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Iron-Catalyzed C−H Alkylation of Heterocyclic C−H Bonds

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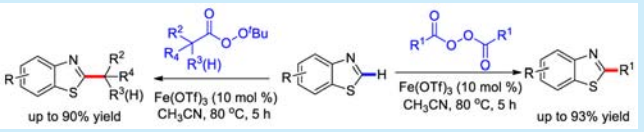
Supporting Information

ABSTRACT: An efficient, iron-catalyzed C−H alkylation of benzothiazoles by using alkyl diacyl peroxides and alkyl *tert*-butyl peresters which are readily accessible from carboxylic acids to synthesize 2-alkylbenzothiazoles is developed. This reaction is environmentally benign and compatible with a broad range of functional groups. Various primary, secondary, and tertiary alkyl groups can be efficiently incorporated into diverse benzothiazoles. The effectiveness of this method is illustrated by late-stage functionalization of biologically active heterocycles.



Carboxylic acids are commercially available, inexpensive, and nontoxic substances extensively used in organic synthesis. The decarboxylative functionalizations of alkyl carboxylic acids are less explored when compared with the aryl carboxylic acids.[1] In the past decade, the development of redox-active esters via carboxylic acid activation became an vital strategy for decarboxylative coupling reactions to construct C_{sp3}−C_{sp3} and C_{sp3}−C_{sp2} bonds.[2−4] Peresters and diacyl peroxides are readily available from carboxylic acids and represent another type of activation of the corresponding carboxylic acids. Combining our interests in alkyl peroxides[5,6] and iron catalysis,[7] we developed vinylic C−H methylation of vinylarenes using alkyl peroxides as alkylating reagents.[8]

Aromatic heterocycles are a class of significant organic molecules that have been extensively used as biologically active molecules, pharmaceuticals, synthetic building blocks, and organic materials.[9] In recent years, C−H functionalization has been developed as one of the most direct strategies for the synthesis of heteroaromatic derivatives.[10] However, the alkylation of heteroaromatic compounds is quite challenging due to the undesired β-H elimination of alkyl intermediates.[11]

Several methods for direct C−H alkylation of heteroaromatic compounds have been established from alkyl halides,[12] olefins,[13] Grignard reagents,[14] potassium alkyltrifluoroborates,[15] organometallic reagents,[16] *N*-tosylhydrazones,[17] and carboxylic acids[18] as alkylating reagents by using transition-metal catalysis (Scheme 1). There is no comprehensive solution to alkylation of benzothiazoles with primary, secondary, and tertiary electrophiles. Herein, we report the unprecedented iron-catalyzed direct C−H alkylation of benzothiazoles by using alkyl diacyl peroxides and alkyl *tert*-butyl peresters as the alkylating reagents which are readily obtainable from the corresponding carboxylic acids.

Our initial investigation commenced with the commercially available benzothiazole (**1a**) and lauroyl peroxide (LPO) (**2a**) as the alkylating coupling partner. In an initial experiment, reaction of **1a** with **2a** in the presence of 10 mol % of $Fe(OTf)_3$ in 1,4-dioxane at 80 °C gave 2-undecylbenzothiazole **3a** in 67% yield (Table 1, entry 1). Other metal catalysts such as $Fe(OTs)_3$, $Cu(OTf)_2$, $In(OTf)_3$, and $Zn(OTf)_2$ catalyzed the reaction with moderate to low efficiency (entries 2−5 and 11). Copper salts cannot catalyze this reaction. Subsequently, solvent effects were also investigated (entries 12−18). Acetonitrile proved to be the most suitable solvent and gave the best result with 86% yield of the desired product **3a** (entry 14). Furthermore, when we reduced the amount of the catalyst to 5, 3, or 1 mol %, lower conversions of **1a** were obtained (entries 19−21). When the reaction was carried out with 30 mol % of HOTf instead of using metal catalyst, the reaction afforded the desired product **3a** in 51% yield (entry 22).

With the optimized reaction conditions in hand, the scope with respect to the benzothiazoles was examined (Scheme 2). The reactivity of different substituted benzothiazoles toward LPO was evaluated. It is noteworthy that the electronic effect

Scheme 1. Direct C−H Alkylation Methods for Alkylated Azole Derivatives

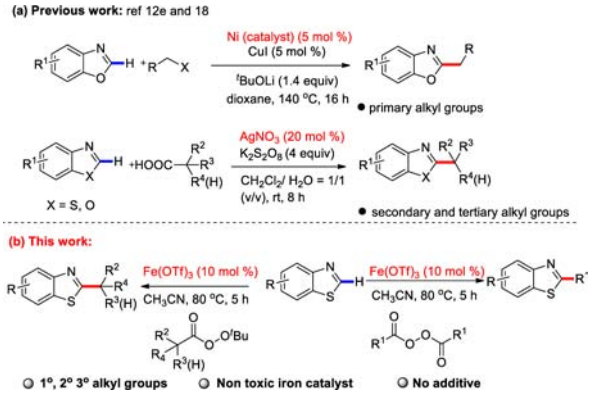


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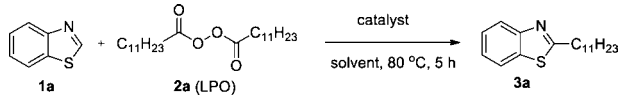
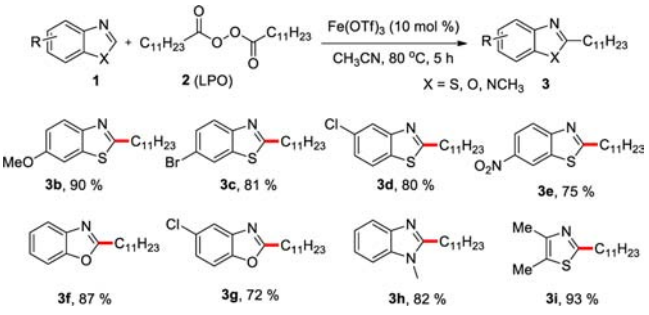
Table 1. Optimization of the Direct C−H Alkylation Conditions[a]



entry	catalyst (mol %)	solvent	yield[b] (%)
1	$Fe(OTf)_3$ (10)	1,4-dioxane	67
2	$Fe(OTs)_3$ (10)	1,4-dioxane	47
3	$Cu(OTf)_2$ (10)	1,4-dioxane	46
4	$In(OTf)_3$ (10)	1,4-dioxane	57
5	$Zn(OTf)_2$ (10)	1,4-dioxane	43
6	CuI (10)	1,4-dioxane	0
7	CuBr (10)	1,4-dioxane	0
8	$Cu(OAc)_2$ (10)	1,4-dioxane	0
9	$CuCl_2$ (10)	1,4-dioxane	0
10	CuTc (10)	1,4-dioxane	0
11	$Fe(acac)_2$ (10)	1,4-dioxane	15
12	$Fe(OTf)_3$ (10)	DMSO	64
13	$Fe(OTf)_3$ (10)	DMF	65
14	$Fe(OTf)_3$ (10)	CH_3CN	86
15	$Fe(OTf)_3$ (10)	toluene	73
16	$Fe(OTf)_3$ (10)	1,2-DCE	61
17	$Fe(OTf)_3$ (10)	THF	71
18	$Fe(OTf)_3$ (10)	H_2O	18
19	$Fe(OTf)_3$ (5)	CH_3CN	59
20	$Fe(OTf)_3$ (3)	CH_3CN	36
21	$Fe(OTf)_3$ (1)	CH_3CN	20
22	TfOH (30)	CH_3CN	51

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), catalyst (10 mol %), solvent (1 mL), 80 °C, 5 h. [b]Yield of the isolated product.

Scheme 2. Substrate Scope of the Heteroaromatic Compounds[a,b]

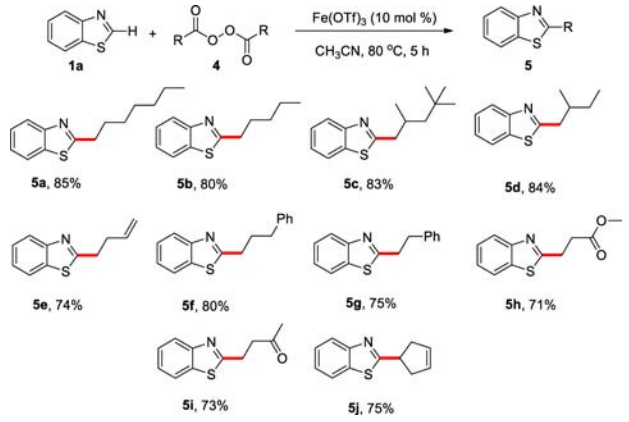


[a]**1** (0.5 mmol), **2** (0.5 mmol), $Fe(OTf)_3$ (10 mol %), solvent (1 mL), 80 °C, 5 h. [b]Yield of the isolated product.

had a noticeable influence on the lauroyl peroxide coupling reactions. Benzothiazole with an electron-donating methoxy group gave 90% yield (**3b**), while the electron-withdrawing bromo-, chloro-, and nitro-substituted alkylated benzothiazoles were obtained with 81% (**3c**), 80% (**3d**), and 75% (**3e**) yields, respectively. It is worth mentioning that the coupling reaction was also tolerable for the alkylation of benzoxazole, 5-chlorobenzoxazole, 1-methylbenzoimidazole, and 4,5-dimethylthiazole, which proceeded smoothly under the standard reaction conditions with good to excellent yields (**3f−i**).

Next, we examined the scope of the alkyl diacyl peroxides (Scheme 3). Alkyl diacyl peroxides (**4**) were prepared in one step from the corresponding carboxylic acids (see the Supporting Information for details).[17] The alkyl diacyl

Scheme 3. Substrate Scope of the Alkyl Diacylperoxides[a,b]

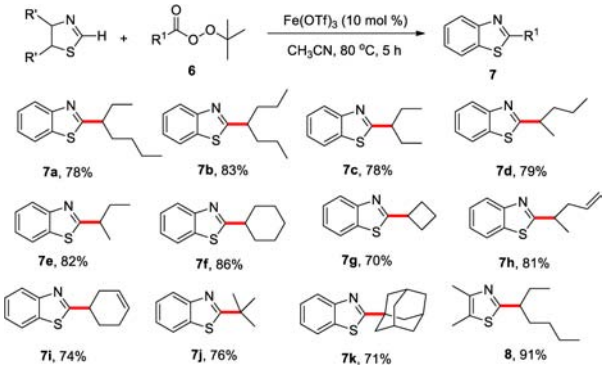


[a]**1** (0.5 mmol), **4** (0.6 mmol), $Fe(OTf)_3$ (10 mol %), solvent (1 mL), 80 °C, 5 h. [b]Yield of the isolated product.

peroxides that contain long-chain alkyl groups and methyl-substituted long-chain alkyl groups afforded the corresponding alkylated products with good yields (**5a−d**). Notably, the alkenyl diacyl peroxide also tolerated the reaction conditions to afford alkenyl derivative of benzothiazole with good yield (**5e**). Furthermore, alkyl diacyl peroxides which contain phenyl groups also gave good yields (**5f** and **5g**). Importantly, alkyl diacyl peroxides bearing ester or ketone groups were well-tolerated (**5h** and **5i**). The reaction of cyclic secondary alkenyl diacyl peroxide afforded cyclopentene ring substituted benzothiazole derivative (**5j**).

Alkyl diacyl peroxides are good reagents for primary and secondary alkylation. To further explore the alkylating reagents for secondary and tertiary alkyl groups, we investigated alkyl *tert*-butyl peresters. Interestingly, the aforementioned optimized reaction conditions were also suitable for alkyl *tert*-butyl peresters to synthesize secondary and tertiary alkylated benzothiazoles. Under similar reaction conditions, we examined the scope of the alkyl *tert*-butyl peresters, which were also synthesized from the corresponding carboxylic acids in moderate to good yields (Scheme 4). The secondary alkylated benzothiazoles (**7a−e**) were obtained with good yields. 2-Cyclohexylbenzothiazole and 2-cyclobutylbenzothiazole were obtained with 86% (**7f**) and 70% (**7g**) yield, respectively.

Scheme 4. Substrate Scope of the Alkyl *tert*-Butyl Peresters[a,b]



[a]**1** (0.5 mmol), **6** (0.6 mmol), $Fe(OTf)_3$ (10 mol %), solvent (1 mL), 80 °C, 5 h. [b]Yield of the isolated product.

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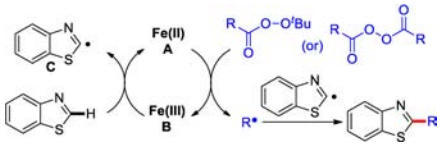
Interestingly, cyclic and acyclic secondary alkylations were also achieved, affording the corresponding products (**7h** and **7i**) in good yields. It is worth mentioning that the tertiary alkyl *tert*-butyl peresters also underwent alkylation smoothly with moderate yields (**7j** and **7k**). Finally, dimethylthiazole also underwent secondary alkylation efficiently under the standard reaction conditions with excellent yield (**8**).

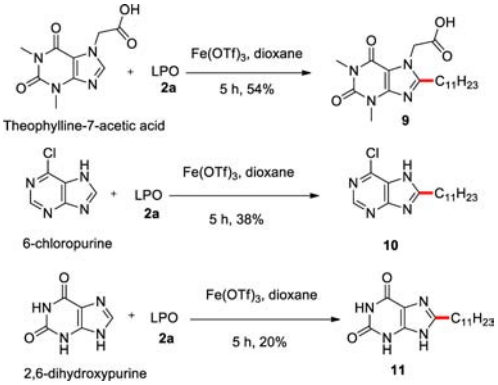
To gain insight into the mechanism of this transformation, we carried out the radical capture reaction by adding a radical-trapping reagent (tetramethylpiperdinyloxy, TEMPO) to the reaction system, and the desired product **3a** was not detected. On the basis of the above results and previous work by Zhao,[18] a plausible mechanism for the C−H alkylation of benzothiazole is proposed via a single-electron transfer catalytic cycle as shown in Scheme 5. This transformation involves Fe(III) (**B**), which is reduced to Fe(II) (**A**) by the benzothiazole or alkyl radicals to form benzothiazole radical **C**. Then Fe(II) (**A**) could be oxidized by the alkyl peroxide or alkyl *tert*-butyl perester through a single-electron transfer to afford the alkyl radical and regenerate Fe(III). Subsequently, the resulting transient alkyl radical reacts with persistent benzothiazole radical **C** to obtain the desired C-2-alkylated benzothiazole.[19]

Scheme 5. Plausible Mechanism for the C-2 Alkylation



To demonstrate the synthetic importance of this method, this catalytic reaction was implemented on biologically important substrates. As shown in Scheme 6, when the commercially available theophylline-7-acetic acid, 6-chloropurine, and 2,6-dihydroxypurine were subjected to LPO (**2a**) under standard reaction conditions (solvent was changed from acetonitrile to dioxane), these substrates underwent C−H alkylation, and alkylated heterocyclic compounds **9**, **10**, and **11** were obtained in 54% (**9**), 38% (**10**), and 20% (**11**) yield, respectively. This result demonstrates the potential applicability of this catalytic method to synthesize analogues of biologically significant molecules.

Scheme 6. C−H Alkylation of Biologically Significant Derivatives



In summary, we have developed an efficient, iron-catalyzed direct C−H alkylation reaction of benothiazoles, benzoxazoles, and thiazole with easily accessible alkyl diacyl peroxides and alkyl *tert*-butyl peresters. This transformation demonstrates a broad range of primary alkyl groups, secondary alkyl groups, and tertiary alkyl groups that can be readily incorporated into benzothiazole with high efficiency. This reaction is environmentally benign and exhibits excellent substrate scope. The applicability of this method is demonstrated by utilizing the reaction for the synthesis of biologically important derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b03287.

Experimental details and NMR spectra are included (PDF)

X-ray data for compound **9** (CIF)

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Notes

The authors declare no competing financial interest.

The X-ray crystallographic coordinates for structure **9** have been deposited at the Cambridge Crystallographic Data Centre under deposition no. CCDC 1510155. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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