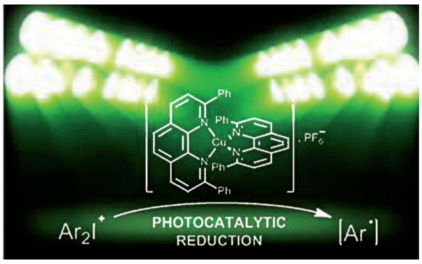
Photocatalyzed reduction of diaryliodonium salts was achieved by using $[Cu(dpp)_2][PF_6]$ as photoactive complex and DIPEA as reductive quench. The application of a copper catalyst allows the generation of aryl radicals under mild conditions and maintains their reactivity for C–C bond formation processes.



Diaryliodonium Salts

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Aryl Radical Formation by Copper(I) Photocatalyzed Reduction of Diaryliodonium Salts: NMR Evidence for a Cu^{II}/Cu^{I} Mechanism

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Aryl Radical Formation by Copper(I) Photocatalyzed Reduction of Diaryliodonium Salts: NMR Evidence for a Cu^{II}/Cu^{I} Mechanism

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Hypervalent iodine chemistry is currently a field of intense development.[1] Thanks to the variety of possible derivatives, iodonium salts have proven to be useful and versatile reagents in organic synthesis.[2] Whereas most investigations focus on electrophilic arylation and alkenylation, homolytic reduction of iodonium salts has rarely been examined. Such transformations have typically been accomplished either by electrochemical or photochemical methods or single electron transfer (SET) reagents.[3] In particular, the ability of diaryl iodonium salts to generate aryl radicals under UV irradiation in the presence of a photocatalyst or by electrochemical reduction has been exploited as a tool to initiate polymerization and for surface functionalization. However, their use in mainstream organic synthetic processes would require milder conditions. The development of new photocatalytic systems may provide a solution to this challenge. Recently, in the context of green chemistry, visible-light photoredox catalysis relying on the use of transition metal complexes for the generation of radicals has witnessed a rebirth.[4,5] For that purpose, a variety of ruthenium(II)[6] and iridium(III)[7] polypyridine complexes have been shown to catalyze single-electron transfer to unsaturated or cyclopropyl ketones,[8] halides,[9] *N*-alkoxyphthalimides,[10] keto epoxydes/azeridines,[11] azides,[12] diazonium,[13] and sulfonium reagents under visible-light.[14] Moreover, the previous work of Lalevée et al.[15] on cationic photopolymerization of epoxides, initiated by the system TTMSS/Ph_2I^+/Ru^{II} or Ir^{III}, suggests that iodonium salts ($E_{1/2}^{red}(Ph_2I^+) = -0.2$ V versus SCE) should be appealing aryl radical precursors under photoreductive conditions. Recently, Sanford et al. and Xue and Xiao et al. took advantage of this property for the C−H arylation of various arenes and heteroarenes with diaryliodonium salts.[16]

The objective of this work is the application of iodonium salts as alternative aryl radical sources to rare-metal-based complexes, with cheaper and more sustainable photocatalysts than ruthenium(II) and iridium(III) complexes but with comparable reductive potentials.[17] In late 1970s, McMillin et al. reported a new family of photoactive copper(I)–bisphenanthroline complexes.[18] Owing to their photophysical properties and electrochemical properties, $[Cu(dap)_2]^+$ (dap = 2,9-bis(*para*-anisyl)-1,10-phenanthroline; **1a**) and $[Cu(dpp)_2]^+$ (dpp = 2,9-diphenyl-1,10-phenanthroline; **1b**; Figure 1) emerged as promising candidates for photoredox catalysis. Particularly, the photoactivated complexes $^*[Cu(dap)_2]^+$ and $^*[Cu(dpp)_2]^+$ show lower reduction potentials than $^*[Ru(bpy)_3]^{2+}$ (−1.43 V and −1.11 V vs. −0.85 V vs. SCE).[19] The first application of such complexes was published by Sauvage et al. and concerns the reductive coupling of *para*-nitrobenzylbromide catalyzed by $[Cu(dap)_2][BF_4]$ under visible light in the presence of triethylamine.[20] More recently, Reiser et al. successfully applied the same photocatalyst to atom-transfer radical addition to olefins and allylation of α-haloketones.[9w] In both cases, a Cu^{II}/Cu^{I} redox systems may be involved through an oxidative quench of the $^*[Cu(dap)_2]^+$ complex. However, the reactivity of the least reducing copper(I) complex $[Cu(dpp)_2]^+$ under visible-light irradiation was never exploited in synthesis. In this context, we explored the photocatalytic reduction of diaryliodonium salts with $[Cu(dpp)_2][PF_6]$, which shows a suitable reduction potential, to generate aryl radicals. The so-formed radicals were engaged in allylation processes with allylsulfones as radical acceptors.

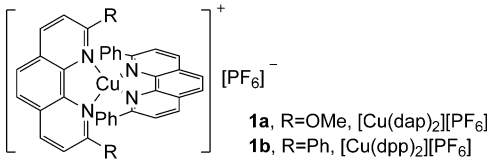

Figure 1. Structures of $[Cu(dap)_2][PF_6]$ and $[Cu(dpp)_2][PF_6]$.

In a typical experiment, diphenyliodonium hexafluorophosphate (**2a**) was irradiated in acetonitrile (0.2 M) in the presence of 0.5 mol % of $[Cu(dpp)_2][PF_6]$, *N*,*N*-diisopropylethylamine (DIPEA, 2 equiv) and allylsulfone **3a** (5 equiv). After 30 min, a full conversion of **2a** was observed and the corresponding allylation product **4a** was formed in 80 % yield (Table 1, entry 1). Considering that this copper complex absorbs between 400 and 600 nm,[19] we selected green

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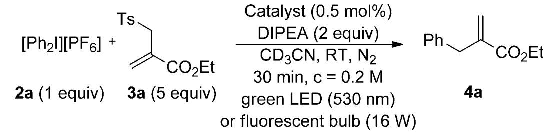
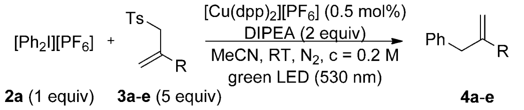
Table 1. Generation of phenyl radical by photocatalytic reduction of diphenyliodonium salts with copper(I) complexes.

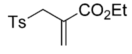
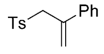
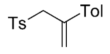
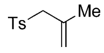
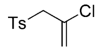


Entry	Catalyst	Conv. [%]	Yield [%][a]
1	$[Cu(dpp)_2][PF_6]$	100	80
2	$[Cu(dpp)_2][PF_6]$	100	80[b]
3	$[Cu(dpp)_2][PF_6]$	100	62[c]
4	$[Cu(dpp)_2][PF_6]$	100	82[d,e]
5	$Ru(bpy)_3Cl_2.6H_2O$	100	81[f]
6	$Ir(ppy)_3$	100	80[f]
7	$[Cu(dap)_2][PF_6]$	100	80
8	$[Cu(dpp)_2][PF_6]$	0	0[g]
9	$[Cu(dpp)_2][PF_6]$	0	0[h]
10	–	0	0[g]
11	–	20	20

[a] NMR yield. [b] $[(Ph)_2I][TfO]$ **2b** was used instead of $[(Ph)_2I][PF_6]$ **2a**. [c] 2 equivalents of **3a** were used. [d] Isolated yield. [e] In acetonitrile. [f] Fluorescent bulb was used as visible light source. [g] Without DIPEA. [h] Without light.

Table 2. Allylation of phenyl radical under photocatalytic reduction conditions.



Entry	Acceptor	Product, yield [%][a]
1	 **3a**	**4a**, 82
2	 **3b**	**4b**, 43[b]
3	 **3c**	**4c**, 64[b]
4	 **3d**	**4d**, 66[b,c]
5	 **3e**	**4e**, 55[d,e]

[a] Isolated yield with full conversion. [b] Full conversion was obtained in 1 h. [c] NMR yield. [d] Full conversion was obtained in 4 h. [e] 1 mol% of catalyst was used.

LED, emitting at 530 nm, far from the UV range, as a suitable light source to limit potential UV side reactions such as photoinduced electron transfer (PET) reactions from DIPEA and degradation of iodoniums. The screening of the experimental conditions was carried out in CD_3CN to follow the conversion and quantify the yield of the transformation with precision by ^1H NMR (butadiene sulfone was the internal standard). Changing the counter anion to triflate has no influence on the reaction. Under the same reaction conditions, diphenyliodonium triflate (**2b**) gave similar results (Table 1, entry 2). These optimized conditions also allowed the reduction of the amount of acceptor to two equivalents (Table 1, entry 3). Full conversion of iodonium salt was observed in 30 min but the yield decreased slightly to 62%. Then, the reaction was scaled to one millimole in order to illustrate the synthetic potential of this transformation (Table 1, entry 4). A reproducible isolated yield of 82% was obtained.

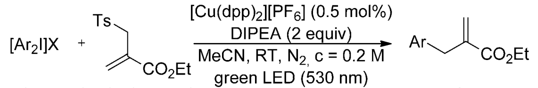
Comparison with known photocatalysts showed that standard $[Ru(bpy)_3]Cl_2$ and $[Ir(ppy)_3]$ catalyzed this transformation with fluorescent light irradiation (Table 1, entries 5 and 6). No significant improvement was observed, demonstrating that $[Cu(dpp)_2]^+$ remains a valuable alternative to known photocatalysts. We also investigated the behavior of $[Cu(dap)_2]^+$ in our photocatalyzed reductive process (Table 1, entry 7). This complex was also effective and **4a** was obtained in 80% yield. This comparison highlights the potential of such complexes either in reductive or oxidative transformations. When $[Cu(dpp)_2]^+$ was used without DIPEA, no **4a** was observed (Table 1, entry 8). The control experiments confirmed that the copper complex, DIPEA and irradiation with visible-light are needed for good conversions (Table 1, entries 9 and 10). Without light, copper salt and DIPEA proved to be inactive in this reduction (Table 1, entry 9) and irradiation with DIPEA gave only 20% of **4a** (Table 1, entry 11) as PET product (95% conversion was observed in 22 h to yield **4a** in 79%).

With the optimized conditions in hand, we extended the scope of the allylation to a range of allyl sulfones (Table 2). When the internal position of the olefin moiety was substituted by a phenyl or a tolyl group (**3b** and **3c**), the yields decreased to 43% and 64%, respectively (Table 2, entries 2 and 3). In these cases, longer times (1 hour) are required for a full conversion of the iodonium salts. The same behavior was observed with a methyl substituent (**3d**). A yield of 66% in **4d** was determined by ^1H NMR due to the volatility of the resulting allylation product (Table 2, entry 4). A chlorine atom at the internal position impacted the course of the reaction and full conversion was reached in 4 h with 1 mol% of the copper catalyst (Table 1, entry 5). The corresponding allylation product, **4e**, was isolated in 55% yield. In our conditions, allyl sulfone **3a** proved to be the best acceptor and we decided to use it to test the scope of diaryliodonium reagents applicable to this reaction.

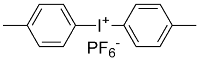
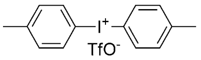
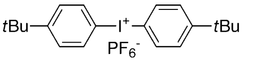
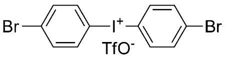
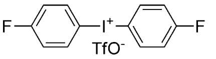
The influence of the aromatic ring substitution on the generation of the corresponding substituted aryl radical was also investigated (Table 3). A range of commercially available diaryliodonium salts was selected. Alkyl substitution did not modify the reaction time to full conversion. Indeed, after 30 min of irradiation, iodonium salts **2c** and **2e** furnished allylated adducts **5** and **6** in 71% and 67% yield, respectively (Table 3, entries 1 and 3). The influence of the counter-ion on the reduction of diaryliodonium salts was negligible as illustrated by the formation of **5** in 67% yield from the triflate salt (Table 3, entry 2). When the aromatic ring was *para*-substituted by a bromine atom, an extended reaction time of 16 h was needed to obtain full conversion (Table 3, entry 4). The corresponding allylated compound **7** was obtained in 63% yield. Interestingly, changing the bromine to fluorine atom allowed to obtain **8** in 64% yield within a shorter reaction time of 1.5 h (Table 3, entry 5).

Dissymmetric iodonium salts have been investigated to test the influence of steric and electronic effects on the for-

Table 3. Scope of diaryliodonium salts as aryl radical sources.

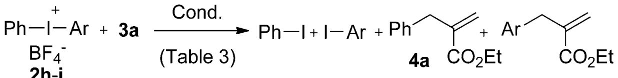


2c-**g** (1 equiv) **3a** (5 equiv) **5**-**8**

Entry	Diaryliodonium salt		Product, yield [%][a]
1		**2c**	**5**, 71[b]
2		**2d**	**5**, 67[b]
3		**2e**	**6**, 67[b]
4		**2f**	**7**, 63[c]
5		**2g**	**8**, 64[d]

[a] Isolated yield with full conversion. [b] Full conversion was obtained in 30 min. [c] Full conversion was obtained in 16 h. [d] Full conversion was obtained in 1.5 h.

mation of aryl radicals (Scheme 1). Iodonium salts **2h**–**j** were applied to the allylation reaction with allylsulfone **3a** as the radical acceptor. Full conversions were obtained in 30 min and NMR analysis of the crude reaction mixture allowed the quantification of both the aryl iodides and the allylation products **4a**, **4h**–**j**. With iodonium salt **2h**, no steric discrimination was observed in the fragmentation step and the aryl radical addition to acceptor **3a**. In the same fashion, no selectivity was obtained in the reduction of iodonium salts bearing either an electron-poor (**2i**) or an electron-rich (**2j**) aryl ring. The lack of selectivity in these cases deterred us from exploring further the reduction of dissymmetric aryl iodoniums.



	Conv.	PhI/ArI	Allylation compounds
Ar = Mes, **2h**	100%	52:48	53:47, **4a**/**4h**
Ar = p-CF$_3$-C$_6$H$_4$, **2i**	100%	60:40	49:51, **4a**/**4i**
Ar = p-MeO-C$_6$H$_4$, **2j**	100%	56:44	64:36, **4a**/**4j**

Scheme 1. Behavior of dissymmetric iodonium salts. Conversions and ratios were determined by ^{1}H NMR spectroscopy (crude NMR spectra are provided in the Supporting Information).

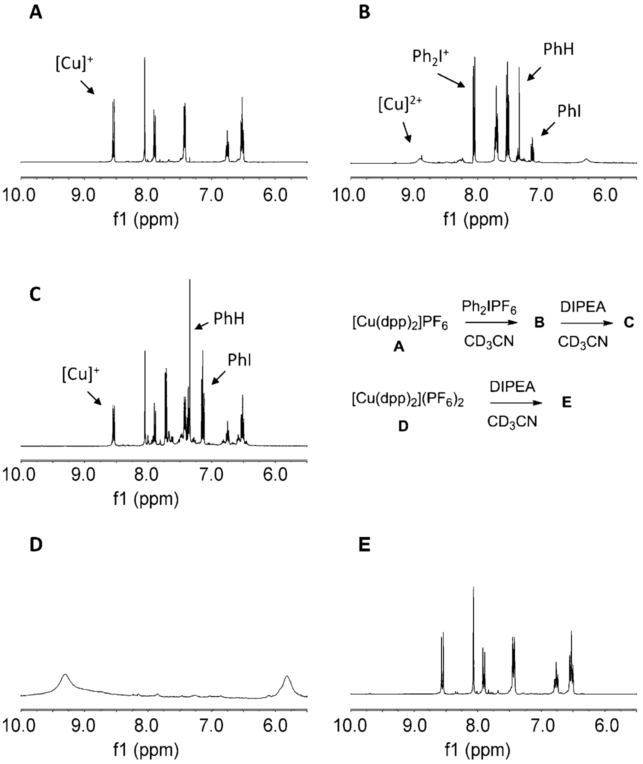
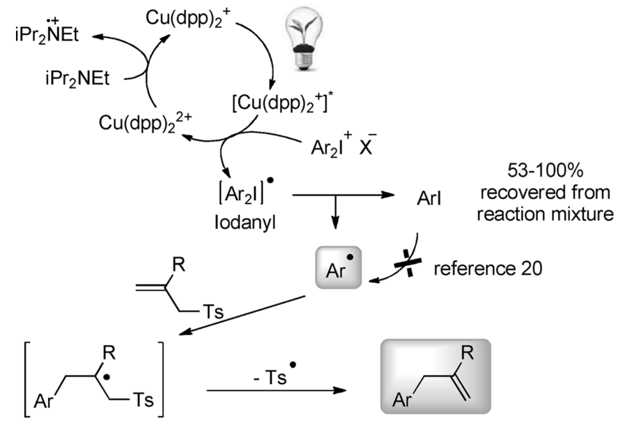


Figure 2. ^{1}H NMR investigations of iodonium photocatalytic reduction (scale: 10–5.5 ppm, full scale spectra are in the Supporting Information).

To gain further insight into the catalytic cycle, we decided to monitor the reduction of diphenyliodonium salt by ^{1}H NMR (Figure 2). [Cu(dpp)$_2$][PF$_6$] (40 mol%) was dissolved in CD$_3$CN (2 mL) and the corresponding ^{1}H NMR spectrum was recorded (Figure 2A). Then, one equivalent of diphenyliodonium hexafluorophosphate was added and the NMR tube was irradiated during 30 min with green LED (Figure 2B). The characteristic signals of [Cu(dpp)$_2$]$^+$ disappeared and signals of PhI and benzene appeared, which indicates the reduction of the iodonium salt into the corresponding iodanyl radical and its subsequent fragmentation to form iodobenzene and phenyl radical. The simultaneous oxidation of the copper(I) complex occurred and no more characteristic signals of the initial complex were visible. Only broad peaks appeared that can be attributed to the corresponding Cu^{II} species were observed and compared with an authentic sample of [Cu(dpp)$_2$][PF$_6$]$_2$ (Figure 2D). Two equivalents of DIPEA were then added and the irradiation was maintained for 30 min (Figure 2C). The total conversion of the iodonium salt was observed concomitantly with an increase in the amount of iodobenzene and benzene. Moreover, the signals of [Cu(dpp)$_2$]$^+$ were recovered without significant modification. In order to support the reduction of Cu^{II} generated during the reduction of iodonium salt, an authentic sample of [Cu(dpp)$_2$][PF$_6$]$_2$ (Figure 2D) was treated with DIPEA without irradiation. The initial dark blue solution immediately turned to dark red suggesting the reduction of Cu^{II} to Cu^{I}. The ^{1}H NMR spectrum of the resulting solution confirmed the formation of [Cu(dpp)$_2$]$^+$ (Figure 2E).

Based on these results, we can propose the following mechanism (Scheme 2). Upon light irradiation, the excited state of [Cu(dpp)$_2$]$^+$ is oxidatively quenched by the iodonium salt to generate [Cu(dpp)$_2$]$^{2+}$ and the intermediate iodanyl radical. Its fragmentation generates the aryl iodide and aryl radical concomitantly. This suggestion is strongly supported by the fact that aryl iodide by-products were isolated from the reaction mixture in 53–100% yields. Conversely, the so-formed aryl radical reacts with the allyl sul-



Scheme 2. Proposed mechanism.

fone acceptor to afford the allylation product. In order to secure this assumption, we checked that the aryl iodide was not an alternative source of aryl radical in such experimental conditions.[21] The catalyst $[Cu(dpp)_2]^+$ is regenerated after reduction of $[Cu(dpp)_2]^{2+}$ by DIPEA.

In summary, we report the photocatalytic reduction of diaryliodonium salts as an efficient way to generate the corresponding aryl radicals. This mild process relies on a copper complex as photocatalyst. The experimental conditions developed are compatible with the radical intermediates invoked. Carbon–carbon bond formation appears to be efficient as illustrated by the formation of allylated products in good yields which suggest the radical character of this transformation. General studies extending to other radical precursors and the use of this copper complex as alternative photocatalyst to polypyridine Ru/Ir complexes will be reported in due course.

Experimental Section

Photoreductive transformation of diphenyliodonium hexafluorophosphate 2a (General Procedure 1): A solution of diphenyliodonium hexafluorophosphate (1 mmol, 428 mg, 1 equiv), $[Cu(dpp)_2][PF_6]$ (0.005 mmol, 4 mg, 0.5 mol%, unless stated otherwise), *N,N*-diisopropylethylamine (2.0 mmol, 350 μL, 2 equiv) and radical acceptor (5 mmol, 5 equiv) in distilled CH_3CN (5 mL) were introduced into a schlenk tube equipped with a magnetic stirring bar. The mixture was degassed by freeze–pump–thaw cycles (×2) then was irradiated with visible light (530 nm LED approximately 2 cm away from the glassware) for 30 min (unless stated otherwise). The reaction mixture was then concentrated under reduced pressure to give the crude product. The residue was purified by flash chromatography on silica gel to afford the desired product **4a**–**4e**.

Photoreductive transformations of iodonium salts (General Procedure 2): A solution of iodonium salt (1 mmol, 1 equiv), $[Cu(dpp)_2][PF_6]$ (0.005 mmol, 4 mg, 0.5 mol%, unless stated otherwise), *N,N*-diisopropylethylamine (2.0 mmol, 350 μL, 2 equiv) and ethyl *p*-toluenesulfonylmethacrylate **3a** (5 mmol, 1,340 g, 5 equiv) in distilled CH_3CN (5 mL) were introduced into a schlenk tube equipped with a magnetic stiring bar. The mixture was degassed by freeze-pump-thaw cycles (×2) then irradiated with visible light (530 nm LED approximately 2 cm away from the glassware) during 30 min (unless stated otherwise). The reaction mixture was then concentrated under reduced pressure to give the crude product. The residue was purified by flash chromatography on silica gel to afford the corresponding product **5**–**8**.

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Keywords: allylation · copper · iodonium · photocatalysis · radical reactions

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