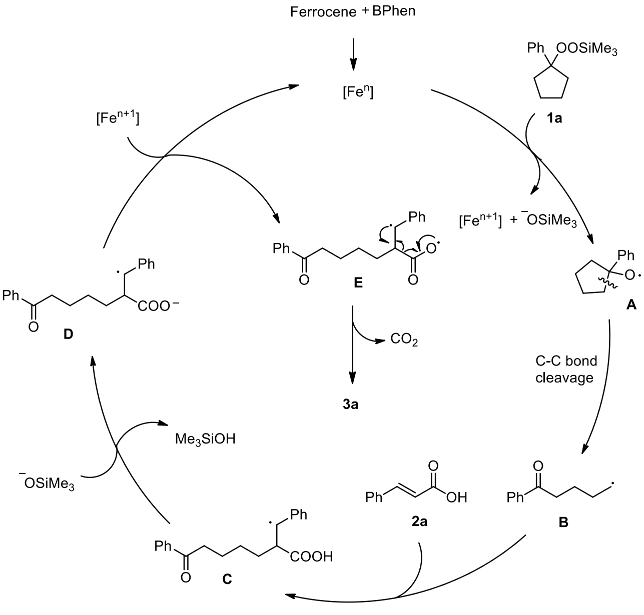
Scheme 3. Control Experiments



delivered the desired product **3a** in only 30% yield. Cyclopentanol **5** could not give the target product **3a** under the standard conditions. Furthermore, it also failed to afford **3a** under different oxidative conditions. When 1.5 equiv of TEMPO was added to the reaction of **1a** and **2a**, the reaction was suppressed completely and the alkyl-TEMPO adduct **7** was isolated in 82% yield. These results suggest that an alkyl radical intermediate is probably involved in this transformation.

On the basis of the above results, a reasonable catalytic mechanism is depicted in Scheme 4.[6e,9h] First, single-electron reduction of cyclopentyl silyl peroxide **1a** by the Fe^n complex, which was generated from Ferrocene and Bphen, gave the alkoxy radicals **A**. Subsequently, β-fragmentation of **A** would generate the corresponding alkyl radical **B**, which attacks the C═C bond of cinnamic acid **2a** regioselectively to afford benzyl radical **C**. Deprotonation of **C** with trimethyl silanolate occurs to give radical **D**, followed by oxidation by Fe^{n+1} to deliver the diradical intermediate **E**. Finally, decarboxylation of **E** gave the desired product **3a** and released CO_2. However, the loss of carbon dioxide through a carbonium ion intermediate could not be excluded at present.[11]

Scheme 4. Plausible Reaction Mechanism



In conclusion, we have developed an efficient iron-catalyzed decarboxylative olefination of unstrained carbon−carbon bonds via an alkoxyl radical-triggered cascade. A variety of cycloalkyl silyl peroxides and α,β-unsaturated carboxylic acids underwent this $C(sp^3)-C(sp^3)$ bond cleavage/$C(sp^3)-C(sp^3)$ bond formation process with excellent functional group tolerance and stereoselectivity. This mild and redox-neutral protocol provided a useful synthetic route to the remotely alkenyl ketones.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b02675.

Experimental details, spectral data, copies of ^1H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Natural Science Foundation of China (No. 21602168), the Fundamental Research Funds of the Central Universities (xjj2017027), and Key Laboratory Construction Program of Xi'an Municipal Bureau of Science and Technology (201805056ZD7CG40). We also thank the Instrument Analysis Center of Xi'an Jiaotong University for the samples analysis.

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