Photocatalytic Rearrangement

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Efficient Aryl Migration from an Aryl Ether to a Carboxylic Acid Group To Form an Ester by Visible-Light Photoredox Catalysis

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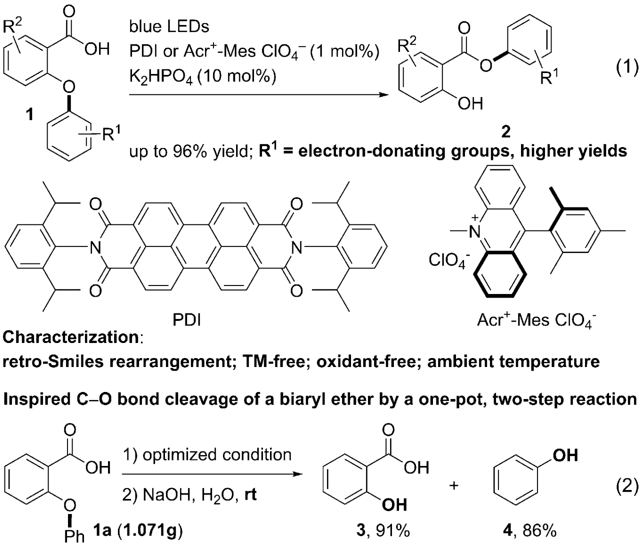
Abstract: *We have developed a highly efficient aryl migration from an aryl ether to a carboxylic acid group through retro-Smiles rearrangement by visible-light photoredox catalysis at ambient temperature. Transition metals and a stoichiometric oxidant and base are avoided in the transformation. Inspired by the high efficiency of this transformation and the fundamental importance of C–O bond cleavage, we developed a novel approach to the C–O cleavage of a biaryl ether to form two phenolic compounds, as demonstrated by a one-pot, two-step gram-scale reaction under mild conditions. The aryl migration exhibits broad scope and can be applied to the synthesis of pharmaceutical compounds, such as guacetisal. Primary mechanistic studies indicate that the catalytic cycle occurs by a reductive quenching pathway.*



Scheme 1. Aryl migration from an aryl ether to a carboxy group to form an ester by visible-light photoredox catalysis and transformation inspired by the rearrangement.

Various aryl-migration reactions have been developed and display broad application.[1] Notably, aryl migration from an aryl ether to form an ester is rare. In 1955, this migration was first observed upon the thermal decomposition of 2-phenoxybenzoyl peroxide in 25% yield by DeTar and Hlynsky.[2] Recently, the migration was promoted by silver catalysis at 130 °C by Hossian and Jana, who used a carboxylic acid as the starting material.[3] However, the stoichiometric strong oxidant $K_2S_2O_8$ and a base were required. Furthermore, the transformation only resulted in up to 64% yield. No clear electronic effects on this aryl migration were observed. Thus, the transformation was identified as a Smiles rearrangement. Herein, we demonstrate a highly efficient aryl migration from an aryl ether to form the ester of a carboxylic acid by visible-light photoredox catalysis at ambient temperature without an oxidant [Scheme 1, Eq. (1)]. Only 1 mol% of a photosensitizer (PDI or Acr$^+$-Mes ClO_4^-) and 10 mol% of a base (K_2HPO_4) were required. Notably, electron-donating groups on the migrating aryl ring generally induced higher yields in this transformation, which differs from the typical Smiles rearrangement[4] and can be understood as a retro-Smiles rearrangement.[4a,5] As this developed aryl migration is the retro-reaction of the reported Smiles rearrangement involving aryl migration from an ester to form an aryl ether.[6] And the Smiles rearrangement always requires a heteroatom as the nucleophilic component and an electrophilic arene activated by strong electron-withdrawing groups, a carbon-based nucleophile, or free-radical attack on the *ipso*-position of sulfonates or sulfonamides.[4] By taking advantage of visible-light photoredox catalysis, transition metals and a stoichiometric amount of an oxidant and a base are avoided, thus leading to an environmentally benign and highly atom economical transformation. Moreover, inspired by the high efficiency of this aryl migration and the fundamental importance of C–O bond cleavage,[4i,7] we demonstrate a novel approach to C–O bond cleavage in biaryl ethers to give two phenolic compounds in a one-pot, two-step reaction under mild conditions as a subsequent transformation [Scheme 1, Eq. (2)].

Visible-light photoredox catalysis is emerging as a powerful tool in organic synthesis and involves the generation of radical intermediates.[8] Thus, the proposed aryl migration would occur by the initial generation of an aryl carboxylic radical intermediate **A** by visible-light redox catalysis with a catalytic base,[9] followed by formation of the cyclic intermediate **B** to afford the final product **2a** (Scheme 2).[3] The formation of the more stable ester C–O bond should be the driving force of this aryl migration, as the C–O bond energies of an aryl ether and an ester are about 78.8 and 87–93 kcal mol^{-1}, respectively.[10]

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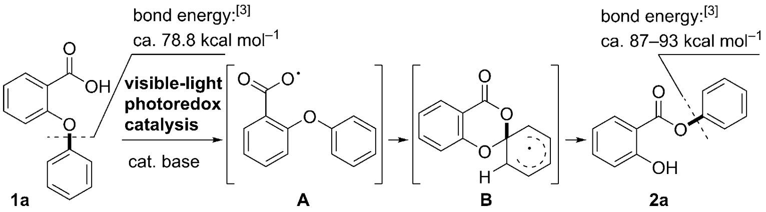
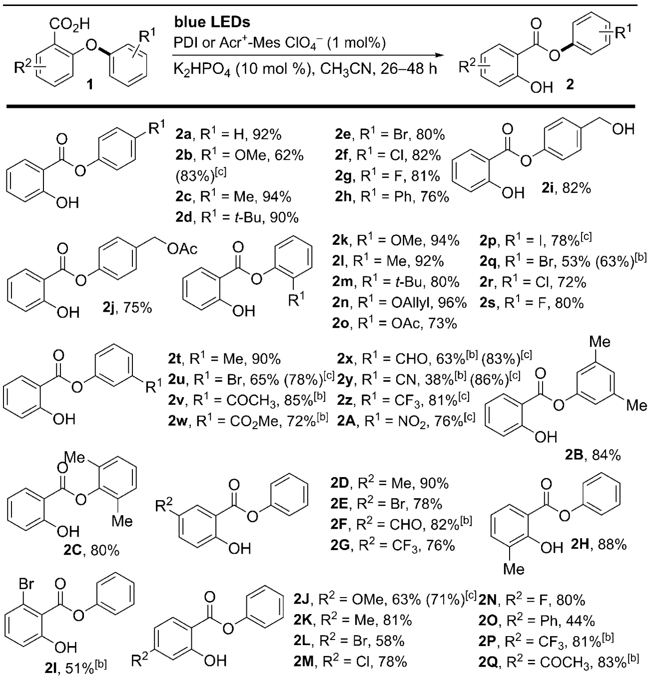


Scheme 2. Possible pathway for the aryl migration by visible-light photoredox catalysis.

Our interest in H_2-releasing transformations[11] led us to attempt to construct dibenzofuran from 2-phenoxybenzoic acid (**1a**) through H_2 release and decarboxylation by photoredox catalysis. To our surprise, a highly efficient 1,5-aryl migration from the aryl ether to the carboxy group (Scheme 2) was observed when Acr$^+$-Mes ClO_4^- or PDI was used as a photosensitizer (1 mol %) in the presence of K_2HPO_4 (10 mol %) in CH_3CN under irradiation with blue LEDs (see Table S1 in the Supporting Information), which led to phenyl 2-hydroxybenzoate (**2a**) in 94 or 96 % yield (as deduced by ^{1}H NMR spectroscopy; **2a** was isolated in 92 % yield when PDI was used). Other ruthenium photosensitizers, such as [Ru(1,10-phen)$_3$Cl$_2$·6 H$_2$O], [Ru(bpy)$_3$Cl$_2$·6 H$_2$O], and [Ru(bpz)$_3$Cl$_2$], did not induce the migration (see Table S1). With [Ir(ppy)$_3$] as the photosensitizer, **2a** was obtained in only 6 % yield (see Table S1). The use of other solvents (DMSO, DMF, MeOH) and bases (DBU, Et_3N, pyridine, K_2CO_3) was investigated with PDI as the photosensitizer, and it was found that MeOH could be used as an alternative solvent (see Table S1). The above-mentioned bases led to slightly lower reaction yields. Without a base, **2a** was obtained in only 22 % yield (see Table S1). Under irradiation with white LEDs, the reaction efficiency decreased significantly. Control experiments showed that light irradiation and a photosensitizer were essential (see Table S1).

The scope of the reaction was investigated under the optimized conditions with PDI or Acr$^+$-Mes ClO_4^- as the photosensitizer. First, the substituents on the migrating aryl ring were investigated (Table 1). With PDI as the photosensitizer, electron-donating groups in the *para* position, such as methyl and *tert*-butyl, but not methoxy (product **2b**), induced excellent yields (products **2c**,**d**). Electron-withdrawing groups, such as halogens and phenyl, decreased the reaction yields to some extent (products **2e**–**h**). Notably, the observed electronic effect of substituents in this aryl migration is contrary to that observed for the typical Smiles rearrangement,[4] in which strongly electron withdrawing groups are required, as mentioned above. Moreover, hydroxy (product **2i**) and acetoxy groups (product **2j**) were well tolerated under the optimized conditions. A similar electronic effect of substituents in the *ortho* position to that of substituents in the *para* position was observed (products **2k**–**s**). A *tert*-butyl group slightly decreased the reaction efficiency (product **2m**), perhaps as a result of steric effects. The influence of substituents in the *meta* position was also investigated. Similar behavior of methyl and bromo substituents was observed (products **2t**,**u**). Notably, electron-withdrawing groups, such as acetyl, ester, and aldehyde groups, in the *meta* position were compatible and resulted in good yields (products **2v**–**x**) after a longer reaction time. Meanwhile, the presence of a strongly electron withdrawing group, such as a cyano group, at this position led to an acceptable yield (product **2y**). Such electron-withdrawing groups in the *para* or *ortho* position resulted in very low yields. The migration of aryl rings with two substituents, such as two methyl groups, in *meta* or *ortho* positions occurred in high yields (products **2B**,**C**).

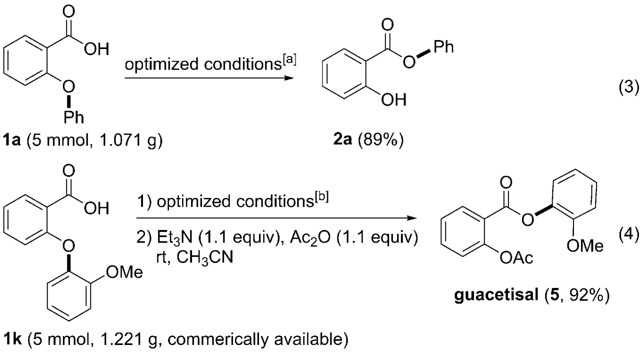
Table 1: Scope of the reaction.[a]



[a] Reaction conditions: **1** (0.20 mmol), PDI (1.0 mol %), K_2HPO_4 (10 mol %), CH_3CN (1.0 mL), irradiation with blue LEDs for 26 h at room temperature under an Ar atmosphere. Yields are for the isolated product. [b] Irradiation for 48 h. [c] Acr$^+$-Mes ClO_4^- was used instead of PDI, and the reaction mixture was irradiated for 26 h with blue LEDs.

Next, the influence of substituents on the other aryl ring was investigated. Methyl, bromo, aldehyde, and trifluoromethyl groups in the *para* position of the aryl ether enabled the transformation to proceed in good to excellent yields (products **2D**–**G**). An *ortho* methyl group on the aryl ether led to an efficient transformation (product **2H**). A bromo group *ortho* to the carboxylic acid and *meta* to the ether oxygen substituent resulted in a moderate yield (product **2I**). Electron-donating and electron-withdrawing groups *meta* to the aryl ether group and *para* to the carboxylic acid were studied. Methyl, chloro, fluoro, trifluoromethyl, and acetal groups were well tolerated (products **2K**, **2M**–**O**, **2Q**). Methoxy, bromo, and phenyl groups resulted in lower yields (**2J**,**L**,**O**), perhaps as a result of coordination effects or solubility. Notably, Acr$^+$-Mes ClO_4^- could act as a complementary photosensitizer to PDI. When Acr$^+$-Mes ClO_4^- was used as the photosensitizer, substrates with methoxy and bromo substituents were transformed in distinctly higher reaction yields (products **2b**,**u**,**J**) and iodine was well tolerated (product **2p**). Furthermore, when more strongly electron withdrawing groups, such as aldehyde, cyano, trifluoromethyl, and nitro groups, were present on the migrating aryl ring, the use of Acr$^+$-Mes ClO_4^- led to significantly higher reaction efficiency or good tolerance (products **2x**–**A**).

Notably, when the reaction was carried out on a gram scale, the excellent yield of **2a** was maintained [Scheme 3, Eq. (3)]. Owing to the importance of C–O bond cleavage, we conducted a one-pot, two-step reaction to cleave the C–O bond of the biaryl ether [Scheme 1, Eq. (2)]. To our delight, **3** and **4** were obtained in excellent yields (91 and 86%, respectively) from a gram-scale reaction of **1a**. Thus, a novel approach to C–O cleavage to give two phenolic compounds was realized under mild conditions. This transformation provides an alternative approach to C–O bond cleavage in biaryl ethers to the generation of a phenolic product and an aryl product by hydrogenation.[7j,k,n] Furthermore, this approach might inspire visible-light photoredox-catalyzed C–O bond cleavage of general aryl ethers by aryl *ipso*-substitution via aryl carboxylic radicals.[12] Moreover, to demonstrate the potential application of this aryl migration, we carried out a gram-scale reaction of commercially available **1k** and obtained guacetisal (**5**), a drug used to treat inflammatory respiratory diseases,[13] in 92% yield in a one-pot, two-step reaction [Scheme 3, Eq. (4)]. As compared with conventional methods,[13b] toxic reagents, such as $SOCl_2$ and $POCl_3$, and intermediate purification are avoided. 2-(Phenylthio)benzoic acid, 2-(phenylamino)benzoic acid, and 2-(methyl(phenyl)amino)benzoic acid were also investigated as starting materials; however, no conversion was observed.



Scheme 3. Gram-scale aryl migration and subsequent transformation. [a] With PDI as the photosensitizer for 32 h. [b] With Acr$^+$-Mes ClO_4^- as the photosensitizer for 11 h.

We conducted a series of experiments under the optimized reaction conditions with PDI as the photosensitizer to provide insight into the reaction mechanism. First, we confirmed that only PDI can act as a photosensitizer from the UV/Vis absorption spectrum of PDI and **1a** (see Figure S1 in the Supporting Information). Second, when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or 2,6-di-*tert*-butyl-4-methylphenol (BHT) was added as a radical scavenger to the reaction mixture, **2a** was obtained in less than 5% yield (see Scheme S1 in the Supporting Information). Meanwhile, the profile of the reaction yield was monitored with the light turned on and off at intervals, and we found that the transformation occurred smoothly under irradiation with blue LEDs and that further conversion stopped in the absence of a visible-light source (Figure 1a). Moreover, the formation of a carboxylic radical is suggested by EPR studies on benzoic acid under the optimized conditions (see Figures S2 and S3). Furthermore, a quantum yield value[9c,14] of $\phi = 0.24$ was determined (see the Supporting Information). Thus, a conclusion could not be reached as to whether the reaction proceeds through a photoredox catalytic pathway or a radical chain pathway at this stage.

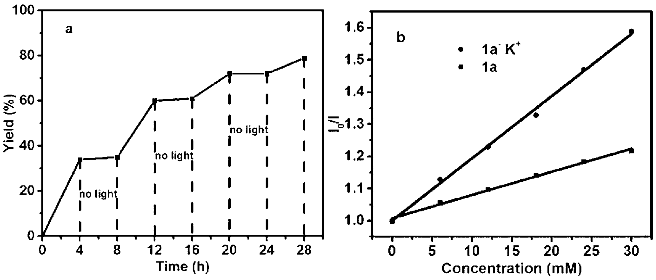
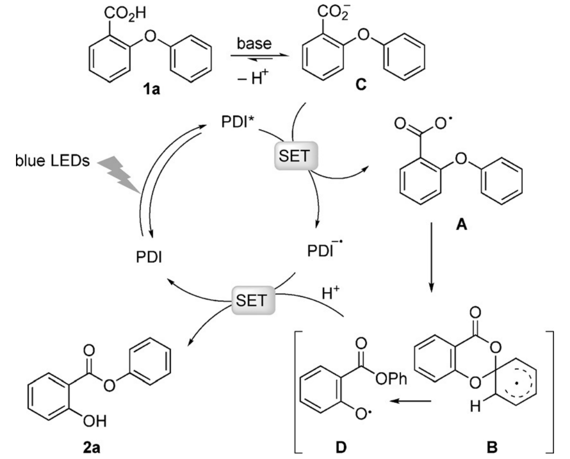


Figure 1. [a] Profile of the formation of **2a** with the light turned on or off at regular intervals. Yields were determined by ^1H NMR spectroscopy with $Cl_2CHCHCl_2$ as an internal standard. [b] Emission-quenching experiments of **1a** and **1a-K**$^+$.

The quenching of the excited state PDI* by the acid or the acid anion was conducted in MeOH because the potassium salt of **1a** has good solubility in MeOH. The results revealed that both **1a** and the anion of **1a** could quench PDI* (Figure 1b; see Figures S5–S7). However, the quenching rate constant of the anion of **1a** is much larger than the rate itself. We deduced that the carboxylate anion, but not **1a**, quenches the PDI*.[9] The quenching of PDI* by **1a** could be attributed to the lower concentration of the **1a** anion produced in MeOH.

The thermodynamic feasibility of the photoinduced electron transfer was analyzed on the basis of the oxidation–reduction potentials. The oxidation potential of $E^{PhOPhCO_2^\bullet/PhOPhCO_2^-}$ and the reduction potential of $E^{PDI/PDI^{-\bullet}}$ in CH_3CN were determined as +1.90 V vs. SCE (see Figure S10) and −0.49 V vs. SCE (see Figure S11), respectively. The excited-state energy E_{00}[15] of PDI was read from the cross-point of the absorption and luminescence spectra at 526 nm (see Figure S8) as 2.36 eV. Therefore, the reduction potential of $E^{PDI*/PDI^{-\bullet}}$ was calculated as +1.87 V vs. SCE ($E^{PDI*/PDI^{-\bullet}} = E^{PDI/PDI^{-\bullet}} + E_{00}$) in CH_3CN, and thus displayed a slight difference to $E^{PDI*/PDI^{-\bullet}} = +1.92$ vs. SCE in DMF.[8i,16] This reduction potential indicates the possibility of the formation of $PDI^{-\bullet}$ and the carboxylic acid radical by single-electron transfer (SET) between PDI* and the carboxylic acid anion.[17]

On the basis of the results described above, we propose the following reaction mechanism (Scheme 4): Initially, irradiation of PDI with blue LEDs leads to the formation of the excited state PDI* as a strong oxidant ($E^{PDI*/PDI^{-\bullet}} =$



Scheme 4. Proposed reaction mechanism.

+1.87 V vs. SCE in CH$_3$CN). PDI* is reductively quenched by the carboxylate anion **C** ($E^{\mathrm{PhOPhCO_2^{\bullet}/PhOPhCO_2^-}} = +1.90$ V vs. SCE in CH$_3$CN), derived from the acid in the presence of a catalytic amount of base, to give PDI$^{-\bullet}$ and the carboxylate radical **A**,[9] which is then transformed into intermediate **B**.[3,12] In the presence of the proton generated from the first step, SET between **B**, or intermediate **D** generated from **B**, and PDI$^{-\bullet}$ affords **2a** and regenerates PDI. On the basis of the efficient transformation with Acr$^+$-Mes ClO$_4^-$ as the photosensitizer and the similar oxidative potentials of $E^{\mathrm{PDI/PDI^{-\bullet}}}$ (−0.49 V vs. SCE) and $E^{\mathrm{Acr^{+}\text{-}Mes\,ClO_4/Acr^{\bullet}\text{-}Mes\,ClO_4}}$ (−0.57 V vs. SCE),[8i,18] it is deduced that the reductive ability of PDI$^{-\bullet}$ is sufficient to lead to SET with **B** or **D** with a proton. Thus, the excitation of PDI$^{-\bullet}$ to PDI$^{*-\bullet}$ is not necessary for the catalytic cycle.[19]

In summary, we have developed a highly efficient aryl migration from an aryl ether to a carboxyl group through visible-light photoredox catalysis in a transformation which can be understood as a retro-Smiles rearrangement. Transition metals and stoichiometric amounts of an oxidant and base are avoided in the transformation. Inspired by the high efficiency of this aryl migration and the fundamental importance of C–O bond cleavage, we demonstrated a novel approach to C–O cleavage into two phenolic compounds by a highly efficient one-pot, two-step reaction under mild conditions. This approach might inspire visible-light photoredox-catalyzed C–O bond cleavage of general aryl ethers by aromatic *ipso*-substitution via aryl carboxylic radicals. The aryl migration exhibits wide substrate scope and can be applied to pharmaceutical synthesis.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aryl migration · C–O bond cleavage · retro-Smiles rearrangement · synthetic methods · visible-light photocatalysis

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