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Photoredox-Catalyzed Alkenylation of Benzylsulfoniums

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Abstract: Visible light-mediated radical alkenylation of benzylsulfoniums was achieved by means of fac-Ir(ppy)₃ as a photocatalyst, giving allylbenzenes as products. A variety of functional groups such as halogen, ester, and cyano groups were well tolerated in this transformation. Starting benzylsulfoniums could be readily prepared from benzyl alcohols via an acid-mediated substitution, increasing the synthetic utility of this transformation.

Organosulfur compounds widely exist in natural compounds, living bodies, pharmaceuticals, and functional materials.^[1] From the viewpoint of organic synthesis, organosulfur compounds can be regarded as important synthetic intermediates, due to their unique reactivities that organohalogen compounds do not have. In order to utilize such characteristics for organic synthesis, recently, transition metal-catalyzed transformations of organosulfur compounds with cleavage of their C–S bonds have been actively explored.^[2]



Scheme 1. Working hypothesis of this work.

Among various transition metal-catalyzed transformations, the Mizoroki–Heck alkenylation is one of the most important reactions in organic synthesis.^[3,4] However, Mizoroki-Heck-type alkenylation of organosulfur compounds has been left unexplored due to the strongly coordinating and potentially catalyst-poisoning nature of leaving anionic sulfur moieties. In order to overcome these problems, utilization of arylsulfoniums instead of aryl sulfides is beneficial because 1) oxidative addition of arylsulfoniums is easier than that of aryl sulfides due to their electron-deficient nature; and 2) leaving neutral sulfides would be less debilitating to the catalyst. Taking advantage of these

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benefits, Zhang's group and our group recently succeeded in developing palladium-catalyzed Mizoroki-Heck-type reactions of arylsulfoniums.^[5] Unfortunately, however, these methods were applicable only to arylsulfoniums, and alkylsulfoniums did not react at all. In order to convert alkylsulfoniums to the corresponding alkene products, we then turned our strategy to photoredox-catalyzed radical-mediated alkenylation.^[6] Recently Lei and co-workers reported photoredox-catalyzed^[7] radicalmediated alkenylation of benzyl bromides under very mild reaction conditions.^[8] We envisioned that Lei's alkenylation would be applicable to benzylsulfoniums. Our working hypothesis is shown in Scheme 1: A) photoexcited catalyst reduces benzylsulfonium to generate benzyl radical and dialkyl sulfide, B) addition of the benzyl radical to alkene takes place, C) single electron transfer from the radical adduct to the oxidized photocatalyst generates cation I, and D) deprotonation affords alkenylation product. Indeed, various benzylsulfoniums and alkenes could be coupled under visible light irradiation. It is worth mentioning that electrochemical,^[9] chemical,^[10] and photosensitized^[11,12] formations of aryl or alkyl radicals from sulfonium salts have been well studied, while its application to organic synthesis has been limited to a-carbonyl or acyanosulfoniums,^[10,12] triarylsulfoniums,[13] and 1trifluoromethyldibenzothiophenium (Umemoto reagent).[14]

Table 1. Optimization of reaction conditions.^[a]

Б	$rac{1}{s}$ + $rac{Ph}{Ph}$ $rac{2}{solv}$	mol% <i>fac</i> -Ir(pp equiv base vent, blue LED,	y) ₃	Ph
1a	2a			3aa
entry	catalyst	base	solvent	NMR yield
1	fac-lr(ppy)₃	Na ₂ CO ₃	DMF	39%
2	fac-lr(ppy)₃	K ₂ CO ₃	DMF	34%
3	<i>fac</i> -Ir(ppy)₃	NaOAc	DMF	16%
4	fac-Ir(ppy)₃	Cs ₂ CO ₃	DMF	0%
5	fac-lr(ppy)₃	Na ₂ CO ₃	DMF	52% ^[b]
6	[lr(ppy) ₂ (dtbpy)](PF ₆)	Na ₂ CO ₃	DMF	0% ^[b]
7	fac-lr(ppy)₃	Na ₂ CO ₃	NMP	64% ^[b]
8	fac-lr(ppy)₃	Na ₂ CO ₃	NMP	71% ^[b,c]
9	-	Na ₂ CO ₃	NMP	0% ^[b,c]
10	fac-lr(ppy)₃	Na ₂ CO ₃	NMP	0% ^[b,c,d]

[a] **1a** (0.50 mmol), **2a** (0.50 mmol), *fac*-lr(ppy)₃ (0.010 mmol), base (1.0 mmol), solvent (2.5 mL). [b] **2a** (1.0 mmol). [c] NMP (1.0 mL). [d] In the dark.

In the presence of 2 mol% of *fac*-lr(ppy)₃ as a photocatalyst, the reaction of 1-benzyltetrahydrothiophenium bromide (**1a**) with 1,1-diphenylethylene (**2a**) was tested under blue LED irradiation. By using Na₂CO₃ as a base and DMF as a solvent, a 39% yield of the alkenylated product **3aa** was obtained (Table 1, entry 1). The use of K₂CO₃ instead of Na₂CO₃ gave the product **3aa** in a slightly lower yield (entry 2). NaOAc was found to be inferior, and **3aa** was not obtained when Cs₂CO₃ was used^[15] (entries 3 and

COMMUNICATION

4). Organic bases such as Et₃N, *i*Pr₂EtN, and DABCO resulted in no or negligible formations of the desired product (See Table S1 in the Supporting Information). By increasing the amount of **2a** to 2 equivalents, the yield of **3aa** increased to 52% (entry 5). Since the reduction potential of the sulfonium salt **1a** is –1.48 V (vs SCE, see Figure S1 in the supporting information), strongly reducing *fac*-lr(ppy)₃ (Ir^{III*}/Ir^{IV} = –1.73 V)^[16] was crucial. As another photocatalyst, [Ir(ppy)₂(dtbpy)](PF₆) having a higher reduction potential (Ir^{III*}/Ir^{IV} = –0.96 V)^[17] did not give **3aa** at all (entry 6). The result of solvent screening revealed that NMP was the best solvent (entry 7 and Table S1). Eventually, the reaction in higher concentration (0.5 M) furnished **3aa** in 71% yield (entry 8). In the absence of either photocatalyst or light, **3aa** was not obtained at all (entries 9 and 10).^[18]

With the optimized reaction conditions in hand, we then tried this alkenylation with various benzylsulfoniums (Scheme 2). The efficiency of the alkenylation depends on the electronic nature of benzylsulfoniums: the yields of the products from electron-deficient sulfoniums were higher than that from **1a**. Functional groups such as ester and cyano groups were well tolerated in this reaction, giving **3ba**, **3ca**, and **3da**, respectively. A methyl substituent on the *ortho* position in **1e** did not retard the reaction. Electron-deficient sulfoniums **1f** and **1g** afforded **3fa** and **3ga** in high yields, respectively. Bromo-substituted benzylsulfoniums **1h** and **1i** were successfully converted to **3ha** and **3ia** without touching their aryl–Br bonds. Substituents on the *meta* positions did not hamper the reaction; products **3ja** and **3ka** were obtained in good yields. π -Extended naphthylsulfoniums **1I** and **1m** also gave alkenylation products **3Ia** and **3ma**.

2 mol% *fac*-Ir(ppy)₃ 2 equiv Na₂CO₃ NMP, blue LED, 16 h

NC

3fa 86%

Ph 人 Ph

3ia 75%

3la 56%

yields, respectively. Styrene derivatives also underwent the present alkenylation and the reaction of 1i with 4-methoxystyrene (2h) afforded 1,3-diarylpropene 3ih in 66% yield as a mixture of E and Z isomers.^[19] Under the standard conditions, less electronrich 4-acetoxystyrene (2i) gave the desired product 3bi in 20% yield along with hydrated alcohol 3bi' in 20% yield. We speculated that benzylic cation I in Scheme 1 would be trapped by a trace amount of water in the reaction mixture to generate 3bi'.[14a,I] Therefore we ran the reaction in the presence of tetrabutylammonium bromide (TBAB) in order to enhance the deprotonation from I by increasing the solubility of the base. As a result, the formation of 3bi' was suppressed and 3bi was obtained in 37% yield. The alkenylation with simple styrene in the presence of TBAB gave 3bj while the yield was lower than that of electronrich styrenes. The reaction with α -methylstyrene (2k) also proceeded while a mixture of three isomers, 3ik', (E)-3ik, and (Z)-3ik, was obtained.



Scheme 2. Scope of benzylsulfonium bromides.

3ka 69%

Br Br

3aa 64%

3da 77%

MeO

P٢

3ha 67%

ÓMe

2a 2 equiv

MeO₂C

3ea 79%

3ba 79%

The scope of alkenes was also investigated (Scheme 3). 1,1-Diphenylethylenes bearing electron-withdrawing fluoro or electron-donating methoxy groups participated in the reaction, giving **3ib** or **3bc** in good yields. The methylsulfanyl groups in **2e** left untouched in the reaction and **3be** was obtained in 77% yield. The alkenylation of **1b** with unsymmetrical 1,1-diarylethylenes **2f** and **2g** afforded *E/Z* mixtures of **3bf** and **3bg** in 87% and 84% **Scheme 3.** Scope of alkenes. [a] With 1.0 equiv of *n*Bu₄NBr.

We then checked the effect of the counteranion of benzylsulfoniums. Instead of benzylsulfonium bromide **1i**, benzylsulfonium triflate **4i** was involved in the reaction (Scheme 4a). As a result, not only the desired product **3ia** but also tertiary alcohol **3ia'** was observed in the crude mixture. We inferred that

Ph

3ca 73%

3ga 80%

3ja 80%

3ma 56%

Ph

Ph

COMMUNICATION

the difference would be derived from the efficiency of the step D in Scheme 1. When 1i is employed, counteranion of the benzylic cation I should be Br⁻ or NaCO₃⁻ (by generating NaBr) and the anion would deprotonate I to afford 3ia. On the other hand, in the case of 4i, far less basic TfO- would be reluctant to deprotonate I. As a result, the reaction of I with water afforded 3ia'. An addition of TBAB was again effective to accelerate the deprotonation and suppress the formation of 3ia', as is the case with 3bi and 3bj, affording 3ia in 72% yield (Scheme 4b, upper). Additionally, we tried to obtain 3ia' selectively by running the reaction in the presence of water. As expected, 3ia' was obtained in 65% yield (Scheme 4b, lower). The reaction in the presence of MeOH gave ether 3ia" in 58% yield. Interestingly, formation of 3ia' is less efficient when 2-bromobenzyl bromide was used instead of 4i: the yield of 3ia' was only 27% and 3ia was the major product. Therefore, it can be emphasized that the synthesis of 3ia' or 3ia" is one feature of using benzylsulfoniums.

chlorobenzyl alcohol could be alkenylated to afford 3na in 69% yield. Electron-rich benzylsulfonium 4o was also converted to 3oa in 54% yield although the yield was lower than those from electron-deficient ones. It is noteworthy that this method allows one to avoid the use of unstable electron-rich benzyl bromides. Alkenylation of 2-arylbenzylsulfonium 4q proceeded in spite of the steric hindrance, giving 3qa in 70% yield. This example shows usefulness of this reaction (Scheme 6); while palladium-catalyzed cross-coupling of 2-bromobenzyl bromide with arylboronic acids was reported to take place at the benzylic C-Br bond (Scheme 6a),^[21] that of 2-bromobenzyl alcohols took place at the aromatic C-Br bonds without any protection of the hydroxy moiety.^[22] After the arylation, the hydroxy group was "activated" to the corresponding sulfonium triflate and then sulfonium 4g was alkenylated under the photoredox catalysis. This arylationactivation-alkenylation sequence would provide a new synthetic strategy for allylbenzene derivatives (Scheme 6b).



Since 1-benzyltetrahydrothiophenium triflates **4** can be synthesized from benzyl alcohols and tetrahydrothiophene,^[20] the scope of 1-benzyltetrahydrothiophenium triflates was also examined (Scheme 5). The sulfonium salt prepared from 2-

Finally, we conducted the present alkenylation in a 1.5 mmol scale; sulfonium bromide **1b** and sulfonium triflate **4i** reacted with **2a**, respectively. In both cases, the corresponding alkenylation

COMMUNICATION

products **3ba** and **3ia** were obtained without loss of the yields (Scheme 7).

In conclusion, we have developed alkenylation of benzylsulfoniums by means of photoredox catalysis. The starting benzylsulfonium triflates could be prepared from the corresponding benzyl alcohols, allowing this transformation valuable. Further development on photoredox-mediated transformations of organosulfur compounds is currently underway in our laboratories.

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Keywords: photoredox catalysis, alkenylation, sulfonium, radical reaction

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- [19] The *E*/*Z* ratio of **3ih** would depend on the reaction time. With a longer reaction time, the ratio of the *E* isomer of **3ih** was increased probably due to *E*/*Z* isomerization.
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Entry for the Table of Contents (Please choose one layout)

Layout 2:

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Visible light-mediated radical alkenylation of benzylsulfoniums was achieved by means of *fac*-lr(ppy)₃ as a photocatalyst, giving allylbenzenes as products. A variety of functional groups such as halogen, ester, and cyano groups were well tolerated in this transformation. Starting benzylsulfoniums could be readily prepared from benzyl alcohols via an acid-mediated substitution, increasing the synthetic utility of this transformation.