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Acyl Radical Smiles Rearrangement To Construct Hydroxybenzophenones by Photoredox Catalysis

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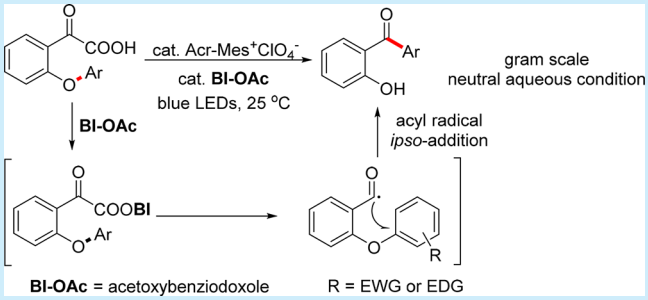
Supporting Information

ABSTRACT: The first visible-light-induced acyl radical Smiles rearrangement to transform biaryl ethers to hydroxybenzophenones under mild and metal-free conditions is reported. Using the dual catalysis of hypervalent iodine(III) reagents and organophotocatalysts, ketoacids readily generate acyl radicals and undergo 1,5-*ipso* addition. This method can construct electron-deficient and electron-rich hydroxybenzophenones with excellent chemoselectivity and on gram scale. The performance of the reaction in neutral aqueous conditions holds potential for future biomolecule applications.

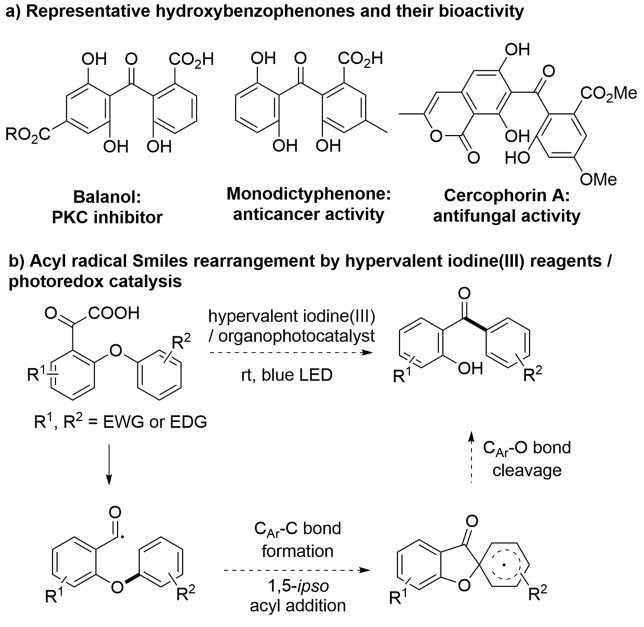


Benzophenones are an important class of natural products, among which the hydroxybenzophenones present widely and carry various bioactivities such as kinase inhibition, antifungal, and anticancer activity (Scheme 1a).[1] Truce−Smiles rearrangement represents an effective approach to synthesize benzophenones; however, the nucleophilic Truce−Smiles rearrangement reactions typically require strong base and heating conditions, which are not chemoselective and incompatible with many functional groups.[2,3] In addition, the migratory aryl groups are limited to electron-deficient arenes, while the electron-rich hydroxybenzophenones are not applicable due to the nucleophilic character of the reaction.[4]

In contrast to ionic Smiles rearrangements, the radical Smiles rearrangement provides alternative reactivity, which may enable synthetic routes for both electron-deficient and electron-rich hydroxybenzophenones.[5] However, there is only one isolated example using di-*tert*-butyl peroxides in refluxing chlorobenzene to generate acyl radicals from aldehydes, in which harsh reaction conditions compromised the functional group compatibility of the reaction and resulted in moderate yields for most substrates.[6] From the bond energy data, the cleavage of the C_{Ar}−O bond (78.8 kcal/mol) should be compensated by the formation of the C_{Ar}−C bond (90.7−98.7 kcal/mol), such that no strong heating or strong oxidants should be required.[7] In this paper, we report the first visible-light-induced acyl radical Smiles rearrangement reaction by dual hypervalent iodine(III)/photoredox catalysis under mild conditions, which is chemoselective and suitable for both electron-deficient and electron-rich aryl migratory groups to construct various hydroxybenzophenones (Scheme 1b).

α-Ketoacids are readily available acyl synthons in organic synthesis; however, its reactivity for 1,5-*ipso* addition is unknown.[8,9] We started the investigation with the ketoacid-substituted biarylether **1a**, which is not applicable for ionic Smiles rearrangement with an electron-rich trimethylbenzene migratory group. With $[Ru(bpy)_3](PF_6)_2$ (0.02 equiv) and the

Scheme 1. Construction of Hydroxybenzophenones by Acyl Radical Smiles Rearrangement



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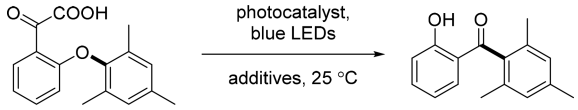
catalytic amount of cyclic iodine(III) reagent acetoxybenziodoxole (BIOAc) (0.2 equiv), we gladly observed the formation of the desired hydroxybenzophenone **2a**, but in low 32% yield (entry 1 in Table 1). The use of cesium carbonate as base to replace BIOAc or the change to $[Ir(ppy)_2(dtbbby)]PF_6$ photocatalyst did not improve the reaction (entries 2 and 3).[10] In contrast, the organic photocatalyst 9-mesityl-10-methylacridinium perchlorate ($Acr\text{-}Mes^+ClO_4^-$) gave the optimal 87% yield of **2a** (84% isolated yield, entry 4).[11] The noncyclic iodine(III) phenyliodine(III) diacetate (PIDA) gave slightly decreased 74% yield of **2a**, while the phenyliodine bis(trifluoroacetate) (PIFA) was ineffective (entries 5 and 6).[12] The combination of $Acr\text{-}Mes^+ClO_4^-$ with sodium carbonates for carboxylate anion formation only gave **2a** in 33% yield, suggesting the unique role of hypervalent iodine(III) for the transformation of ketoacids (entry 7).[9c,d,13] The photocatalyst, cyclic iodine(III), and light are all essential for the reaction (entries 8–10).

Table 1. Optimization of the Acyl Radical Smiles Rearrangement Reaction



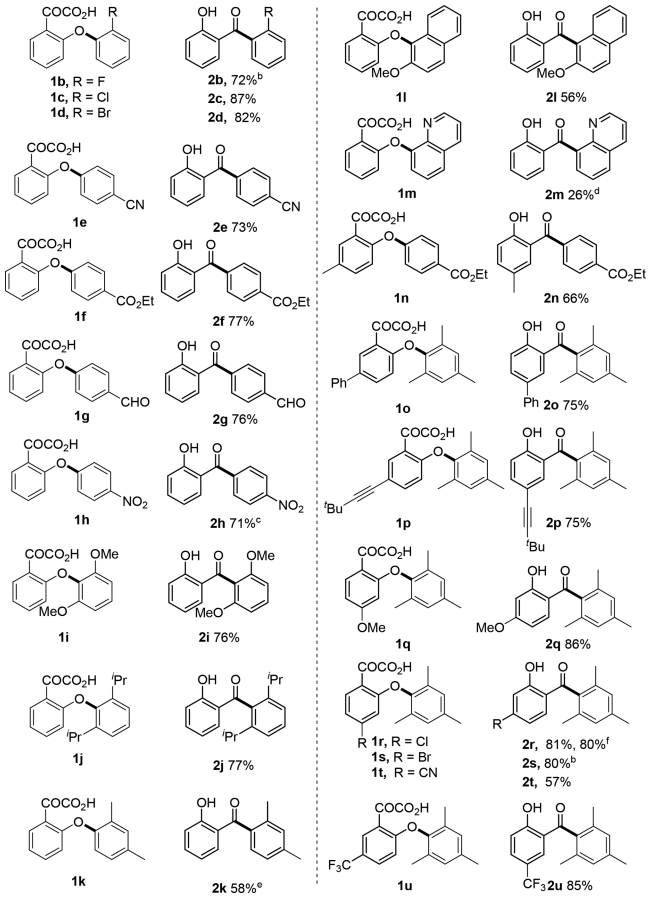
1a **2a**

entry	photocatalyst	additive	conv[c] (%)	yield of **2a**[c] (%)
1	$[Ru(bpy)_3](PF_6)_2$	BIOAc	48	32
2	$[Ru(bpy)_3](PF_6)_2$	Cs_2CO_3	<5	<5
3	$[Ir(ppy)_2(dtbbpy)]PF_6$	BIOAc	34	12
4	$Acr\text{-}Mes^+ClO_4^-$	BIOAc	>95	87 (84)
5	$Acr\text{-}Mes^+ClO_4^-$	PIDA	>95	74
6	$Acr\text{-}Mes^+ClO_4^-$	PIFA	<5	<5
7	$Acr\text{-}Mes^+ClO_4^-$	Na_2CO_3	75	33
8	$Acr\text{-}Mes^+ClO_4^-$		6	5
9		BIOAc	<5	0
10[b]	$Acr\text{-}Mes^+ClO_4^-$	BIOAc	<5	0

[a]Reaction conditions: **1** (0.10 mmol, 1 equiv), photocatalysts (0.002 mmol, 0.02 equiv), and additive (0.02 mmol, 0.2 equiv) in 2.0 mL of acetone under nitrogen with 4 W blue LED irradiation at 25 °C for 12 h, unless otherwise noted. [b]Dark treatment. [c]Conversions and yields were determined by ^1H NMR analysis, and isolated yields are in parentheses. BI = benziodoxole.

We next explored the scope of migratory aryl groups in different substrates (Scheme 2). The ortho-substituted halides **1b–d** gave fluoro-, chloro-, and bromo-substituted 2-hydroxybenzophenones **2b–d** smoothly in 72–87% yields.[4] The para-substituted cyanide **1e** and ester **1f** gave the corresponding products **2e,f** in 73–77% yields. Significantly, the reactive aldehyde group in NHC catalysis method was not affected in this reaction condition to give **2g** in 76% yield,[14] and the nitro group is also tolerated to give **2h** in 71% yield.[15] The highly electron-rich **1i** with dimethoxyl substitutions gave **2i** in 76% yield, which widely presents in many bioactive natural products but remains inaccessible with nucleophilic Smiles rearrangement reactions.[1,2b,c,3] The sterically hindered diisopropyl substitution did not inhibit the reaction to give the hindered **2j** in 77% yield,[16] which is very difficult to prepare from cross-coupling reactions.[17] The 2,4-dimethyl substitution gave 58% yield of **2k**.[18] The bicyclic naphthalene **1l** resulted in 56% yield of **2l**, and quinolone **1m** gave a decreased 26% yield of **2m** due to the side products from decomposition. The ketoacid scope was next explored, and various electron-rich or electron-deficient aryl substitutions including methyl, methoxyl, phenyl, halide, cyanide, alkynyl, and trifluoromethyl groups were all tolerated to give **2n–u** in 57–81% yields. We also performed the gram-scale reaction with **1r**, and the 2-hydroxychlorobenzophenone **2r** was obtained in 80% yield in 1.21 g.

Scheme 2. Substrates Scope[a]



[a]Entry 4, Table 1. [b]16 h. [c]24 h. [d]Acetone/HFIP = 1:1 as solvent. [e]0.4 equiv of BIOAc. [f]5.5 mmol scale.

The reaction mechanism was then investigated by testing the reaction of the preformed benziodoxole–ketoacid complex **3** (Scheme 3a).[19] The formation of **2a** in 60% yield without the addition of BIOAc confirmed the critical role of the BI–ketoacid complex for the reaction.[9c,d,20] In addition, the combination of the preformed benziodoxole–ketoacid complex **3** (0.2 equiv) and the ketoacid **1a** (0.8 equiv) afforded **2a** in 79% yield, which suggested the catalytic turnover of the benziodoxole–ketoacid complex **3**. We also measured the cyclic voltammetry of the benziodoxole–ketoacid complex **3** and obtained the oxidation potential at 0.82 V, which was well below the photoexcited $Acr\text{-}Mes^{+*}$ (E^*_{red} = 2.06 V).[9c,21] The cyclic voltammetry of benziodoxole–ketoacid complexes from ketoacids **1f**, **1h**, and **1i** were also measured, which were in the range of 0.83–1.02 V. In contrast, the corresponding ketoacids did not show peak anodic currents at these oxidation potentials, which confirmed the benziodoxole coordination is critical for the ketoacid oxidation.[19]

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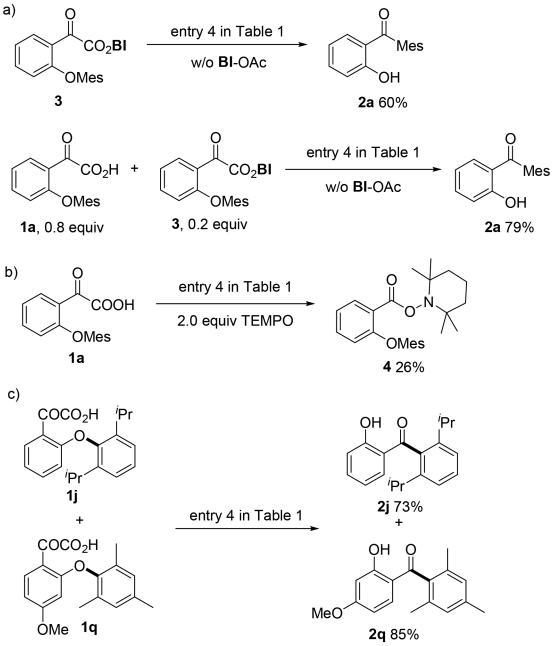
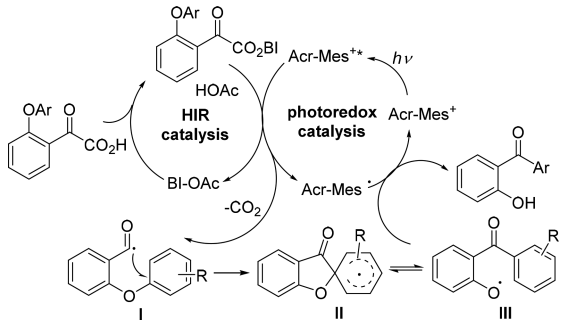
Scheme 3. Mechanistic Investigations of the Acyl Smiles Rearrangement



The TEMPO was next added to the reaction conditions (Scheme 3b). The complete inhibition of the reaction with the acyl-TEMPO adduct **4** formation in 26% yield suggested the acyl radical intermediate.[21] The crossover experiment with **1j** and **1q** resulted in the unscrambled products **2j** and **2q**, which suggested the intramolecular acyl radical addition reactions rather than the intermolecular reactions (Scheme 3c). The quantum yield of the reaction was measured as 50% by the standard ferrioxalate actinometry, which indicated the radical-chain mechanism was unlikely.[22]

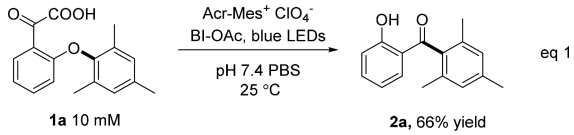
Based on the mechanistic investigations above, we propose the reaction is initiated by the BI-ketoacid complex formation in situ, which can be oxidized readily by the photoexcited Acr-Mes$^+$* to the ketoacid radical (Scheme 4).[11a,23] The ketoacid

Scheme 4. Mechanistic Proposals



radical then eliminates the carbon dioxide to form the acyl radical **I**, and BI-OAc is released for the next catalytic activation of ketoacids. The acyl radical **I** next undergoes 1,5-*ipso* addition to form the dearomatized radical intermediate **II**, which is in equilibrium with the C_{Ar}–O bond-cleaved phenoxyl radical **III**. The radical intermediate **II** or **III** (phenoxyl radical E_{red} ~ 0.9 V) then undergoes single-electron reduction by the Acr-Mes radical (E_{red} = −0.57 V) to form the hydroxybenzophenone with the turnover of the Acr-Mes$^+$ catalyst.[11a,23,24]

With the mild and metal-free reaction conditions, we next tested the reaction under neutral aqueous conditions for potential future biomolecule applications.[9c,20d,25] In pH 7.4 phosphate-buffered saline (PBS) solutions with 1.0 equiv of BI-OAc, the ketoacid-substituted biarylether **1a** in 10 mM concentration readily underwent the structure rearrangement to give hydroxybenzophenone **2a** in 66% yield, which will be very valuable for the photomanipulation of bioactive molecule in biological studies (eq 1).[26]



In conclusion, we have developed the first acyl radical Smiles rearrangement by dual hypervalent iodine(III)/photoredox catalysis to transform various biarylethers to hydroxybenzophenones. The metal-free reaction conditions are mild and tolerate various functional groups, working with both electron-deficient and electron-rich migratory aryl groups. The reaction is suitable for gram-scale synthesis and works in neutral aqueous reaction conditions, suggesting future preparative and biomolecule applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b00353.

Mechanistic experiments, optimization tables, experimental methods, and additional experimental data (PDF)

NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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(12) Entries 4 and 5 of Table 1 with 0.4 equiv trifluoroacetic gave significantly decreased 22% and 10% yields, respectively. See the Supporting Information for details.
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(16) The 1,6-ipso addition adduct was observed in 16% yield; see the Supporting Information for details.
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