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Visible Light Photocatalytic Reduction of *O*-Thiocarbamates: Development of a Tin-Free Barton–McCombie Deoxygenation Reaction

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Abstract: The Barton–McCombie deoxygenation is one of the most important transformations in the toolbox of organic chemists which has been the subject of a number of methodological developments. In this study, we report a photocatalyzed redox deoxygenation of secondary and tertiary alcohols from thiocarbamate precursors under visible light activation. The iridium complex $Ir(ppy)_3$ proved to be the most efficient catalyst in the presence of Hünig's base as sacrifial electron donor. A mechanistic investigation is presented based on fluorescence quenching experiments and cyclic voltammetry.

Keywords: deoxygenation; photocatalysis; photoreduction; radical reactions; thiocarbamates

Since the development of modern radical chemistry, a number of related transformations have entered mainstream chemistry and proved to be highly efficient tools for chemists in molecular and material sciences.^[1] Indeed, applications in surface functionalization,^[2] polymer preparation^[3] or organic synthesis^[4] have highlighted the strong impact of this field and demonstrated its ability to act at the interface of different scientific domains. Among the large number of known radical reactions, those dedicated to functional group transformations have certainly been the most intensively studied for methodological development and total synthesis. Notably, the Barton–McCombie deoxygenation is one of the most used radical reactions since it allows the reduction of an alcohol function to the corresponding alkane.^[5] The reaction usually proceeds in two steps through the preliminary formation of an intermediate thiocarbonyl precursor such as xanthate, thiocarbonate, thiocarbamate (Scheme 1). In the original version, the radical chain reaction was initiated by AIBN under thermal conditions and $(n-Bu)_3$ SnH was used as chain mediator.^[5a]

Related protocols have been proposed by changing the initiation process and substituting the toxic tin hydride mediator by silanes,^[6] phosphorus derivatives,^[7] boranes^[8,9] or cyclohexadienyl compounds.^[10] Deoxygenation reactions have also been investigated through the reduction of benzoyl derivatives by organometallic redox processes^[11] as well as photoin-

Classical radical deoxygenation





photoredox catalysis

Scheme 1. Photoreduction of *O*-thiocarbamate: A photocatalytic alternative to the classical Barton–McCombie deoxygenation reaction

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duced electron transfer sensitized by *N*-alkylcarbazoles under Hg-lamp irradiation.^[12] As an efficient alternative to stoichiometric redox reactions or harsh UV conditions, visible light photoredox catalysis has re-emerged in the last decade.^[13] A lot of groups including ours have taken an active part in the development of new catalytic processes based on visible light to activate organic or organometallic photocatalysts able to promote electron transfers and radical reactions.^[14,15] Very few of them have been dedicated to the challenging reductive cleavage of the C–O bond because of its high bond strength.

Recently, Falvey reported a photorelease of carboxylic acids based on a formal deoxygenation reaction.^[16] Stephenson combined the iodination of primary and secondary alcohols with the photoreduction of the so-formed aliphatic iodides to the corresponding alkanes in a one-pot two-step sequence.^[17] Finally, Overman developed a photoredox-catalyzed fragmentation of tertiary alkyl *N*-phthalimidoyl oxalates aiming at C–C bond formation.^[18] Based on all these considerations, we surmised that the development of an efficient tin-free deoxygenation reaction that would use visible light activation of a photoredox catalyst is of primary importance for the chemical community.

Thus, we decided to investigate the photoreduction of thiocarbonyl derivatives and to focus our attention on the very easy to access imidazolyl-l-thiocarbonyl (ITC) substrates (Scheme 1). This functional group has been introduced by Barton and McCombie^[5a] and gave comparable yields with methyldithiocarbonyl (MDC), and thiobenzoyl (TB) counterparts. ITC substrates have been, for instance, used by Rasmussen for the deoxygenation of carbohydrates.^[19] *O*-Thiocarbamates **1a–j** (structures are reported in Table 2) were obtained in high yields (63–84%) from the corresponding secondary and tertiary alcohols and *N,N'*thiocarbonyldiimidazole (1.2 equiv.) with a catalytic amount of DMAP (0.4 equiv.) (Scheme 2).

We selected *O*-thiocarbamate **1a** for the optimization of the reaction parameters. We investigated the photoreductive conditions catalyzed by polypyridine ruthenium or iridium complexes in the presence of Hünig's base [(*i*-Pr)₂NEt] as sacrificial electron donor under blue LED light (Table 1).^[20] We first tested the



Scheme 2. One-step synthesis of *O*-thiocarbamates from alcohols and commercially available reagents.

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Table 1. Optimization of the reaction conditions for the pho-tocatalytic reduction of O-thiocarbamate 1a into 2a.



Ешиу	(mol%)	<i>i</i> [h]	$(l-PI)_2$ NEt [equiv.]	conc. ^[f]	[%] ^[a]
1	A (5)	24	10	CH ₃ CN C ₁	NR
2 ^[b]	B (5)	24	10	CH ₃ CN C ₁	20
3	C (5)	24	10	CH ₃ CN C ₁	47
4	C (5)	18	10	DMPU C ₁	51
5 ^[c]	C (5)	24	10	NMP C ₁	27
6 ^[c]	C (5)	48	10	DMF C_1	42
7	C (5)	48	10	DMSO C ₁	47
8 ^[c,e]	C (5)	48	10	acetone C ₁	ND
9 ^[c]	C (5)	48	10	DCM C ₁	29
10	C (5)	24	10	CH ₃ CN C ₂	53
11 ^[c]	C (5)	24	10	CH ₃ CN C ₂	53
12	C (2)	24	10	CH ₃ CN C ₂	54
13	C (2)	24	5	CH ₃ CN C ₂	53
14	C (1)	24	5	CH_3CNC_2	53
15	C (5)	24	5	DMPU C_1	50
16	C (1)	24	-	CH ₃ CN C ₂	3
17	_	24	5	CH ₃ CN C ₂	NR
18	$C(1)^{[d]}$	24	5	CH ₃ CN C ₂	NR

^[a] Isolated yield.

^[b] NMR yield.

^[c] Fluorescent bulb, 14 W.

^[d] Reaction performed in the dark.

^[e] Not determined, only traces of **2a** were observed.

^[f] $C_1 = 0.1 \text{ M}, C_2 = 0.067 \text{ M}.$

usual $Ru(bpy)_3Cl_2$ (5 mol%) with 10 equivalents of (*i*-Pr)₂NEt in acetonitrile without success (Table 1, entry 1). Under the same conditions, the use of the slightly more reductive $[Ir(dtbppy)(ppy)_2]PF_6$ established the viability of our photoreductive approach affording 2a in 20% yield (Table 1, entry 2). The most reductive $- Ir(ppy)_3 - of$ the catalyst set proved to be superior and yielded the reduced product 2a in 47% (Table 1, entry 3). Then, we settled on this catalyst for the rest of the study. Changing acetonitrile to DMPU (N,N'-dimethylpropyleneurea) gave comparable yield (Table 1, entry 4) but any other solvent modification (NMP, DMF, DMSO, acetone and DCM; Table 1, entries 5-9) did not improve the photoreduction process. Fluorescent bulb lamp (14 W) and blue LED gave similar results (Table 1, entries 10 and 11) which is consistent with a visible light activation of the catalyst. The next step was to decrease the catalyst concentration and the stoichiometry of the (i-Pr)₂NEt (Table 1, entries 12–14). Thus, the $Ir(ppy)_3$ loading was fixed to only 1 mol% in the presence of 5 equivalents of Hünig's base. The reaction was conducted in acetonitrile during 24 h under blue LED irradiation and 2a was obtained in 53% isolated yield (Table 1, entry 14, conditions A). We decided to set alternative conditions involving DMPU that could be a helpful solvent for the deoxygenation of very lipophilic substrates. A higher catalyst loading (5 mol%) was necessary to keep the same efficiency of the reduction (Table 1, entry 15, conditions B).

Control reactions have been pursued in order to secure the role of each reagent. Only 3% of 2a was obtained when (i-Pr)2NEt was omitted (Table 1, entry 16). No reaction occurred in the absence of Ir- $(ppy)_3$ and without visible light activation (Table 1, entries 17 and 18).

Our photocatalytic conditions were compared to the conventional Barton-McCombie reaction. The deoxygenation of **1a** was run in refluxing toluene (c =0.02 mM) with a slow addition of AIBN (10 mol%) and (n-Bu)₃SnH (2 equiv.) solution over 4 h. Complete conversion was observed after two additional hours and 2a was obtained in 46% (NMR yield) (Scheme 3). This finding was highly suggestive that a photocatalytic Barton-McCombie deoxygenation could be competitive with the original method and constitute a versatile tool for applications in organic synthesis.

Then, we investigated the scope of the reaction by applying the optimized conditions to a series of O-thiocarbamate derivatives **1a**-j (Table 2). The model substrate was modified by changing the N-sulfonyl group to a Boc carbamate (1b) that was also compatible with the reaction conditions and 2b was obtained in a comparable yield of 53%. The isolation of 2c (41%) was a bit tedious due to its relative volatility but the benzylidene acetal was tolerated under such mild reduction conditions. Due to its poor solubility in acetonitrile, lithocholic acid derivative 1d was reduced under conditions B. Indeed, DMPU was more suitable for this reaction and the corresponding deoxy compound was obtained in 65% yield. Other very interesting chemoselectivities were highlighted in the reduction of 1e and 1f. Indeed, the diacetonide-D-glucofuranose derivative 1e was deoxygenated at the 3position to afford the corresponding 3-deoxy com-



Scheme 3. Tin-mediated radical reduction of O-thiocarbamate 1a to 2a.

Table 2. Scope of the reaction.



[b] Isolated yield.

[c] Conditions B.

[d] Conditions A with 2 equiv. of (*i*-Pr)₂NEt.

Ratio meso/DL = 1/1.

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[e]

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Scheme 4. Reaction in absence of the $(i-Pr)_2NEt$: *O*-Thiocarbamate transfert to *S*-thiocarbamate.

pound in 56% yield. Even more interestingly, the benzoyl group at the 5-position of xylofuranose derivative 1f stayed untouched and the reduction proceeded well in 70% yield.^[11] Secondary aliphatic O-thiocarbamate 1g was smoothly deoxygenated in 51% yield. Secondary benzylic and allylic alcohols were engaged in this photocatalyzed deoxygenation sequence. Benzhydrol derivative 1h was reduced under conditions A to afford 1,1-diphenylmethane **2ha** (21%) and dimer 1,1,2,2-tetraphenylethane 2hb (37%), characteristic of benzylic radical reactivity. Interestingly, 1i was efficiently reduced to afford the corresponding dimerization compound 2i in quantitative yield as a 1:1 mixture of DL and meso diastereoisomers.^[21] The reduction of the tertiary O-thiocarbamate 1j coming from the quinic acid exhibited the potentiality of the method to deoxygenate functionalized tertiary substrates in good yield (2i, 60%).

In order to gain insights into the mechanism of this reaction and understand the role of each constituent, we engaged *O*-thiocarbamate **1a** without $(i-Pr)_2NEt$ as sacrificial donor (Scheme 4). Very interestingly, this reaction allowed us to obtain the deoxygenated product **2a** (3%) and the *S*-thiocarbamate **3** in 15% yield while **1a** was recovered in 65% yield, as determined by ¹H NMR with 3-sulfolene as internal standard.

The formation of 3 presumably originates from a thiocarbamate group radical transfer. Thus, valuable information can be deduced: without $(i-Pr)_2NEt$, the carbon-centered radical is formed and the (*i*-Pr)₂NEt plays an important role in the terminal hydrogen transfer to afford the resulting reduced product.^[22] Indeed, in the absence of the Hünig's base, the carbon-centered radical would add on the sulfur atom of **1a** to propagate the radical chain reaction. This chain reaction seems to be moderately efficient because 1 mol% of photocatalyst resulted in 15% of the group transfer compound 3 but is quite interesting in terms of mechanistic implications and perspectives. At that stage, questions arose: How can 1a be reduced by $Ir(ppy)_3$? and how does $(i-Pr)_2NEt$ act in the catalytic process? We decided to answer these questions by carrying out fluorescence quenching studies of $Ir(ppy)_3^*$ (Figure 1).



Figure 1. Fluorescence quenching studies of $Ir(ppy)_3^*$ with *O*-thiocarbamate **1a**.

Fluorescence quenching has been done by addition of thiocarbamate **1a** to a solution of $Ir(ppy)_3$ in DMF.^[23] The fluorescence signal was recorded under excitation at 385 nm for a maximum of emission at 528 nm (Figure 1). To a 1 mM solution of $Ir(ppy)_3$ maintained in the dark, **1a** was added to obtain 0.6, 0.7 and 0.99 mM as final concentrations. The corresponding fluorescence spectra showed a significant decrease of the intensity while the concentration of **1a** increased. The fluorescence intensity ratio (I₀/I) at 528 nm was plotted against **1a** concentration. A linear variation was observed and followed a Stern–Volmer law that supports the energy or electron transfer process between $Ir(ppy)_3^*$ and **1a** with a quenching rate constant kq = $6.5 \times 10^5 M^{-1} s^{-1}.^{[24]}$

To balance these two processes, we did cyclic voltammetry that allowed us to determine the reduction potentials of a representative set of thiocarbamates (Table 3).^[25] For substrates **1a**, **1b**, **1f** and **1j**, these potentials are in the range of -1.56 to -1.73 V (SCE). **1i** appeared to be more favorably reduced at -1.11 V (SCE). These measurements support that $Ir(ppy)_3$ * $\{E_{1/2} ([Ir(ppy)_3]^+/Ir(ppy)_3^*)=-1.73$ V (SCE)} is able to reduce the *O*-thiocarbamates to the corresponding radical anions. Moreover, no reduction wave is observed for the *S*-thiocarbamate **3** up to -2 V. This is consistent with the observed radical thiocarbamate group transfer (Scheme 4) when the reaction is conducted without Hünig's base and confirms that Ir-(ppy)₃* is not able to reduces *S*-thiocarbamates.

Based on all these findings, we were able to propose a mechanistic pathway for the photocatalyzed deoxygenation of imidazolyl O-thiocarbamate (Scheme 5). Under visible light activation, $Ir(ppy)_3$ is able to reach an excited state that could transfer one

Table 3. Reduction potential of thiocarbamates.^[a]

Substrate (Sub)	1 a	1b	1f	1i	1j	3
E _{red} (V) ^[b] [Sub]/[Sub]	-1.68	-1.73	-1.67	-1.11	-1.56	<-2

^[a] For cyclic voltammograms, see the Supporting Information.

^[b] The redox potentials are given in volt *versus* SCE.



Scheme 5. A proposed mechanism.

electron to the thiocarbamate moiety.^[26] This reduction process leads to the oxidation of Ir(III) to Ir(IV) species that would be reduced in turn to Ir(ppy)₃ by $(i-Pr)_2NEt$ and starts a new catalytic cycle. Then, the thiocarbamate radical anion decomposes by fragmentation to afford the intermediate carbon-centered radical. The hydrogen transfer occurs either from the amine radical cation coming from the reduction of iridium catalyst or directly by $(i-Pr)_2NEt$.^[22] This mechanism is supported by the fluorescence quenching experiments and the fact that in the absence of "Hdonor", the thiocarbamate transfer is observed.

In conclusion, we report a novel photocatalyzed deoxygenation method based on the activation of Ir-(ppy)₃ by visible light under reductive conditions. This transformation allowed us to convert secondary and tertiary aliphatic and benzylic alcohols to the corresponding alkanes in good yields. Interesting functional group tolerances were observed. A preliminary mechanistic study based on fluorescence suggested the role of the thiocarbamate substrates as oxidative quenches of Ir(ppy)₃ excited state. Moreover, the thiocarbamate transfer reaction would open new perspectives to highly versatile transformations in the fields of organic synthesis and polymer sciences.

Experimental Section

Conditions A

Into a Schlenk tube were introduced the *O*-thiocarbamate (0.5 mmol), $\text{Ir}(\text{ppy})_3$ (3.3 mg, 0.005 mmol), then CH₃CN (7.5 mL) and $(i\text{-Pr})_2$ NEt (0.435 mL, 2.5 mmol). The mixture was degassed using the freeze-pump-thaw method (3 cycles) and irradiated by blue LEDs (470 nm) until completion of the reaction (monitored by TLC). The mixture was concentrated under vacuum and the crude was purified by flash column chromatography.

Conditions B

Into a Schlenk tube were introduced the *O*-thiocarbamate (0.5 mmol), $Ir(ppy)_3$ (16.4 mg, 0.025 mmol) then DMPU (5 mL) and $(i\text{-}Pr)_2$ NEt (0.435 mL, 2.5 mmol). The mixture was degassed using the freeze-pump-thaw method (3 cycles) and irradiated by blue LEDs (470 nm) until completion of the reaction (monitored by TLC). Water was added and the mixture was extracted with Et₂O. (3×25 mL). The organic phases were gathered, dried over MgSO₄, filtered and concentrated under vacuum. The crude was purified by flash column chromatography.

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