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Photoinduced Aerobic Iodoarene-Catalyzed Spirocyclization of *N*-Oxy-Amides to *N*-Fused Spirolactams

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In memory of Professor Kilian Muñiz (1970–2020)

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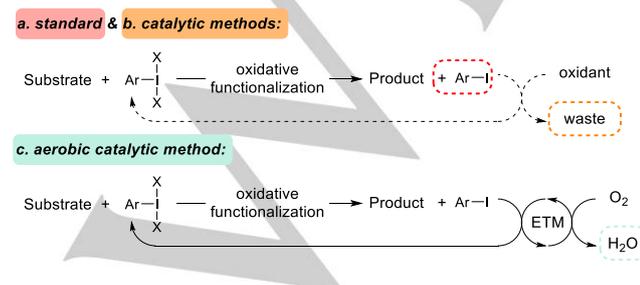
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Abstract: Iodoarene catalysis is a powerful methodology that usually requires an excess of oxidant, or of redox mediator if the terminal oxidant is dioxygen, to generate the key hypervalent iodine intermediate to proceed efficiently. We report that, using the spirocyclization of amides as a benchmark reaction, aerobic iodoarene catalysis can be enabled by relying on a pyrylium photocatalyst under blue light irradiation. This unprecedented dual organocatalytic system allows the use of low catalytic loading of both catalysts under very mild operating conditions.

Hypervalent iodine(III) compounds have been known for 130 years,^[1] yet interest in their reactivity was very modest until the 80's, before witnessing a dramatic surge in the 2000's.^[2–4] They possess many advantages in terms of versatility, high selectivity and lack of toxicity; however, their use as a stoichiometric reagent remains a drawback. Indeed, the driving force behind their reactivity is the final release of one equivalent of iodoarene (Scheme 1a), such as iodobenzene. The liberation of a stoichiometric amount of organic waste is in total contradiction with the need for greener and more responsible processes. In order to circumvent these hurdles, the more general and sought after strategy is based on the in situ re-oxidation of the iodoarene into a reactive iodine(III) species. This approach, pioneered by Ochiai & Miyamoto^[5] and by Kita^[6] in 2005, *de facto* establishes iodoarenes as a particular subclass of organocatalysts,^[7–9] with many synthetic applications, including asymmetric versions.^[10,11]

Apart from anodic oxidation, which, more than 20 years after the pioneering studies by Fujita,^[12] currently receives increasing attention,^[13–19] iodoarene catalysis requires the use of a stoichiometric oxidant,^[8] thus generating an equimolar quantity of inorganic or organic waste (Scheme 1b). A more desirable alternative is the use of molecular oxygen as a widely available and cheap stoichiometric oxidant that would only generate aqueous waste (Scheme 1c). Since the single electron oxidation potential of iodobenzene is much higher (half peak potential: $E_{p/2} = 2.17$ V vs SCE)^[20] than the reduction potential of oxygen (-0.33 V vs SHE, for single electron reduction at pH = 7),^[21] resorting to an electron-transfer mediator^[22] (ETM) is mandatory. This strategy was eventually implemented in 2017 by Miyamoto & Uchiyama^[23] and Powers^[24] who independently reported the first examples of aerobic oxidation of iodoarenes. Both approaches are based on the formation of a suitable oxidant during the O₂-mediated autoxidation of aldehydes,^[25–27] although the protocols slightly differ. The Miyamoto-Uchiyama protocol requires a sterically hindered aldehyde and was applied to the glycol scission of 1,2-diols and the Hofmann rearrangement of primary amides with only 3 to 5 equivalents of *iso*-butyraldehyde and 5 to 20 mol% of pentamethyliodobenzene.^[23] Powers' method, which was further refined for the formation of iodine(V) reagents,^[28] uses 10 equivalents of acetaldehyde and 1 mol% of CoCl₂ as the initiator to promote the synthesis of (diacetoxy)iodoarenes from the corresponding aryl iodides in acetic acid. This system was named "oxidase catalysis" by the authors.^[29] Five distinct examples of catalytic applications were presented, necessitating between 10 to 20 mol% of diiodobenzene and one equivalent of iodobenzene to work efficiently. Despite the spectacular improvement that these aerobic strategies bring to iodoarene catalysis, yet they still require a rather large excess of aldehyde and, in some cases, even a stoichiometric amount of the iodobenzene catalyst.

With the goal of developing an aerobic system that would only require a substoichiometric amount of the O₂-mediator we sought to employ a visible-light photoredox catalyst to reoxidize the iodoarene into an iodine(III) derivative. Since the 2011 study by Lalevée on the use of a ruthenium photocatalyst with a diphenyliodonium to form phenyl radicals,^[30] the interplay



Scheme 1. Stoichiometric iodoarene oxidative transformation (a), iodoarene catalysis (b) and aerobic iodoarene catalysis (c).

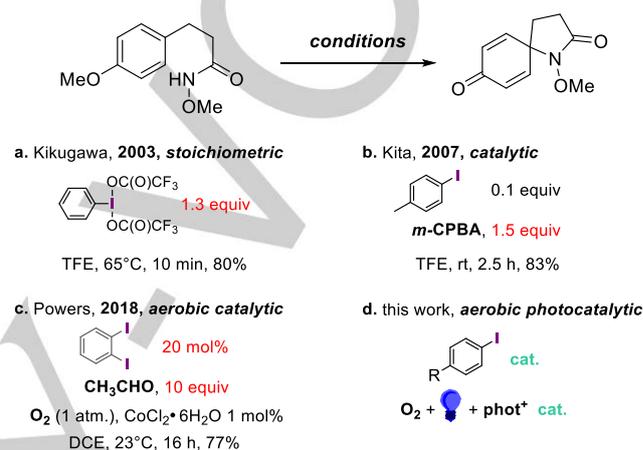
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between visible-light photoredox catalysis and hypervalent iodine(III) derivatives has been increasingly studied.^[31] However, all these studies rely on the reduction of iodine(III) reagents to give an aryl iodide by-product while there is no report of a photoredox oxidation of an iodoarene into an iodine(III) derivative. The oxidation potential of aryl iodides being quite high,^[20] it precludes the use of most Ru- and Ir-based complexes^[32] in favor of organic dyes^[33–35] such as acridinium (Fukuzumi's catalyst Acr⁺) or pyrylium (pyr⁺) salts.

To explore this dual (iodoarene/photocatalyst) catalytic system, the spirocyclization of amides into *N*-fused spiroactams was chosen as a benchmark reaction. After their initial work on the generation of nitrenium ions from chloramides,^[36] this transformation was then developed by Kikugawa in 2003 using a stoichiometric amount bis(trifluoroacetoxy)iodo]benzene (PIFA) in trifluoroethanol (TFE) (Scheme 2a).^[37] This reaction was later reported using anodically generated iodine(III) by Nishiyama.^[38] In 2007, Kita described a catalytic version, using 10 mol% of iodotoluene in the presence of 1.5 equivalents of *m*-CPBA (Scheme 2b)^[39] while Togo used Oxone.^[40] Kita later refined this method using 2 mol% of a diiodobiaryl with 2 equivalents of peracetic acid.^[41] Finally, this reaction was one of the examples that Powers^[24] implemented in an aerobic fashion with 20 mol% of diiodobenzene and 10 equivalents of acetaldehyde (Scheme 2c). For our part, we set to establish the feasibility of this transformation under aerobic conditions with an iodoarene catalyst, which would be oxidized using an organic photocatalyst (phot⁺) under irradiation (Scheme 2d).

The reaction was first studied with *N*-Methoxy amide **1a** as the starting material using a high catalyst loading of iodobenzene (50 mol%) in the presence of 2.5 mol% of 2,4,6-triphenylpyrylium tetrafluoroborate (TPT, $E_{1/2} P^*/P^* = 2.30$ V vs. SCE)^[42] as the photocatalyst, under one atmosphere of dioxygen and irradiation

at 455 nm (Table 1). The influence of the solvent was dramatic as no reaction was observed in dichloroethane (DCE) or acetonitrile, while trifluoroethanol (TFE) and hexafluoroisopropanol (HFIP) enabled the formation of the desired spiro-adduct in 10% and 18%, respectively. Doubling or tripling the reaction time allowed to double the yield to 37%. As the TPT catalyst is known for its poor photo-stability, we used the more robust and more oxidizing mesityl-2,6-diphenylpyrylium tetrafluoroborate (MDPT, $E_{1/2} P^*/P^* = 2.62$ V vs. SCE) recently developed by Beeler.^[43] This led to a slight improvement of the yield to 43%. On the contrary, the use of 9-mesityl-10-phenylacridinium tetrafluoroborate (Ph-Acr, $E_{1/2} P^*/P^* = 2.20$ V vs. SCE)^[44] did not permit the reaction to proceed.



Scheme 2. Spirocyclization of amides to *N*-fused spiroactams using a stoichiometric iodine(III) reagent (a), iodoarene catalysis (b), aerobic iodoarene catalysis (c) and dual aerobic photo- and iodoarene catalysis (d, this work).

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

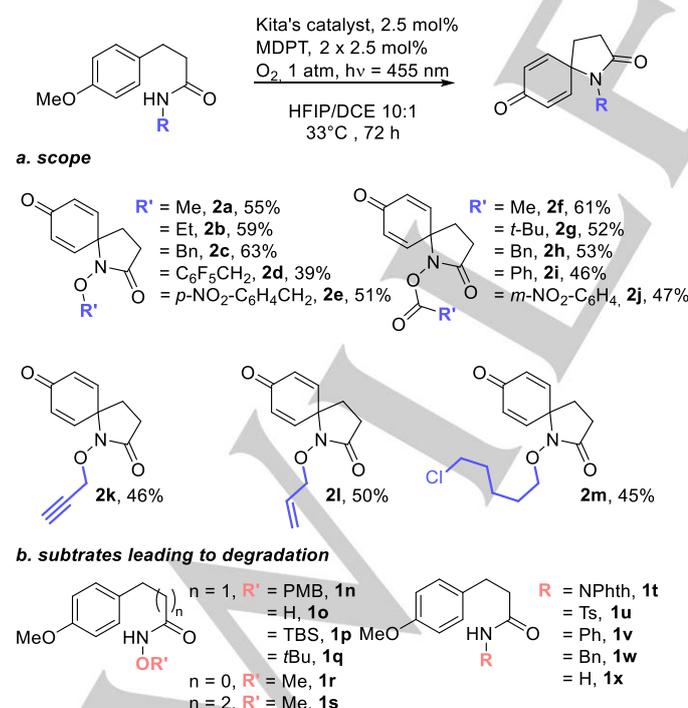
Reaction Conditions		iodoarene	photocatalyst	Yield 2 (%) ^[b]	
Iodoarene (mol%)	Photocatalyst (mol%)	Solvent	Time (h)	Yield 2 (%) ^[b]	
PhI (50)	TPT (2.5)	DCE	24	N. R. ^[c]	
PhI (50)	TPT (2.5)	MeCN	24	N. R.	
PhI (50)	TPT (2.5)	TFE	24	10	
PhI (50)	TPT (2.5)	HFIP	24	18	
PhI (50)	TPT (2.5)	HFIP	48	37	
PhI (50)	TPT (2.5)	HFIP	72	37	
PhI (50)	MDPT (2.5)	HFIP	72	43	
PhI (50)	Ph-Acr (5.0)	HFIP	72	N. R.	
PhI (50)	MDPT (2.5 x 2) ^[d]	HFIP	72	49	
IBA (20)	MDPT (2.5 x 2) ^[d]	HFIP	48	58	
1,2-DIB (50)	MDPT (2.5 x 2) ^[d]	HFIP	48	46	
Kita (20)	MDPT (2.5 x 2) ^[d]	HFIP/DCE 10:1	72	52	
Kita (2.5)	MDPT (2.5 x 2)^[d]	HFIP/DCE 10:1	72	55	

[a] All reactions were carried out with 0.28 mmol of **1a**, stirred in 1.5 mL of solvent under 455 nm irradiation. [b] isolated yields. [c] no reaction. [d] The reaction was started with 2.5 mol% of catalyst, another 2.5 mol% was added after half the reaction time.

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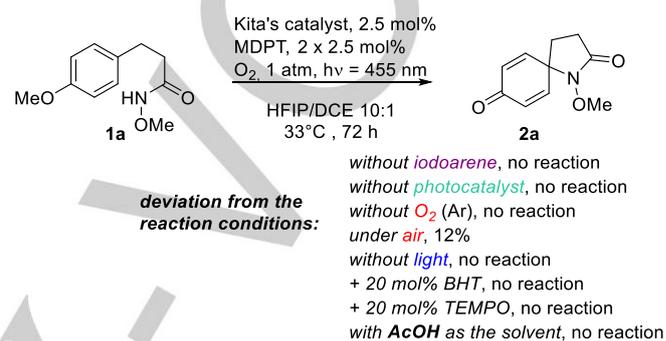
To favor the oxidation of the iodoarene, derivatives bearing a substituent in *ortho* were then assayed. Using 20 mol% of iodobenzoic acid (IBA), which could lead to a transient benziodoxole intermediate,^[45–47] spiro adduct **2a** could be isolated with a 58% yield. 1,2-Diiodobenzene, that can form μ -oxo intermediates,^[48] was less effective and a 46% yield was obtained. Finally, Kita's bis iodoarene catalyst^[41] was employed (DCE was added to HFIP to increase its solubility) and a 55% yield could be obtained with a catalyst loading of only 2.5 mol%. Being almost as efficient as with 20 mol% of IBA, these conditions were selected as optimal since only 2.5 mol% of the iodoarene catalyst and 5 mol% of the photocatalyst are needed to promote the spirocyclization.

When the *N*-methoxy group was changed for an ethoxy, or a benzyloxy group the corresponding spiro-adducts **2b** and **2c** were obtained with 59% and 63% yield, respectively (Scheme 3a). While electron-rich groups were not suitable for the reaction (*vide infra*), electron-poor benzyloxy groups such as pentafluorobenzyl and *para*-nitrobenzyl groups were compatible and yielded **2d** (39%) and **2e** (51%). The spirocyclization also proceeded smoothly with various *N*-acyloxy amides, whether an acetate (**2f**, 61%), a pivalate (**2g**, 52%), a phenyl acetate (**2h**, 53%), a benzoate (**2i**, 46%) or a *meta*-nitrobenzoate (**2j**, 47%). More diversely substituted *N*-alkoxy derivatives also underwent the spirocyclization, including the propargyl and allyl derivatives (**2k**, 46% and **2l**, 50%) and the chloropentanyl compound (**2m**, 45%). Yet for several substrates the reaction only led to a complex mixture, although it could not be determined if it was due to a decomposition of the starting material, the final product or both (Scheme 3b). These included *N*-oxy derivatives with an electron-rich group (**1n**), a hydroxyl functionality (**1o**), a silyl group (**1p**) or a tertiary ether (**1q**). In contrast with what was observed by Kita,



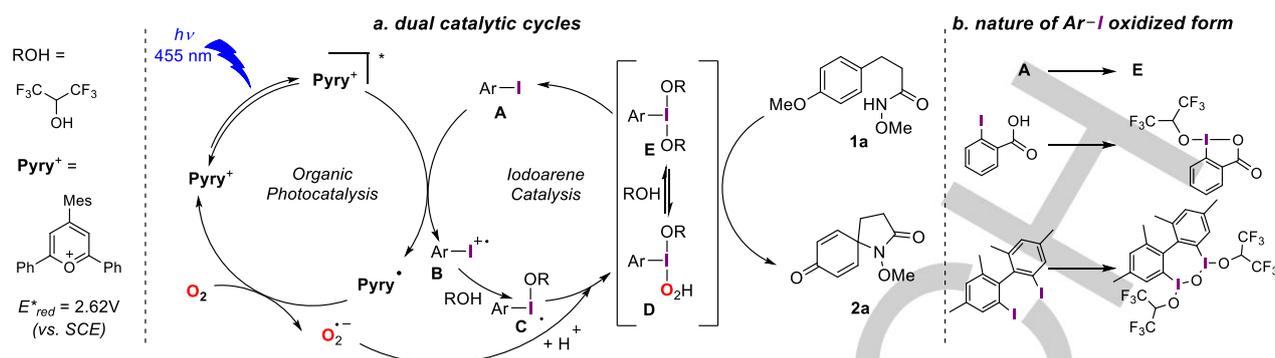
Scheme 3. Scope and limitations of the spirocyclization of amides to *N*-fused spiro lactams under photoinduced aerobic iodoarene catalysis.

substrates **1r** and **1s**, which would have furnished the 4-membered and 6-membered spiro derivatives, respectively, only led to decomposition. Other types of substituent that could help stabilize a putative radical intermediate on the nitrogen such as a phthalimide (**1t**),^[39,41] a tosyl (**1u**) or a phenyl (**1v**) were also ineffective, and so was an alkyl group (**1w**) or an unprotected amide (**1x**). Control experiments (Scheme 4) showed that the reaction did not proceed in the absence of either catalyst, oxygen or light, nor in the presence of 20 mol% of a radical quench such as BHT and TEMPO. When air was used instead of pure dioxygen, the reaction only yielded 12% of **2a**. Finally, acetic acid was used as a highly polar and protic solvent but no reaction took place.



Scheme 4. Control experiments.

These observations led us to propose a plausible mechanism based on a dual organocatalytic system (Scheme 5). Photoexcitation of the pyrylium **Pyry*** would generate the highly oxidizing **Pyry**** (E^*_{red} vs SCE = 2.62 V)^[43] that could promote the oxidation of iodoarene **A** into iodoaryl radical cation **B** and form **Pyry***. Oxidation of the latter into **Pyry*** by the dioxygen would close the photoredox catalytic cycle and generate the superoxide ion.^[49] Iodoaryl radical cation **B** has been proposed as an intermediate in the anodic generation of iodine(III) reagents^[19] and could serve as a precursor to iodonium radical **C**,^[27] upon reaction with the solvent. After combination with the superoxide and protonation peroxy-iodinane **D** could be formed. Eventually, full solvolysis could occur leading to iodane **E**.^[13,14] This spirocyclization has been proposed to occur through the initial formation of a nitrenium ion^[39] but a *N*-centered radical, stabilized by the alkoxy group,^[50] could also be operative. This means that all three species **C**, **D** and **E** could promote the transformation of **1** into **2**, by triggering the formation of a reactive nitrogen intermediate. In all cases, this would regenerate the starting iodoarene, thus closing the second catalytic cycle. Control experiments demonstrate that several factors are essential for this dual catalytic system to be operative. As evidenced by the absence of reactivity in non-fluorinated solvent, including the highly polar and protic AcOH, HFIP solvent is essential, a feature that has already been noted for electrochemical generation of iodine(III) species,^[17–19] presumably via multiple roles. First, its superior solvation properties for charged species^[51] such as arene radical cations generated in photoredox process,^[52] would favor the formation of **B** and **C**. Moreover, when apically bound to the iodine in λ^3 -iodanes **D** or **E**, its strong electron-withdrawing character would enhance the stabilization of the 3-center 4-electron hypervalent bond.^[53]



Scheme 5. Mechanistic proposal: (a) dual catalytic cycles and (b) putative structure of the solvolyzed Ar(I) species.

The stability of the can also be further enhanced by The substituents on the aryl group of A, can play a crucial role in the stabilization of the hypervalent iodine(III) reagents generated. From IBA, the formation of a cyclic benziodoxole would occur for both the peroxy- λ^3 -iodane D^[64] and HFIP-derived E (Scheme 5b). For Kita's bis iodoarene catalyst,^[41] the stabilization would come from the formation of μ -oxo species, here depicted for the fully solvolyzed adduct E.

Using the spiro-cyclization of amides as a model reaction, we have thus demonstrated that aerobic iodoarene catalysis can be enabled by relying on a pyrylium photocatalyst under blue light irradiation. This unprecedented dual organocatalytic system allows the use of low catalytic loading of both catalyst under very mild operating conditions. We are currently pursuing more thorough study of this dual catalyst system to gain a deeper understanding of the reaction pathway by experimental and theoretical methods, with a particular focus on determining the nature of the oxidized iodoarene species. This will allow to expand the range of transformations that can be accomplished using this strategy, including the development of asymmetric reactions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: hypervalent iodine • pyrylium • aerobic photoredox reaction • dual organocatalysis

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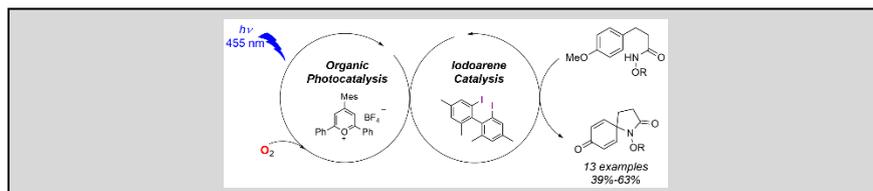
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