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Photoinduced transition-metal- and external-photosensitizer-free intramolecular aryl rearrangement *via* C(Ar)–O bond cleavage†

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The use of photochemical reactions that do not require expensive photocatalysts or transition metals is an environmentally friendly strategy for accomplishing a variety of structural transformations. Herein, we report a protocol for photoinduced transition-metal- and external-photosensitizer-free intramolecular heteroaryl/aryl rearrangement reactions of 2-heteroaryl/aryloxybenzaldehydes. The protocol was compatible with a variety of functionalities, including methyl, methoxy, cyano, ester, trifluoromethyl, halogen, and heteroaromatic rings. Control experiments suggested that the reaction proceeded *via* a photoinduced intramolecular heteroaryl/aryl rearrangement process involving photoexcitation of the aldehyde carbonyl group, radical addition, C–C bond formation and C(Ar)–O bond cleavage.

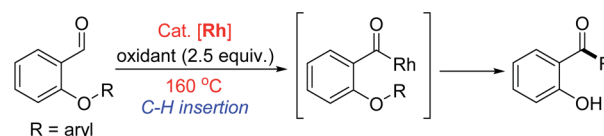
Introduction

Catalytic cleavage of C(Ar)–O bonds is among the most promising methods for degradation and transformation of renewable naturally occurring aromatic resources such as lignins,¹ which can thus serve as sustainable alternatives to aromatic halides. For example, transition-metal-catalyzed cross-coupling reactions involving C(Ar)–O bond cleavage have become a powerful tool for modification of the functional groups of aromatic compounds.² In particular, reactions involving transition-metal-catalyzed activation of the C(Ar)–O bonds of phenol derivatives (*e.g.*, sulfonates,³ esters,⁴ and carbamates⁵) have been extensively explored. However, compared with these phenol derivatives, aryl ethers are more readily available (owing to their presence in naturally occurring, renewable lignins), and their use allows for more step-economical cross-coupling reactions.⁶ Considerable progress has been made in developing methods for the coupling of aromatic alkyl ethers with various nucleophiles by means of direct transition-metal-catalyzed activation of C(Ar)–O bonds. Notably, *ortho* functional groups with chelating ability can facilitate C(Ar)–OMe bond cleavage and eliminate the need for an external ligand bearing a directing group.⁷ This strategy was recently used to accomplish the challenging task of cleaving the 4-O-5 linkage of a lignin model compound, despite the fact that this diaryl ether C(Ar)–O bond

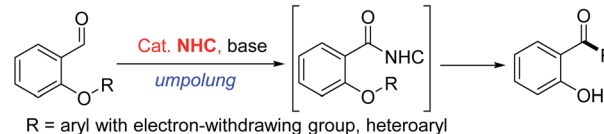
has a high dissociation energy and good stability.⁸ In addition, we reported the Pd/C-catalyzed conversion of diaryl ethers to amines *via* a process involving C(Ar)–O bond cleavage and C–N bond formation.⁹

Recently, *ortho*-functional group assisted cleavages of the C(Ar)–O bond of diaryl ethers *via* an intramolecular rearrangement have been reported. For example, Rao and Li developed a rhodium-catalyzed rearrangement of 2-aryloxybenzaldehydes involving cleavage of the C(Ar)–O bond of a diaryl ether, aldehyde C–H bond insertion, and an intramolecular chelation-

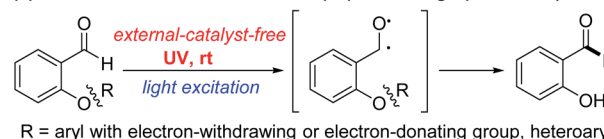
(a) Rh-catalyzed intramolecular C(Ar)–O cleavage



(b) NHC-catalyzed intramolecular C(Ar)–O cleavage



(c) Photo-induced intramolecular C(Ar)–O cleavage (This work)



■ Transition-metal- and photocatalyst-free ■ C(Ar)–O cleavage
■ Photo-induced arrangement ■ Broad substrate scope

Scheme 1 Strategies for the cleavage of the C(Ar)–O bonds of diaryl ethers.

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Table 1 Evaluation of reaction conditions^a

Entry	Additive	Solvent	Yield of 2a ^b /[%]
1	TFA	CH ₃ CN	23
2	TFA	DCE	29
3	TFA	H ₂ O	Trace
4	TFA	EtOAc	76
5	TfOH	EtOAc	n.p.
6	HCl	EtOAc	10
7	H ₂ SO ₄	EtOAc	14
8 ^c	TFA	EtOAc	90 (83 ^d)
9 ^e	TFA	EtOAc	85
10 ^c	Zn(OTf) ₂	EtOAc	28
11 ^c	Sc(OTf) ₃	EtOAc	9
12 ^c	In(OTf) ₃	EtOAc	6
13 ^c	Yb(OTf) ₃	EtOAc	78
14 ^{c,f}	TFA	EtOAc	13
15 ^{c,g}	TFA	EtOAc	19
16 ^{c,h}	TFA	EtOAc	n.r.
17 ^{c,i}	—	EtOAc	15

^a General conditions: **1a** (0.2 mmol) and the additive (1.0 equiv.) in the solvent (1.0 mL) was irradiated at 254 nm for 24 h at room temperature under argon. ^b Yields were determined by ¹H NMR spectroscopy using nitromethane as an internal standard; n.r. = no reaction. ^c EtOAc (2.0 mL). ^d Isolated yield. ^e EtOAc (4.0 mL). ^f 405 nm. ^g 385 nm. ^h In the dark. ⁱ No additive.

assisted S_NAr process in the presence of a stoichiometric oxidant at high temperature¹⁰ (Scheme 1a). Recently, the Glorius's group reported a N-heterocyclic carbene-catalyzed intramolecular arylation reactions of aldehyde C–H bonds involving cleavage of the C–O bonds of diaryl ethers (Scheme 1b).¹¹ However, in these reactions, the migrating groups are limited to heteroaryl or aryl rings bearing electron-withdrawing groups.

Progress in photochemistry research has led to the development of methods for photoinduced transition-metal- and photosensitizer-free functionalization of C(Ar)–O bonds,¹² which results in the formation of new C–C, C–N, C–P, and C–B bonds. Herein, we report that photoexcitation of the aldehyde carbonyl group of 2-aryl/heteroaryloxybenzaldehydes under transition-metal- and external-photosensitizer-free conditions generates C–O diradicals that undergo C(Ar)–O bond cleavage via an intramolecular Minisci¹³-rearrangement process (Scheme 1c).

Results and discussion

For our preliminary studies, we selected 2-(pyridin-2-yl)benzaldehyde (**1a**) as a model substrate. Its UV-vis absorption spectrum indicated that the wavelength of its absorption maximum was approximately 254 nm (see ESI†), which was thus chosen as the excitation wavelength. To our delight, when an acetonitrile solution of **1a** containing trifluoroacetic acid (TFA)

as a proton source was UV-irradiated (254 nm) at room temperature, C(Ar)–O bond cleavage and rearrangement product **2a** was detected (23% yield; Table 1, entry 1). The effects

Table 2 Substrate scope of the photoinduced heteroaryl group rearrangement reaction^a

 2a, 83%	 2b, 81%	 2c, 71% ^b
 2d, 90%	 2e, 96%	 2f, 57%
 2g, 80%	 2h, 72%	 2i, 67%
 2j, 47%	 2k, 57% ^c	 2l, 81% ^c
 2m, 76%	 2n, 85%	 2o, 51% ^d
 2p, 78%	 2q, 82%	 2r, 79%
 2s, 95%	 2t, 89%	 2u, 68%
 2v, 54%	 2w, 93%	 2x, R = 1-isoquinolinyl, 0% 2y, R = 2-quinolinyl, 0%

^a Reaction conditions: **1** (0.2 mmol) and TFA (0.2 mmol) in EtOAc (2 mL) was irradiated at 254 nm for 24 h at room temperature under argon; isolated yields are provided. ^b Yb(OTf)₃ (0.1 mmol) was used instead of TFA. ^c No Additive. ^d 48 h.



of varying the solvent were subsequently investigated (entries 1–4), and EtOAc was found to give the best yield of the rearrangement product (76%, entry 4). We also explored different proton sources (TfOH, HCl, and H₂SO₄), all of which gave lower yields than TFA (entries 5–7). Decreasing the concentration of **1a** to 0.1 M increased the yield to 90% (entry 8), but further dilution slightly lowered the yield (85%, entry 9). When TFA was replaced with one equivalent of a Lewis acid (Sc(OTf)₃, Zn(OTf)₂, In(OTf)₃, or Yb(OTf)₃), **2a** was still obtained, albeit in a lower yield (6–78%, entries 10–13). Using a different irradiation wavelength (405 or 385 nm) gave an inferior yield (entries 14 and 15), and control experiments revealed that both light and the additive were essential for the rearrangement (entries 16 and 17).

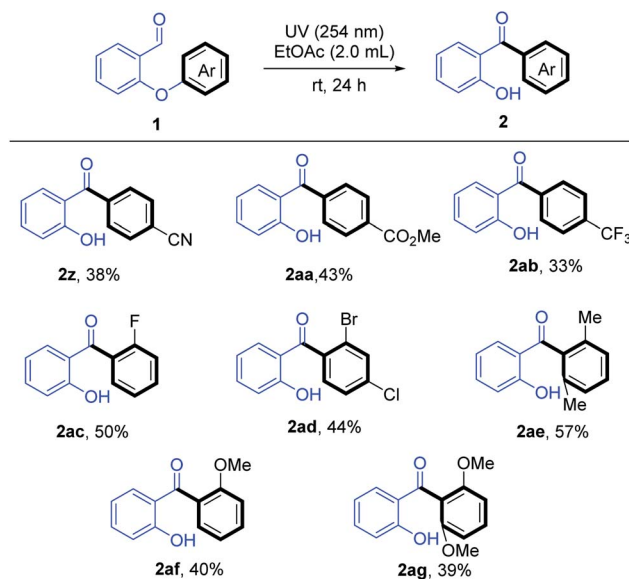
We explored the substrate scope of this rearrangement (Table 2) under the optimized reaction conditions (Table 1, entry 8). Firstly, various substituents on the migrating heteroaryl ring were investigated. Substrates with pyridine rings bearing an electron-donating group such as methoxy or methyl provided up to 96% yields of the desired rearrangement products (**2b–2f**). Interestingly, substrates containing a halogen atom (F, Cl, or Br) successfully underwent the reaction upon UV irradiation, giving moderate to high yields of products with their photosensitive C–halogen bonds¹⁴ intact (**2g–2i**). The rearrangement also proceeded smoothly when the pyridine ring bore a strongly electron-withdrawing trifluoromethyl group, giving **2j** in moderate yield. In addition to pyridine, we tested substrates with a benzothiazole and a pyrazine ring, which smoothly afforded products **2k** and **2l**, respectively, even in the absence of TFA.

Next we elucidated the effects of substituents on the salicylaldehyde portion of the substrate. Both electron-donating and electron-withdrawing substituents (methyl, methoxy, and halide) were tolerated; and the products **2m–2r** were obtained in 51–85% yields. In addition, we assessed substrates with a substituent on both the heteroaryl ring and the salicylaldehyde moiety and found that such compounds were suitable for the rearrangement, providing the products (**2s–2w**) with good yields (54–95%). However, no products (**2x** and **2y**) were detected and the starting materials were recovered when 1-isquinolinyl and 2-quinolinyl were used as the migrating groups, possibly due to the fact that the fused-ring has a stronger absorption of the light than the carbonyl group and inhibits the reaction.

We also explored the use of substrates bearing various substituted aryl groups (Table 3). To our delight, we found that in the absence of TFA, the substrates underwent the desired C(Ar)–O bond cleavage/rearrangement in EtOAc upon irradiation at 254 nm. A variety of functional groups were tolerated: including electron-withdrawing ester, cyano, trifluoromethyl, fluoro, chloro, and bromo, and electron-donating methoxy and methyl groups (**2z–2ag**). Interestingly, even substrates that had substituents at both of the *ortho* positions of the migrating ring afforded the desired rearranged products (**2ae** and **2ag**), despite such substrates being sterically hindered.

To gain insight into the mechanism of this photoinduced intramolecular heteroaryl/aryl rearrangement, we carried out

Table 3 Substrate scope of the photoinduced aryl group rearrangement reaction^a



^a Reaction conditions: **1** (0.2 mmol) in EtOAc (2.0 mL) was irradiated at 254 nm for 24 h at room temperature under argon; isolated yields are provided.

a series of control experiments. First, we determined the effect of periodically turning the light on and off on the time course of the yield of product **2a** (Fig. 1a). We observed that the reaction proceeded smoothly when the light was on and that there was no increase in the product yield during periods when light was off. These results demonstrated that the UV light was necessary. In addition, we monitored the time course of the amounts of **1a** and **2a** (Fig. 1b) and found that the yield of **2a** reached 80% after only 4 h of reaction time, after which point the reaction rate decreased. Kinetic isotope effect experiments ($K_H/K_D = 1.2$) carried out under the standard conditions (Scheme 2a) suggested that the C–H cleavage of the aldehyde is not involved in the rate-limiting step. This finding also indicated that an aryl formyl free radical of aldehyde **1** was unlikely to have been generated. Moreover, we found that the model reaction was suppressed only

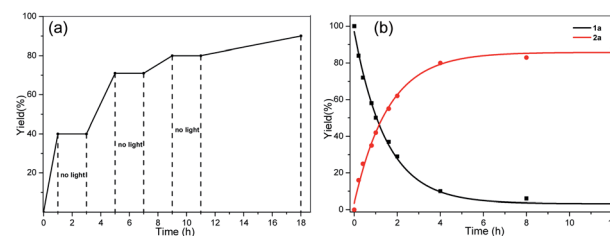
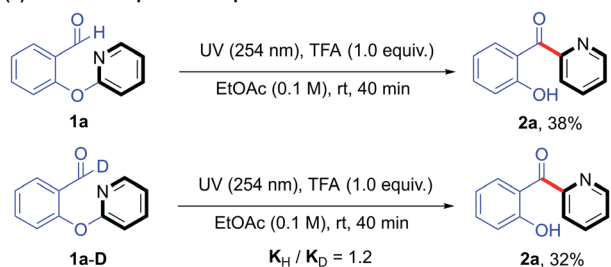


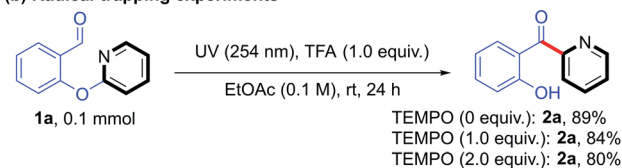
Fig. 1 (a) Time course of the yield of **2a** for a reaction of **1a** during which the light was periodically turned on and off. (b) Time course of the yield of **2a** and consumption of **1a** during a reaction under the standard conditions.



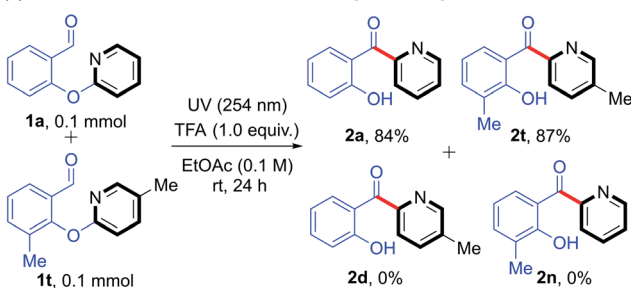
(a) Kinetic isotope effect experiments



(b) Radical-trapping experiments



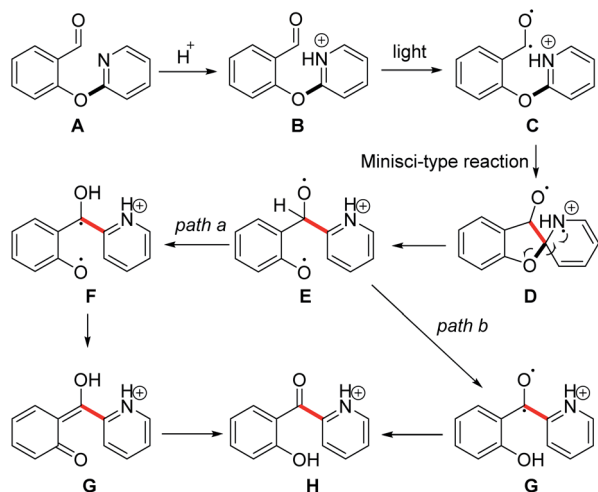
(c) Intramolecular and intermolecular competitive experiment



Scheme 2 Mechanistic studies.

slightly when a radical inhibitor (2,2,6,6-tetramethyl-1-piperidinyloxy) was added, implying that the rearrangement did not involve an intermolecular free-radical process (Scheme 2b). Finally, no cross-rearrangement products were detected when a mixture of **1a** and **1t** was subjected to the standard conditions (Scheme 2c), confirming that the photoinduced rearrangement was an intramolecular process.

On the basis of the above-described control experiments, a plausible mechanism for this photoinduced rearrangement is



Scheme 3 The plausible mechanism.

proposed in Scheme 3. Substrate **A** reacts with acid to form organic salt **B**. Photoirradiation generates diradical **C**, and subsequent intramolecular attack of the carbon radical on the pyridine ring generates cation radical **D** via a Minisci-type reaction. Rearomatization of **D** accompanied by homolytic cleavage of the C–O bond forms diradical **E**. Further transformation can proceed by one of two paths. In path a, abstraction of a hydrogen radical from the benzyl position by one of the oxygen radicals generates diradical **F**, which tautomerizes to form *ortho*-quinone **G**. Tautomerization of **G** generates intermediate **H**, which affords neutral product **2a** upon workup. Alternatively, in path b, a hydrogen radical is abstracted from the benzyl position of **E** by the other oxygen radical to generate diradical **G**, which then forms intermediate **H**.

Conclusions

In summary, we have developed a photoinduced aldehyde-mediated rearrangement reaction that involves C(Ar)–O bond cleavage and C–C bond formation. This efficient protocol affords rapid access to 2-hydroxybenzophenone derivatives under transition-metal- and external-photosensitizer-free conditions at room temperature and is thus environmentally friendly. The protocol is compatible with a variety of functional groups and is suitable for substrates bearing heteroaryl and electron-deficient or -rich aryl migrating groups. Mechanistic studies confirmed that the reaction proceeds by means of an intramolecular rearrangement.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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