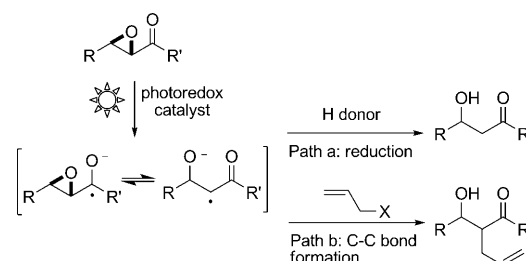


Visible-Light-Induced Photoreductive Generation of Radicals from Epoxides and Aziridines**

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As a result of its unique features, radical chemistry has become a reliable and efficient tool for synthetic chemists over the last fifty years.^[1] Nowadays, the necessity to devise eco-compatible alternatives for the generation of radical species has stimulated intense research efforts.^[2] The development of single-electron transfer (SET) redox processes using catalytic amounts of metal complexes would be a significant advance. For that purpose, the use of visible light and a photoredox catalyst such as [Ru(bpy)₃]Cl₂^[3] has lately appeared to offer very promising possibilities.^[4] Thus, following the pioneering findings of Cano-Yelo and Deronzier,^[5] recent contributions from the research groups of Yoon, MacMillan, and Stephenson have demonstrated that enones,^[6] perfluorated iodides,^[7] as well as activated chlorides and bromides^[8] are suitable substrates for the formation of radicals by visible light-catalyzed reductive electron transfers.

Because epoxides are exquisite substrates for radical transformations,^[9] we envisioned to expand the scope of visible light photoredox catalysis to the ring opening of these moieties, and access a formal photocatalytic Nugent–Rajan-Babu–Gansäuer^[10] reaction. Owing to their low redox potential (−2.35 V for stilbene oxide vs. Ag/AgI)^[11] compared to [Ru(bpy)₃]²⁺/[Ru(bpy)₃]⁺ (−1.33 V vs. SCE), we quickly abandoned our initial approach based on direct electron transfer to the oxirane, but we installed an α-carbonyl moiety as a relay. Ring opening of α-ketoepoxides^[12] has been sporadically reported under UV irradiation^[13] and our goal was first to develop an alternative using low-energy visible-light activation. Then, the photogenerated radical could be



Scheme 1. Photocatalytic reductive ring opening of epoxides and subsequent carbon–carbon bond formation.

exploited in the context of carbon–carbon bond formation (Scheme 1).^[14] Our results are presented herein.

Our preliminary investigation was carried out on epoxy-chalcone **1a** (Table 1). First, we tested the Stephenson conditions used for dehalogenation^[8b] (i.e. [Ru(bpy)₃]Cl₂·(H₂O)₆ (5 mol %), *i*Pr₂NEt (2 equiv), and Hantzsch ester (1.1 equiv) in DMF). After 36 hours of irradiation with a

Table 1: Optimization of the photoreduction conditions for epoxy-chalcone **1a**.^[a]

Entry	Solvent	<i>n</i>	<i>t</i> [h]	Conv. [%] ^[b]	Yield [%] ^[c]
1	DMF	2	36	76	74
2	MeCN	2	36	30	10
3	Et ₂ O	2	36	0	0
4	DMSO	2	3	100	86
5	DMSO	0	3	100	91

[a] Reaction conditions: **1a** (0.1 mmol, 0.1 M in solvent), **3** (0.11 mmol), [Ru(bpy)₃]Cl₂·(H₂O)₆ (0.005 mmol), irradiation with a 14 W fluorescent light bulb at room temperature. [b] Conversion determined by ¹H NMR analysis. [c] Yield of isolated product. bpy = 2,2'-bipyridine, DMF = *N,N*-dimethylformamide, DMSO = dimethyl sulfoxide.

14 W fluorescent lamp, β-hydroxyketone **2a** was obtained in 74 % yield with incomplete conversion of **1a**.

A rapid solvent screening indicated that DMSO was the best solvent. Finally, it became apparent that the Hantzsch ester could be both the reductive quencher and the hydrogen and proton donor. Indeed, in a typical reduction, **1a** led to 91 % of **2a** after 3 hours of irradiation at room temperature in DMSO, in the presence of the Hantzsch ester (1.1 equiv) and [Ru(bpy)₃]Cl₂·(H₂O)₆ (5 mol %) only.^[15]

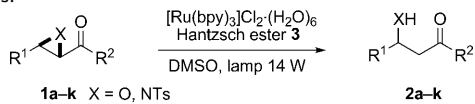
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[**] We thank UPMC, CNRS, IUF (L.F., M.M.), and ANR (grant “Credox”). M.-H.L. was awarded a graduate fellowship by the Région Ile-de-France, which is gratefully acknowledged. We warmly thank Dr. Carlos Afonso (IPCM) for technical assistance (LC-MS measurements). Analytical equipment was generously offered through FR 2769.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201007571>.

Table 2: Scope of the epoxide ring-opening reaction and extension to aziridines.^[a]



Entry	X	R ¹	R ²	t [h]	Yield [%] ^[b]
1	O	C ₆ H ₅	C ₆ H ₅	3	2a , 91
2	O	C ₆ H ₅	4-MeOC ₆ H ₄	7	2b , 76
3	O	C ₆ H ₅	4-CF ₃ C ₆ H ₄	5	2c , 76
4	O	C ₆ H ₅	4-CO ₂ MeC ₆ H ₄	20	2d , 55
5	O	C ₆ H ₅	napht	10	2e , 42
6	O	4-CF ₃ C ₆ H ₄	C ₆ H ₅	4	2f , 78
7	O	4-ClC ₆ H ₄	C ₆ H ₅	3	2g , 86
8	O	C ₄ H ₉	C ₆ H ₅	24	2h , 52
9	NTs	C ₆ H ₅	C ₆ H ₅	3	2i , 94
10	NTs	C ₆ H ₅	4-MeOC ₆ H ₄	3	2j , 81
11	NTs	C ₄ H ₉	C ₆ H ₅	3	2k , 78

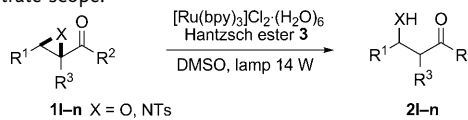
[a] Reaction conditions: substrate (0.2 mmol, 0.1 M in DMSO), **3** (0.22 mmol), [Ru(bpy)₃]Cl₂·(H₂O)₆ (0.01 mmol), irradiation with a 14 W fluorescent light bulb at room temperature. [b] Yield of isolated product. naphth = naphthyl, Ts = 4-toluenesulfonyl.

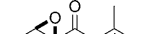
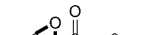
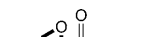
With the optimized conditions in hand, we examined the scope of the process (Table 2). The ring opening worked smoothly with epoxychalcones bearing electron-donating (Table 2, entry 2), or -withdrawing substituents (Table 2, entries 3, 4, and 6) on both aromatic rings. The mild conditions were compatible with a range of functionalities including an ether (Table 2, entry 2), an ester (Table 2, entry 4), an aromatic halide (Table 2, entry 7), or a naphthyl ring (Table 2, entry 5). When the carbonyl substituent R^2 was an alkyl chain, no conversion could be observed. However, when the oxirane substituent R^1 was a butyl chain, the desired reduction proceeded as desired. Interestingly, tosylaziridines were reduced under the same conditions in quite high yields (Table 2, entries 9–11). To our knowledge, these represent the first examples of photocatalyzed ring opening of aziridines which are substrates that have not been yet reported to be reactive in titanocene chemistry.

Limitations were encountered with sterically hindered β -epoxyketones. To bypass this problem, we first reintroduced $i\text{Pr}_2\text{NEt}$ as a better reductive quench than Hantzsch ester **3** (Table 3, conditions B). We were pleased to observe that the desired reduction of substrate **1l** bearing a bulky mesityl substituent occurred, even if the conversion remained incomplete after 72 hours of irradiation (75 % conversion, 55 % yield; Table 3, entry 2). Anticipating that a stronger reductant would favor the photoreductive process, we switched the catalyst from $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot (\text{H}_2\text{O})_6$ to $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ complex^[16] (-1.51 V vs. SCE for $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]^+ / [\text{Ir}(\text{dtbbpy})(\text{ppy})_2]$; conditions C).^[17] Pleasingly, we obtained a full conversion for **1l** after 15 hours of irradiation (100 % conversion, 75 % yield, entry 3). Then, applying those conditions to substrates **1m** and **1n** bearing a substituent in the α position to the ketone, we were delighted to observe that the photoreduction took place with a total conversion and synthetically useful yields (Table 3, entries 5 and 7).

We next attempted to engage the photogenerated radical in an allylation process (Table 4). Introduction of 10 equiv-

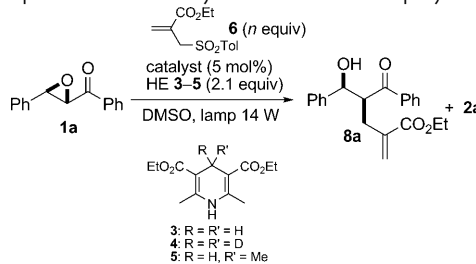
Table 3: Influence of the nature of the photocatalyst and the additives on the substrate scope.



Entry	Substrate	<i>t</i> [h]	Conditions ^[a]	Yield [%] ^[b]
1		15	A	2l , 0
2		72	B	2l , 55
3		15	C	2l , 75
4		15	A	2m , 0
5		15	C	2m , 83 (d.r.=54:46)
6		15	A	2n , 0
7		4	C	2n , 87 (d.r.=76:24)

[a] Conditions A: substrate (0.2 mmol, 0.1 M in DMSO), **3** (0.22 mmol), [Ru(bpy)₃]Cl₂·(H₂O)₆ (0.01 mmol); Conditions B: substrate (0.2 mmol, 0.1 mM in DMSO), **3** (0.22 mmol), *i*Pr₂NEt (0.22 mmol), [Ru(bpy)₃]Cl₂·(H₂O)₆ (0.01 mmol); Conditions C: substrate (0.2 mmol, 0.1 mM in DMSO), **3** (0.22 mmol), *i*Pr₂NEt (0.22 mmol), [Ir(dtbppy)(ppy)₂]PF₆ (0.01 mmol) [b] Yield of isolated product. dtbppy = 4,4'-di-*tert*-butyl-2,2'-bipyridine, ppy = 2-phenylpyridine.

Table 4: Optimization of the allylation conditions on epoxychalcone **1 a**.^[a]



Entry	<i>n</i>	Catalyst	HE	<i>t</i> [h]	Yield of 2a [%] ^[b]	Yield of 8a [%] ^[b]
1	10	[Ru(bpy) ₃]Cl ₂ ·(H ₂ O) ₆	3	5	30	41
2	10	[Ru(bpy) ₃]Cl ₂ ·(H ₂ O) ₆	4	12	23	51
3	10	[Ru(bpy) ₃]Cl ₂ ·(H ₂ O) ₆	5	24	0	0
4	10	[Ir(dtbbpy)(ppy) ₂]PF ₆	5	48	< 5	65
5	3	[Ir(dtbbpy)(ppy) ₂]PF ₆	5	48	< 5	67

[a] Reaction conditions: substrate (0.2 mmol, 0.1 M in DMSO), **3-5** (0.42 mmol), catalyst (0.01 mmol), irradiation with a 14 W fluorescent light bulb at room temperature. [b] Yield of isolated product. HE = Hantzsch ester, Tol = tolyl.

alents of allylsulfone **6** prior to irradiation under conditions A led to α -allyl ketone **8a** in 41 % yield, albeit together with 30 % of directly reduced **2a** (Table 4, entry 1). We decided to take advantage of the kinetic isotope effect to favor allylation over reduction^[18] and switched to 4,4'-[D₂]-Hantzsch ester **4**. This led to an improved ratio of allyl product (2:1; Table 4, entry 2). Reasoning that the substitution at the 4-position of Hantzsch esters might be determining for the balance between direct reduction and allylation, we also tested 4-Me-Hantzsch ester **5**. No conversion was observed when [Ru(bpy)₃]Cl₂·(H₂O)₆ was used (Table 4, entry 3). However,

the use of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ allowed us to selectively obtain the allylation product **8a** (Table 4, entry 4). Pleasingly, lowering the amount of allylating agent to only 3 equivalents of allyl sulfone did not affect this good selectivity (Table 4, entry 5).

The scope of this new radical allylation sequence was examined next (Table 5). A variety of β -epoxyketones (Table 5, entries 1–4 and 7) and tosylaziridines (Table 5,

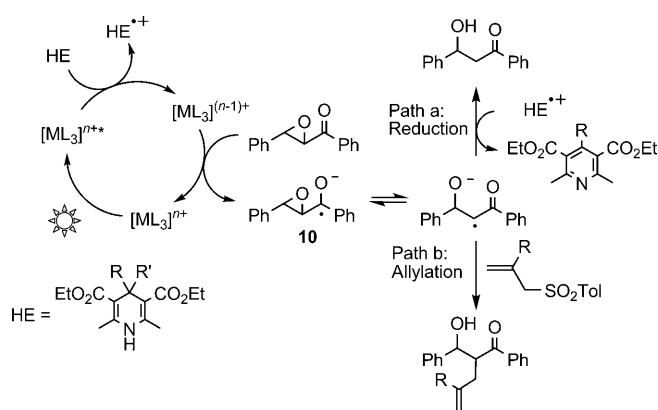
Table 5: Scope of the photoallylation process.^[a]

1a–j		6: R = CO ₂ Et 7: R = Me		8a–j: R = CO ₂ Et 9a,i: R = Me	
Entry	X	Sulfone	R ¹	R ²	d.r. ^[b] Yield [%] ^[c]
1	O	6	C ₆ H ₅	C ₆ H ₅	96:4 8a , 67
2	O	6	C ₆ H ₅	4-MeOC ₆ H ₄	93:7 8b , 73
3	O	6	C ₆ H ₅	napht	> 95:5 8e , 51
4	O	6	C ₄ H ₉	C ₆ H ₅	> 95:5 8h , 70
5	NTs	6	C ₆ H ₅	C ₆ H ₅	> 95:5 8i , 49
6	NTs	6	C ₆ H ₅	4-MeOC ₆ H ₄	> 95:5 8j , 46
7	O	7	C ₆ H ₅	C ₆ H ₅	90:10 9a , 60
8	NTs	7	C ₆ H ₅	C ₆ H ₅	87:13 9i , 43

[a] Conditions: substrate (0.2 mmol, 0.1 M in DMSO), **5** (0.42 mmol), allyl sulfone (0.6 mmol), $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (0.01 mmol), irradiation with a 14 W fluorescent light bulb at room temperature. [b] Diastereomeric ratio (d.r.) was determined from the ¹H NMR analysis of the crude and isolated products and confirmed by LC-MS analysis. [c] Yield of isolated product.

entries 5, 6, and 8) could be reduced and then allylated with fair to good yields, and excellent diastereoselectivities. Allyl sulfone can be substituted by an electron-withdrawing (Table 5, entries 1–6) as well as -donating (Table 5, entries 7–8) group without loss in efficiency, although diastereoselectivities for **9a** and **9i** are slightly altered. Notably, such radical allylation would presumably not be possible in the classical Ti^{III} conditions because formation of the keto-enolate as a result of the two-electrons reduction is fast.^[12] A suitable crystal was obtained for aminoketone **8i**, whose structure was determined by X-ray analysis (see the Supporting Information).^[19] The major diastereomer was shown to be *syn* which is consistent with Guindon's model for the radical allylation of β -alkoxy esters under nonchelation control.^[20]

A plausible mechanism is proposed for both transformations—simple reduction and reductive allylation—as depicted in Scheme 2. The excited state $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]^{+*}$ (or $[\text{Ru}(\text{bpy})_3]^{2+*}$) obtained upon visible-light irradiation of $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]^+$ (or $[\text{Ru}(\text{bpy})_3]^{2+}$) would be reductively quenched by the Hantzsch ester to form the strong reductant $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]$ (or $[\text{Ru}(\text{bpy})_3]^+$). Single-electron transfer to epoxychalcone **1a** would then take place, thus regenerating the iridium(III) (or ruthenium(II)) complex to provide the radical anion **10**. This radical anion would undergo ring opening and either subsequent reduction by Hantzsch ester or trapping by the allyl sulfone derivative.



Scheme 2. Proposed mechanism for both photocatalyzed reduction and reductive allylation of **1a**.

To conclude, we have extended the scope of visible-light photoredox catalysis to the generation of radicals from epoxides and aziridines. To perform this process, we used either $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]^+$ or $[\text{Ru}(\text{bpy})_3]^{2+}$ as the photocatalyst in combination with a Hantzsch ester derivative as both quencher and hydrogen donor. Then, we took advantage of the reactivity of the photogenerated radical to create new carbon–carbon bonds through a highly diastereoselective radical ring-opening/allylation tandem process. Extension to other radical acceptors and related mechanistic studies are still underway. Further work will examine cyclizations and the viability of asymmetric approaches by simply starting from corresponding enantioenriched epoxides or for the desymmetrization of *meso*-epoxides.

Experimental Section

Synthesis of 8a: Hantzsch ester **5** (112 mg, 0.42 mmol, 2.1 equiv), allyl sulfone **6** (161 mg, 0.6 mmol, 3 equiv), epoxychalcone **1a** (44 mg, 0.2 mmol, 1 equiv), and $[\text{Ir}(\text{dtbbpy})(\text{ppy})_2]\text{PF}_6$ (9.1 mg, 0.01 mmol, 5 mol %) were added to a dried Schlenk tube equipped with a stir bar. The Schlenk tube was evacuated and backfilled with argon three times, before degassed DMSO (2 mL) was added under argon. The yellow reaction mixture was irradiated at RT with a 14 W fluorescent light bulb for 48 h. The reaction was quenched with water (15 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over MgSO₄, concentrated in vacuo, and purified by flash chromatography on silica gel to afford **8a** as a colorless oil (45 mg, 67 %).

Received: December 2, 2010

Revised: February 15, 2011

Published online: April 12, 2011

Keywords: allylation · aziridines · epoxides · photocatalysis · photoreduction

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