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Photoinduced Oxidative Cross-Coupling for O–S Bond Formation: A Facile Synthesis of Alkyl Benzenesulfonates

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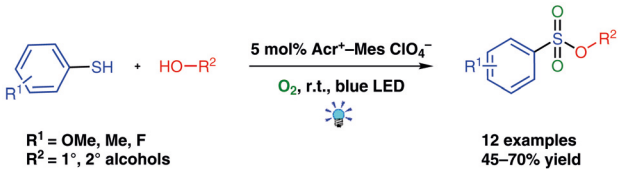

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Abstract We have developed a photoinduced oxidative cross-coupling of thiophenols with alcohols for O–S bond formation. The protocol uses visible light, a metal-free photocatalyst, and oxygen as the oxidant for the selective synthesis of alkyl benzenesulfonates; no ligand co-additive is necessary. Mechanistic studies suggested that the disulfide and alkyl benzenesulfinate are involved as intermediates and that the transformation proceeds by a radical pathway.

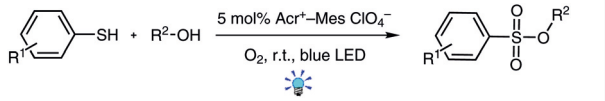
Key words photoredox catalysis, alkyl benzenesulfonates, C–S bond formation, dioxygen, oxidative coupling.

In the past year, cross-coupling reactions have emerged as one of the most powerful tools and a fundamental methodology for the construction of carbon–carbon and carbon–heteroatom bonds in modern synthesis.[1] Various conventional coupling reactions of two functionalized starting materials have been replaced by the improved oxidative coupling reactions, because they are environmentally benign and do not require prior functionalization of the substrate.[1e,2] Numerous oxidative cross-coupling processes have been developed for the construction of carbon–carbon and carbon–heteroatom bonds in the last few years. However, only a few methods are available for the construction of heteroatom–heteroatom bonds, and these are restricted to P–N and P–O bonds.[1e] Therefore, the development of versatile and selective oxidative cross-coupling reactions for the construction of heteroatom–heteroatom bonds would offer a useful strategy and would be a welcome move.

Since the first contribution on the photooxidation of a simple sulfide by Schenck and Krauch in 1962,[3] the photooxidation of organosulfur compounds has been extensively studied, because such compounds are ubiquitous in natural biological systems.[4] In biological systems, organosulfur compounds play key roles in the activities of some enzymes, and these enzymes are often deactivated by active oxygen species.[5] For example, the photooxygenation of methionine causes deactivation of several important enzymes.[4k,6]

Although the photooxidation of organosulfur compounds has been investigated for a long time with a variety of reagents, the photooxidative cross-coupling of thiols with alcohols has never been studied, though it is of current interest. The photooxidation of sulfur with oxygen is complex because of the number of oxidation states of sulfur and it can give rise to a variety of oxidized oxysulfur compounds, depending on the reaction conditions.[7] In continuation of our efforts in photocatalysis and oxidative cross-coupling reactions,[2a–c,2e,g,i] we became interested in the development of photoinduced oxidative cross-coupling reactions of thiophenols and alcohols for O–S bond formation. Here, we report a photooxidative cross-coupling of thiols with alcohols for a selective and ecofriendly synthesis of alkyl benzenesulfonates (Scheme 1). The sulfonates are useful intermediates in organic synthesis, medicinal chemistry, and polyether chemistry.[8] They are widely used as precursors of cyclic crown ethers, aza crown ethers, and lariat ethers.[8] Conventional methodologies, which use tosyl chloride, tosyl anhydride, or *p*-toluenesulfonic acid as moisture-sensitive and reactive sulfonylating reagents for the synthesis of sulfonates, require an equimolar amount of base or Lewis acid or an expensive alkylating agent, which generate significant amount of byproducts in the form of dissolved salts that then require a high level of biological and chemical oxygen demand.[9] The tight restrictions on the release of waste or toxic emissions, to reduce environmental pollution, have induced a paradigm shift in the development of new synthetic strategies. In this context, a visible-light-induced cross-coupling reaction that uses oxygen as a

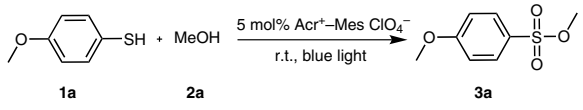
green oxidant would provide an economical, energetically beneficial opportunity for clean processing and pollution prevention.[2,10]



Scheme 1 Visible-light-promoted synthesis of alkyl benzenesulfonates

In the initial stages of our work, we selected 4-methoxybenzenethiol (**1a**) and methanol (**2a**) as model substrates, and, on the basis of earlier reports, the 9-mesityl-10-methylacridinium ion (Acr$^+$–Mes) as a photocatalyst. We chose Acr$^+$–Mes for our optimization studies because it has been shown to be an efficient photoredox catalyst in various photooxidative transformations, as a result of its high oxidizing ability and reducing ability.[11] After a series of screening studies on the reaction conditions (for details, see Supporting Information, Tables S1, S2, S3, and S4), we found that use of 5 mol% of 9-mesityl-10-methylacridinium perchlorate with 3 mL of methanol (**2a**) and 4-methoxybenzenethiol (**1a**; 1.0 mmol) delivered the maximum yield (70%) of methyl 4-methoxybenzenesulfonate **3a** (see Supporting Information, Table S3, entry 9). In addition, we performed a series of control experiments to confirm the necessary parameters for the reaction, such as catalyst, air, and visible light (Table 1). Control experiments indicated that no desired product was observed when light, photocatalyst, or oxygen were absent.

Table 1 Control Experiments to Confirm the Necessary Parameters of the Reaction[A]

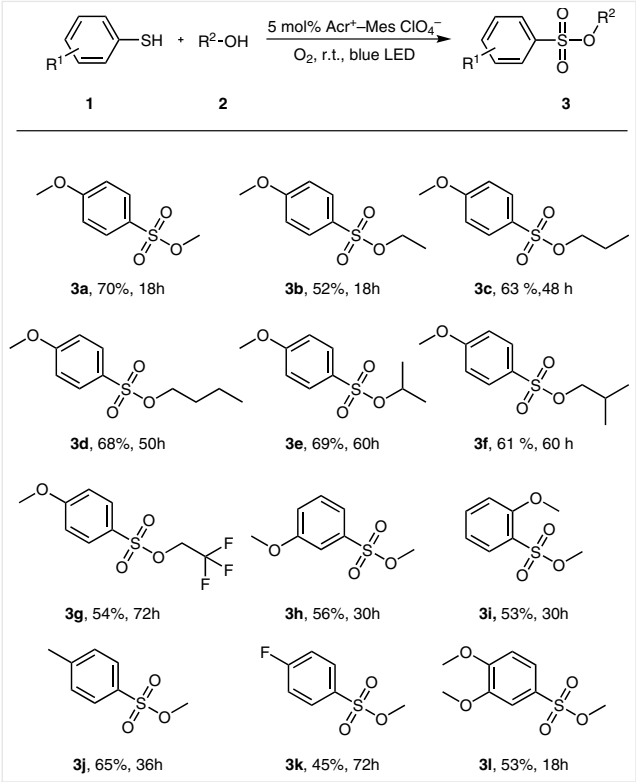


1a **2a** **3a**

Entry	Photocatalyst	Oxidant	Blue light	Yield[b,c] (%)
1	+	O_2	+	72 (70)
2	+	air	+	trace
3	–	O_2	+	no
4	+	O_2	–	no
5	+	N_2	+	no

[a] Reaction conditions: **1a** (1.0 mmol), photocatalyst (5.0 mol%), MeOH (**2a**; 3.0 mL), r.t., oxidant, 3 W blue LED illumination, 18 h.
[b] Determined by GC using biphenyl as an internal standard; the yield in parentheses is the isolated yield.
[c] Yield calculated on the basis of two moles of the thiophenol **1a** being required for conversion into one mole of product **3a**.

With the optimized reaction conditions in hand, we next examined the substrate scope and limitations of this process by changing the alcohol and thiophenol. The results are illustrated by the examples detailed in Scheme 2.[12] To evaluate the scope of the alcohol, various alcohols **2** were treated with 4-methoxybenzenethiol (**1a**) under the standard optimized conditions for oxidative cross-coupling to give an O–S bond. As shown in Scheme 2, a range of primary alcohols, including 2,2,2-trifluoroethanol, participated in the O–S coupling and gave the corresponding benzenesulfonates in good yields. The secondary alcohol substrate propan-2-ol could also be employed in the reaction, giving isopropyl 4-methoxybenzenesulfonate (**3e**) in 69% yield. The scope with tertiary alcohols was also examined, but the desired product was not obtained under the optimized conditions. We then examined the scope of the reaction for the synthesis of sulfonates **3h–l** by using various thiophenols **1**. A series of functional groups on the thiophenol, including methyl, methoxy, or fluoro were tolerated under the mild reaction conditions.



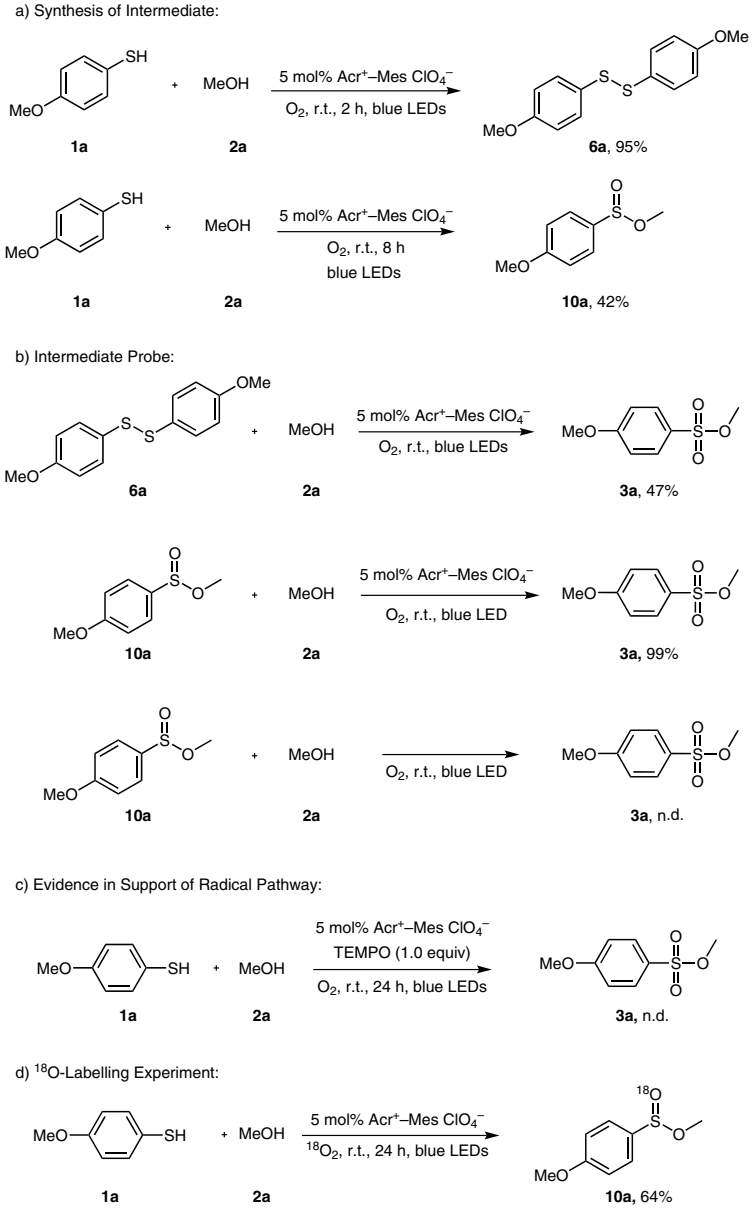
Scheme 2 Exploration of the substrate scope for the synthesis of alkyl benzenesulfones **3**. *Reagents and conditions*: thiophenol **1** (1.0 mmol), photocatalyst (5.0 mol%), alcohol **2** (3.0 mL), O_2, 3 W blue LEDs, r.t., 18–72 h. Isolated yields were calculated for the conversion of two moles of the thiophenol **1** into one mole of the corresponding product **3**.

We conducted a number of experiments to gain a reasonable insight into the reaction mechanism (Scheme 3). Initially, we studied the progress of reaction with 4-methoxybenzenethiol (**1a**, 1.0 mmol) and 9-mesityl-10-methylacridinium perchlorate (5.0 mol%) as model substrate and photocatalyst, respectively, in methanol (**2a**, 3 mL) at r.t., and we monitored the progress of the reaction by TLC. After

two and eight hours, new spots appeared on TLC, and the corresponding intermediate products were isolated in 95% and 42% yield, respectively; these were confirmed to be 1,1′-disulfanediylbis(4-methoxybenzene) (**6a**) and methyl 4-methoxybenzenesulfinate (**10a**), respectively (Scheme 3, a).

To confirm that **6a** and **10a** were intermediates in the reaction, we subjected these compounds to the standard reaction conditions and obtained the product methyl 4-methoxybenzenesulfonate (**3a**) in 47% and 99% yields, respectively (Scheme 3, b). When methyl 4-methoxybenzenesulfinate (**10a**) was oxidized with dioxygen without a photocatalyst, only a trace of product **3a** was obtained (Scheme 3, b). These experiments confirmed that the reaction proceeds via 1,1′-disulfanediylbis(4-methoxybenzene) (**6a**) and methyl 4-methoxybenzenesulfinate (**10a**) as intermediates, and that these compounds participate in the catalytic cycle.

To confirm that a radical process is involved in this reaction, we performed radical-trapping and EPR experiments. The radical-trapping experiment was performed by adding the conventional radical scavenger TEMPO under the standard reaction conditions. The reaction was completely inhibited, and methyl 4-methoxybenzenesulfonate (**3a**) was



Scheme 3 Preliminary mechanistic investigations

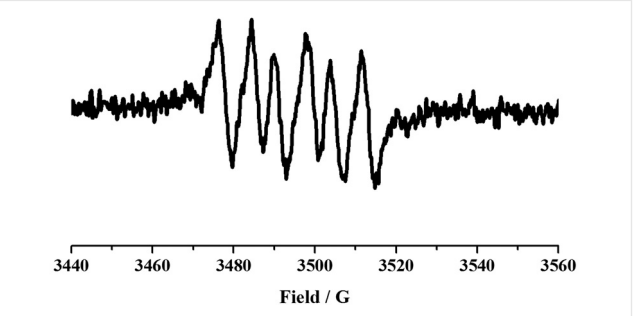
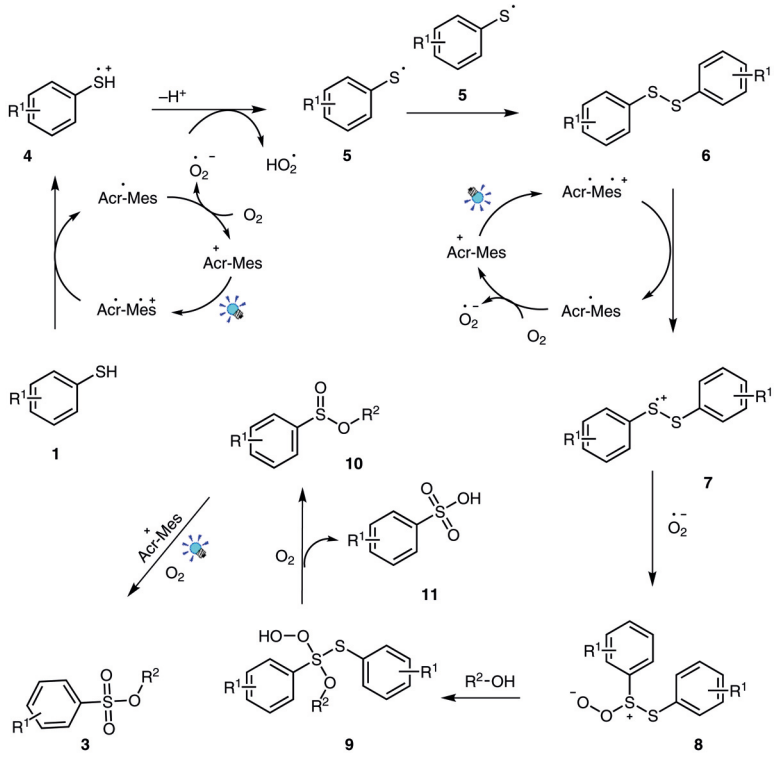


Figure 1 EPR studies of radical species in the oxidative reaction

not formed at all (Scheme 3, c). Electron paramagnetic resonance (EPR) experiments were also conducted to gain an insight into the mechanism. The EPR spectrum of a mixture of 4-methoxybenzenethiol (**1a**, 0.25 mmol), 9-mesityl-10-methylacridinium perchlorate (5 mol%), and methanol (**2a**, 3 mL) displayed a resonance characteristic of an organic radical (g = 2.0070, α^N = 13.3 G,α_β^H = 7.9 G) (Figure 1). We propose that this might correspond to an oxygen-centered radical–5,5-dimethylpyrroline *N*-oxide (DMPO) adduct. The results of the trapping and EPR experiments indicated the participation of organic radicals in the reaction.

We also performed oxygen-labelling experiments. In the presence of $^{18}O_2$ labelled dioxygen, the ^{18}O-labelled product methyl 4-methoxybenzenesulfinate (**10a**) (from the *m*/*z*) was obtained in 64% yield, confirming that dioxygen took part in this transformation, and that the S–O bond originates from the dioxygen (Scheme 3, d).

On the basis of these control experiments, a possible mechanism for this photoinduced cross-coupling reaction for the synthesis of alkyl benzenesulfonates is shown in Scheme 4. The photocatalytic reaction is initiated by intramolecular photoinduced electron transfer from the mesitylene moiety to the singlet excited state of the Acr^+ moiety of Acr^+–Mes, which affords $Acr^{\bullet}$–$Mes^{\bullet+}$. The $Mes^{\bullet+}$ moiety can oxidize the thiophenol **1** to produce the radical cation **4**, whereas the $Acr^{\bullet}$ moiety can reduce O_2 to $O_2^{\bullet-}$. The resulting thiophenol radical cation **4** gives the corresponding thiyl radical **5** through deprotonation. The thiyl radical **5** then undergoes homocoupling to form a disulfide **6**. Disulfide **6** undergoes a further one-electron oxidation to form a disulfide radical cation **7**, which is oxidized to form the thiopersulfinate **8**. This is simultaneously attacked by the alcohol to form intermediate **9**, which then undergoes photooxidative fragmentation to form alkyl benzenesulfinate **10** and benzenesulfonic acid **11** (confirmed by HRMS). Benzenesulfinate **10** is further oxidized to afford the benzenesulfonate product **3**.



Scheme 4 Plausible mechanism for the photoinduced cross-coupling of thiophenols and alcohols for the synthesis of alkyl benzenesulfonates

In conclusion, we have described the first photoinduced oxidative cross-coupling reaction of thiophenols with alcohols for the mild synthesis of alkyl benzenesulfonates in moderate to good yields. A simple and metal-free precatalyst is employed, and no ligand co-additive is necessary. A series of mechanistic studies suggests that the photoinduced O–S coupling proceeds through an SET/radical pathway. An advantage of our method over reported methods is that it does not require an expensive alkylating agent, a Lewis acid, or an equimolar amount of base.

Acknowledgment

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0036-1588728.

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(12) **Alkyl Benzenesulfonates 3; General Procedure**
An oven-dried Schlenk tube equipped with a magnetic stirrer bar was charged with Acr^+–Mes ClO_4^- (5.0 mol%), capped with a septum, and evacuated. A balloon filled with O_2 was connected to the Schlenk tube through the side arm, and thiophenol **1**(1.0 mmol) and alcohol **2** (3.0 mL) were successively injected into the reaction tube. The mixture was irradiated with light from blue LEDs (3.0 W) and vigorously stirred at r.t. for 18–72 h (see Scheme 2). When the reaction was complete (TLC), the product was purified by flash column chromatography (silica gel, PE–EtOAc).