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Sulfur Imidations by Light-Induced Ruthenium-Catalyzed Nitrene Transfer Reactions

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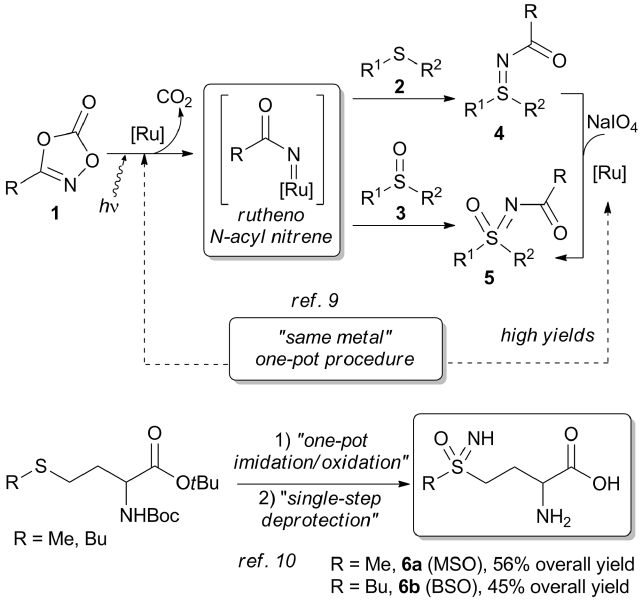
N-Acyl nitrenes have been generated from a range of heterocyclic precursors, and their applications in light-induced ruthenium-catalyzed sulfur imidations have been studied. Analyzing the reaction scope and determining the structural requirements of the in situ formed electrophilic nitrogen species for effective nitrene transfer allowed a mechanistic scheme to be proposed. The mechanistic conclusions were substantiated by the identification of potential intermediates.

Introduction

The development of original synthetic methods for the preparation of highly functionalized molecules is an ongoing challenge. Sulfimides[1] and sulfoximines[2] are characterized by core fragments with a high heteroatom content.[3] Recently, newly discovered biological properties led to a clear recognition of the value of such compounds in medicinal chemistry[4] and crop protection.[5] In the preparation of sulfimides and sulfoximines, sulfur imidations play a prominent role.[6–12] Surprisingly, only a few procedures allow the direct conversion of a sulfide or sulfoxide into the corresponding *N*-acyl sulfimide or sulfoximine. A common feature of such reactions is the involvement of an *N*-acyl nitrene or a metallo-nitrenoid.[7] In this context, an early finding by Sauer and Mayer caught our attention.[8] While investigating the reactivity of 3-substituted 1,4,2-dioxazol-5-ones **1** under photochemical or thermal conditions they found that heating **1** to 150 °C in dimethyl sulfoxide (DMSO) resulted in decarboxylation and formation of the corresponding *N*-acyl sulfoximine **5**. Hypothesizing that improvements to such a decarboxylative imidation process may be possible by applying a combination of metal catalysis and photoinitiation, we recently discovered an advanced procedure allowing the conversion of a wide range of sulfides **2** and sulfoxides **3** by utilizing a combination of **1** as *N*-acyl nitrene precursor and a catalytic amount of a ruthenium(II) porphyrin under irradiation with visible light.[9] By using this strategy, the corresponding *N*-acyl sulfimides **4** and sulfoximines **5** could be obtained in good to excellent yields (up to 99%) at ambient temperature. Noteworthy was the broad substrate scope, which allowed products with a wide range of sulfur substituents to be accessed (dialkyl, diaryl, and alkyl aryl). In addition, a "one-pot" sulfur imidation/oxidation sequence was developed by taking advantage of the same metal (ruthenium) in the reaction mixture for both oxidative steps. Accordingly, *N*-acyl sulfoximines **5** could be rapidly accessed in yields of up to 99% under mild reaction conditions starting from the corresponding sulfides **2** (Scheme 1, top). This protocol was subsequently applied to the synthesis of methionine sulfoximine (MSO, **6a**) and buthionine sulfoximine (BSO, **6b**),[10] which are two well-established chemotherapeutic agents that are known to reduce the level of glutathione in cells (Scheme 1, bottom). A comparison of the "one-pot" imidation/oxidation pro-



Scheme 1. Ruthenium-catalyzed sulfur imidation/oxidation by light-induced decarboxylation of **1** (top); application of this protocol to the synthesis of MSO and BSO (bottom).

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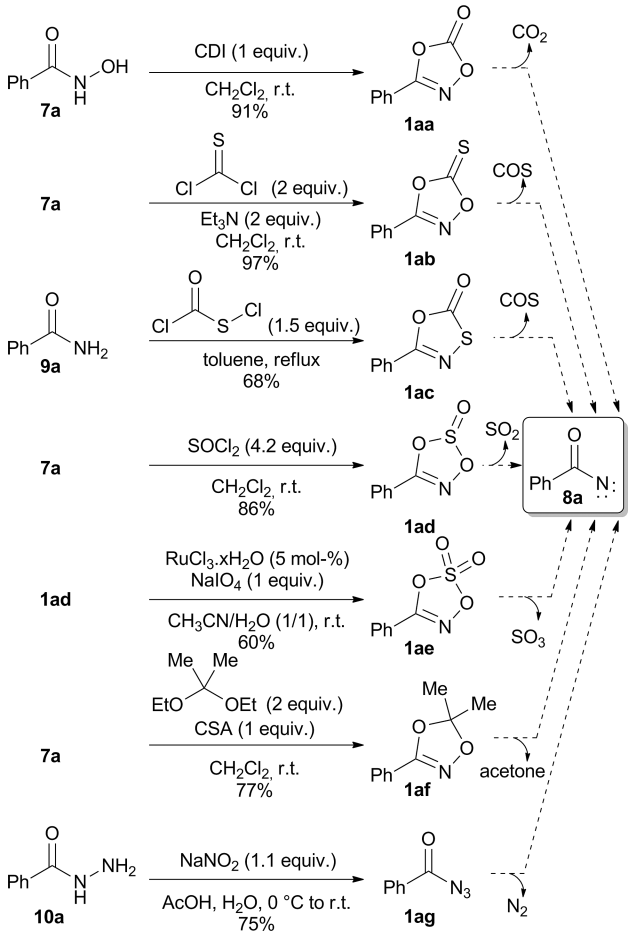
cedure with alternative approaches towards MSO/BSO revealed the superiority of the former method.

Herein, we report the details of our investigation and describe the results of mechanistic studies leading to an improved understanding of the light-induced catalytic sulfur imidation.

Results and Discussion

Choice of the *N*-Acyl Nitrene Precursor

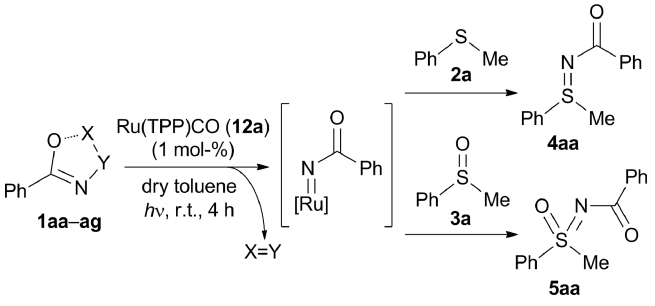
The study was initiated by the synthesis and evaluation of phenyl-substituted compounds **1aa**–**ag** (Scheme 2), which we considered to be potential sources for *N*-benzoyl nitrene (**8a**). In this series, the only variation came from the nature of the leaving group: CO_2 for **1aa**, COS for **1ab** and **1ac**, SO_2 for **1ad**, SO_3 for **1ae**, acetone for **1af**, and N_2 for **1ag**. Most of these heterocycles were obtained from *N*-hydroxybenzamide (**7a**), which was treated with a specific reagent (Scheme 2). Those were carbonyldiimidazole (CDI) for the synthesis of 3-phenyl-1,4,2-dioxazol-5-one (**1aa**; 91% yield), thiophosgene in the presence of triethylamine for 3-phenyl-1,4,2-dioxazole-5-thione (**1ab**; 97% yield), thionyl chloride to give 5-phenyl-1,3,2,4-dioxathiazole 2-oxide (**1ad**; 86% yield), and 2,2-diethoxypropane in the presence of 10-camphorsulfonic acid (CSA) providing 5,5-dimethyl-3-phenyl-1,4,2-dioxazole (**1af**; 77% yield). 5-Phenyl-1,3,4-oxathiazol-2-one (**1ac**) was prepared from benzamide (**9a**) in 68% yield by treatment with an excess of chlorocarbonylsulfenyl chloride in refluxing toluene. 5-Phenyl-1,3,2,4-dioxathiazole 2,2-dioxide (**1ae**) was obtained from **1ad** in 60% yield by using a mild ruthenium-catalyzed oxidation under phase-transfer conditions. Finally, reaction of benzohydrazide (**10a**) with sodium nitrite in the presence of acetic acid led to benzoyl azide (**1ag**) in 75% yield (Scheme 2).



Scheme 2. Syntheses of heterocycles **1aa**–**ag** to be used as precursors of *N*-benzoyl nitrene (**8a**).

The potential of compounds **1aa**–**ag** to serve as a source for *N*-benzoyl nitrene (**8a**) in photochemically-induced ruthenium-catalyzed amidations was tested in reactions with thioanisole (**2a**) and methylphenylsulfoxide (**3a**). The expected products were *N*-benzoyl sulfimide **4aa** and *N*-benzoyl sulfoximine **5aa**, respectively. As catalyst, 1 mol-% Ru(TPP)CO (**12a**) was applied. As reported previously,[9] **1aa** was a highly efficient precursor of **8a**, leading to **4aa** and **5aa** in essentially quantitative yields after 4 h of irradiation at room temperature (Table 1, entry–1). Its C=S analogue **1ab** showed moderate reactivity, affording **4aa** and **5aa** in yields of 87 and 56%, respectively (entry–2). In contrast, 5-phenyl-1,3,4-oxathiazol-2-one (**1ac**), which is an O/S isomer of **1ab**, did not react under these conditions. The S=O analogue of **1aa**, compound **1ad**, showed a low reactivity, giving **4aa** and **5aa** in only 36 and 5% yield, respectively (entry–4). Almost no reaction occurred by applying heterocycles **1ae** and **1af** (entries 5 and 6). Finally, the use of benzoyl azide (**1ag**), which is a common source of *N*-benzoyl nitrene (**8a**), was tested; again, the yields of **4aa** (5%) and **5aa** (10%) were low (entry–7).

Table 1. Light-induced ruthenium-catalyzed imidations of **4aa** and **5aa** with heterocycles **1aa**–**ag**.[a]



Entry	1a	X = Y	Yield of **4aa** [%][b]	Yield of **5aa** [%][b]
1	**1aa**	CO_2	99	99
2	**1ab**	COS	87	56
3	**1ac**	COS	0	0
4	**1ad**	SO_2	36	5
5	**1ae**	SO_3	5	0
6	**1af**	acetone	0	0
7	**1ag**	N_2	10	5

[a] Reaction conditions: **1a** (0.25 mmol), **2a** or **3a** (0.25 mmol), toluene (1 mL), irradiation with a 125 W high-pressured mercury lamp, room temperature, 4 h. [b] After column chromatography.

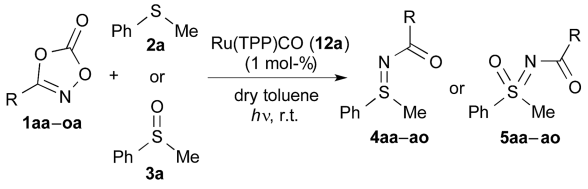
The data presented in Table 1 show that 1,4,2-dioxazol-5-one **1aa** was superior to the other heterocycles in generating an intermediate with relevance for the applied light-induced ruthenium catalysis. Generally, sulfide **2a** appeared to be more reactive than sulfoxide **3a**.

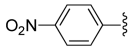
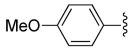
Scope and Reactivity of 1,4,2-Dioxazol-5-ones

The application of 1,4,2-dioxazol-5-ones **1ba**–**oa**, having substituents other than phenyl (as in **1aa**) at the 3-position of the heterocycle, were then studied (Table 2). Based on our earlier findings in imidations of variously substituted sulfur reagents,[9] sulfide **2a** and sulfoxide **3a** were selected as representative model substrates. High efficiencies of the photochemically-induced ruthenium-catalyzed imidations were observed, with heterocycles **1aa** and **1ba** providing the corresponding *N*-benzoyl and *N*-acetyl sulfimides (**4aa** and **4ba**) and sulfoximines (**5aa** and **5ba**) in yields up to 99% (entries 1 and 2). Applying 1,4,2-dioxazol-5-one **1ca**, having a strong electron-withdrawing CF_3 group at C3, gave less satisfactory results (entry–3). Only sulfide **2a** reacted in the expected manner, providing **4ca** in 57% yield. Mixing of **1ca** with sulfoxide **3a** led to deoxygenation of the sulfur reagent and sulfide **2a** was formed with strong effervescence. Apparently, 1,4,2-dioxazol-5-one **1ca** was highly reactive towards traces of water or other nucleophiles, rendering further studies with this heterocycle unattractive. The use of 3-ethyl- and 3-benzyl-substituted 1,4,2-dioxazol-5-one derivatives **1da** and **1ea** in the imidations of sulfide **2a** led to sulfimides **4da** and **4ea** in 92 and 86% yield, respectively, indicating that a moderate increase in size of the substituent at C3 of the 1,4,2-dioxazol-5-one had only a minor effect on the reactivity towards the sulfide. This behavior was in sharp contrast to that observed in imidations of sulfoxide **3a**, which showed low conversions in reactions with **1da** and **1ea**, providing the corresponding products **5da** and **5ea** in only 30 and 7% yield, respectively.

The same trend was observed when 1,4,2-dioxazol-5-ones **1fa** (with a 3-isopropyl) and **1ga** (with a 3-*tert*-butyl group) were treated with **2a** and **3a** (Table 2, entries 6 and 7). From these four experiments, only a single product (**4fa**) could be isolated, and the yield of this sulfimide remained moderate (57%). No products were obtained from the other three reactions. Imidations of sulfide **2a** with 1,4,2-dioxazol-5-ones bearing 2-furyl (**1ha**) and 2-thiofuranyl substituents (**1ia**) worked well, providing sulfimides **4ha** and **4ia** in 96 and 64% yields, respectively (entries 8 and 9). The analogous reactions with sulfoxide **3a** were less effective, resulting in yields of only 14% for **5ha** and 12% for **5ia**. Applying pentafluorophenyl-substituted 1,4,2-dioxazol-5-one **1ja** in the imidations of **2a** and **3a** led, to our delight, to the previously unreported *N*-pentafluorobenzoylated sulfimide **4ja** and sulfoximine **5ja** in excellent yields (entry–10). The formation of products **4ka** and **5ka** starting from **1ka** with a *p*-nitro-substituted aryl group also proceeded well (entry–11). Changing the electron-withdrawing *para*-nitro group to a *para*-methoxy substituent and using **1la** as nitrene source had a positive effect on the imidation of sulfide **2a** but rendered the conversion of sulfoxide **3a** more difficult. As a consequence, sulfimide **4la** was obtained in 99% yield, whereas sulfoximine **5la** could only be isolated in 35% yield (entry–12). This difference in reactivity between the sulfide and the sulfoxide was also revealed in attempts to imidate **2a** and **3a** with *ortho*-methoxy-substituted dioxazolone **1ma**. In this case, only sulfide **2a** reacted, and sulfoxide **3a** remained untouched. Presumably, the steric effect of the *ortho* substituent of **1ma** was responsible for the low yield (40%) of sulfimide **4ma** (entry–13). No reaction took place

Table 2. Applications of **1aa**–**oa** in the imidations of sulfide **2a** and sulfoxide **3a**.



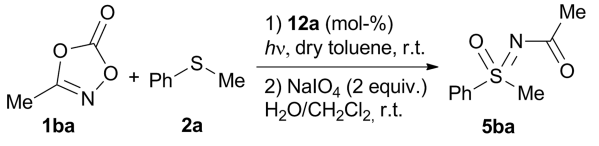
Entry	R	1	4	Yield of 4 [%][a]	5	Yield of 5 [%][a]
1	Ph	**1aa**	**4aa**	99	**5aa**	99
2	Me	**1ba**	**4ba**	98	**5ba**	95
3	CF_3	**1ca**	**4ca**	57	**5ca**	0
4	Et	**1da**	**4da**	92	**5da**	30
5	Bn	**1ea**	**4ea**	86	**5ea**	7
6	*i*Pr	**1fa**	**4fa**	57	**5fa**	0
7	*t*Bu	**1ga**	**4ga**	0	**5ga**	0
8		**1ha**	**4ha**	96	**5ha**	14
9		**1ia**	**4ia**	64	**5ia**	12
10		**1ja**	**4ja**	95	**5ja**	92
11		**1ka**	**4ka**	72	**5ka**	62
12		**1la**	**4la**	99	**5la**	35
13		**1ma**	**4ma**	40	**5ma**	0
14[b]		**1na**	**4na**	0	**5na**	0
15[b]		**1oa**	**4oa**	0	**5oa**	0

[a] Yield after column chromatography. [b] The 1,4,2-dioxazol-5-one is poorly soluble in toluene.

with either 2-hydroxyphenyl- or 4-pyridinyl-substituted heterocycles **1na** and **1oa** with either sulfide **2a** or sulfoxide **3a** (entries 14 and 15). Assuming that the lack of reactivity was due to the poor solubility of these two 1,4,2-dioxazol-5-ones in toluene, *N*,*N*-dimethylformamide (DMF) was added to the reaction mixture. As expected, the heterocycles dissolved, but, unfortunately, no reactions occurred. We assume that the heteroatoms of the pyridinyl and the phenol substituents of **1na** and **1oa** interacted with the ruthenium complex, resulting in catalyst inhibition.

Reviewing and evaluating the data presented in Table 2 led to the conclusion that the light-induced ruthenium catalysis for sulfur imidations was highly effective in providing a wide range of *N*-acylated sulfimides and sulfoximines in moderate to excellent yields. Particularly noteworthy are the sulfide imidations because they lead to products that are commonly difficult to prepare by alternative routes because they require *N*-acylation reactions of rather unstable and difficult to handle *N*H-sulfimides.[11]

The initially described one-pot sulfur imidation/oxidation sequence (Scheme 1) allows the direct transformation of sulfides into *N*-acyl sulfoximines under essentially neutral conditions.[9] Both reaction steps are catalyzed by the same ruthenium source. We then investigated how much the catalyst loading could be reduced in up-scaled reactions; the results are shown in Scheme 3. Under the original reaction conditions involving the use of 1 mol-% Ru(TPP)CO (**12a**) as catalyst on a 0.25 mmol scale, product **5ba** was obtained in 92% yield. To our delight, increasing the reaction scale to 2.5 mmol allowed the amount of catalyst to be reduced to 0.2 and 0.1 mol-%, providing **5ba** in even higher yields of 97 and 95%, respectively. Furthermore, an improved reactivity in the imidation step was observed, leading to complete sulfide conversion after only 4–5 h. Although the subsequent oxidation was comparably slow (overnight), it is clear that this newly developed one-pot procedure is superior to the existing methods towards *N*-acyl sulfoximines. This is particularly true for sensitive compounds, which benefit from the neutral conditions of both of the aforementioned oxidative transformations.

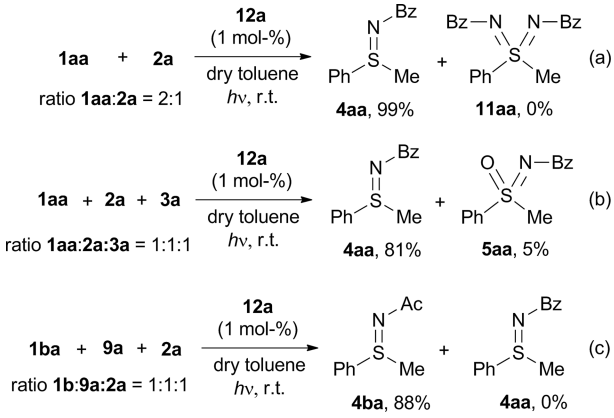


Scale (mmol)	**12a** (mol-%)	Yield **5ba** (%)
0.25	1	92
2.5	0.2	97
2.5	0.1	95

Scheme 3. Scale and required catalyst loadings.

Mechanistic Investigations

With the goal of gaining deeper mechanistic insights, competition experiments were performed. First, the imidating power of the 1,4,2-dioxazol-5-ones was addressed by taking **1aa** as a representative example (Scheme 4). As described before (Table 1, entry–1), reactions with equimolar amounts of **1aa** and sulfide **2a** afforded sulfimide **4aa** in 99% yield. Given that **4aa** could be further oxidized to sulfoximine **5aa**, it was hypothesized that sulfondiimide **11aa** might be formed in reactions of **2a** with an excess of the imidating agent (Scheme 4, a). However, this was not the case; even with 2 equiv. **1aa**, sulfondiimide **11aa** remained undetected and the yield of sulfimide **4aa** was unchanged (99%). Apparently, compared with the sulfide sulfur in **2a**, the mono-imidated sulfur in **4aa** was not sufficiently nucleophilic to be imidated for a second time, rendering the overall process highly selective even in the presence of an excess of the imidating agent.



Scheme 4. Comparative sulfur imidations.

The same trend was observed when the catalysis was performed with a mixture of equimolar amounts of **1aa**, sulfide **2a**, and sulfoxide **3a** (Scheme 4, b). In this case, sulfimide **4aa** was also the main product (81% yield), and the yield of sulfoximine **5aa** was only 5%.

The importance of using a well chosen *N*-acyl nitrene source was demonstrated by a crossover experiment involving 3-methyl-1,4,2-dioxazol-5-one (**1ba**), benzamide (**9a**), and sulfide **2a**. Applying these compounds in an equimolar ratio led to the exclusive formation of sulfimide **4ba** by reaction of **1ba** with **2a** (Scheme 4, c). The lack of reactivity of **9a** was confirmed in a separate experiment with **2a** as substrate. Again, none of the expected product **4aa** was observed, showing that for the newly developed sulfur imidation, the use of compounds such as 1,4,2-dioxazol-5-one **1** was essential.

In our initial work we demonstrated that the combination of ruthenium and light was essential for achieving sulfur imidations.[9] We now wondered whether the applied ruthenium porphyrin [Ru(TPP)CO, **12a**] could be replaced by another photocatalyst (Figure 1). The first answers were given by performing imidations with ruthenium complexes having ligands with substituted aryl groups.[9,13] As for **12a** with phenyl substituents, the use of porphyrin **12b**, having tolyl groups, revealed an exceptionally high catalytic activity in the *N*-benzoyl nitrene transfer from **1aa** onto **2a**, leading to **4aa** in 99% yield. In contrast, mesityl-bearing ruthenium porphyrin **12c** showed low reactivity, providing

sulfimide **4aa** in only approximately 10%. Most likely the eight *ortho*-methyl substituents on the four arenes led to steric hindrance at the metal core, hampering the formation of relevant intermediates. Ruthenium porphyrin **12d**, with pentafluorophenyl substituents, also showed a low catalytic activity, which we interpreted as a hint for the requirement of having a metal center with reasonable electron density. When the latter was reduced by the presence of strongly electron-withdrawing substituents on the ligand, the catalytic activity was diminished. When the ruthenium catalyst was replaced by the non-metallic photosensitizers Rose Bengal (**13a**) and Rose Bengal lactone (**13b**), no reactions occurred.[14] This observation strengthened our hypothesis that N-bound nitrene/ruthenium species were relevant for the success of the imidation process.[15,16]

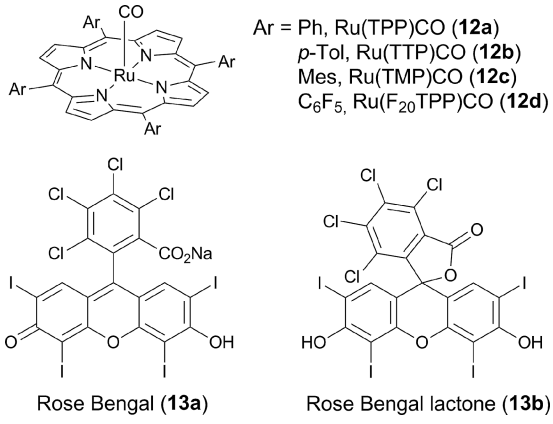


Figure 1. Ruthenium prophyrins and non-metallic photocatalysts applied in the imidation process.

Commonly, a high-pressure mercury lamp (200–600 nm) was used for the photochemical activation of the catalyst. Given that the maximum absorption (λ_{max}) of **12a** was determined to be at 410 nm, it was envisaged that the efficiency of the catalysis could be increased by performing the reaction in a photochemical reactor with a fixed wavelength at 400 nm. However, this attempt proved unfruitful. First, the reactivity was essentially unchanged, confirming our assumption that the reaction was induced by visible light. Second, the temperature increase in the photochemical reactor led to unproductive side reactions (such as Curtius rearrangements), rendering this approach synthetically less attractive.

Hypothesizing that the light-induced decarboxylation of **1** involved electron transfer processes, which could be affected by good electron acceptors, the imidation of **3a** with **1aa** was performed in the presence of 20 mol-% *p*-dinitrobenzene. As a result, the yield of **5aa** decreased to only 23%. Using 20 mol-% terephthalonitrile as electron acceptor led to the formation of **5aa** in 29% yield. Almost the same result (22% yield of **5aa**) was observed when the radical scavenger 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO; 1 equiv.) was added to the reaction mixture. Formation of a TEMPO adduct was not observed. Taking the results together, we regard the decreased yields in these experiments as evidence for electron transfer events playing a significant but not necessarily decisive role in the newly discovered imidation reaction.

With the goal of identifying possible ruthenium-containing intermediates such as rutheno *N*-acyl nitrenes,[16] high-resolution mass spectrometry (MS) experiments were performed. After mixing of **12a** and **1ba** in a 1:20 ratio under visible light irradiation, aliquots of the reaction mixture were taken after 10, 30, and 60 min. The samples were then dissolved in acetonitrile and analyzed by MS spectrometry using the electrospray ionization mode.[17] After 10 min, MS analysis (Figure 2) showed a predominance of the starting ruthenium complex **B** with a cluster peak at *m*/*z* 744.13312 (*m*/*z* calcd. 744.14576). Another weaker signal at *m*/*z* 714.13564 (*m*/*z* calcd. 714.13520) indicated the formation of a ruthenium complex **A** formed from **B** by loss of CO. Of main significance was the cluster peak at *m*/*z* 796.18869 (*m*/*z* calcd. 796.16208), which we attributed to a rutheno *N*-acyl nitrene complex (with an associated Na^+) **C**, formed from complex **A** and **1ba** upon loss of CO_2. After 30 and 60 min, similar cluster peaks were obtained along with other signals above *m*/*z* 1400, probably stemming from fragmentations and associations of the aforementioned species in the spectrometer. Although no rutheno bis(*N*-acyl nitrene) complex was detected in this ESI-MS experiment, the formation of such species cannot be ruled out.[17] An attempt to apply phenyl-substituted 1,4,2-dioxazol-5-one **1aa** (instead of **1ba**) in an analogous MS study was unsuccessful. Presumably due to a rapid Curtius-type rearrangement of the intermediately formed phenylacyl nitrene, no related rutheno species could be detected.

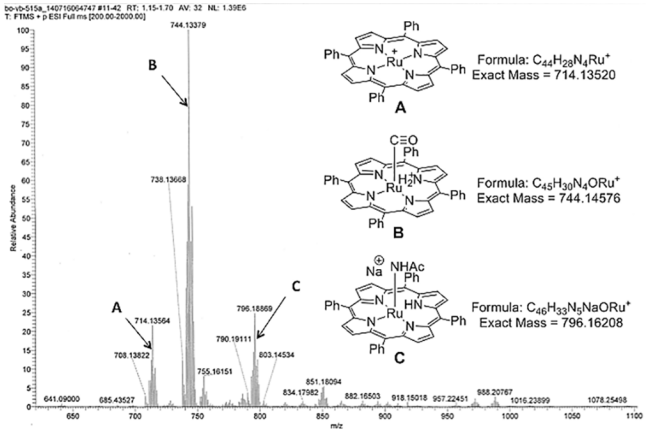
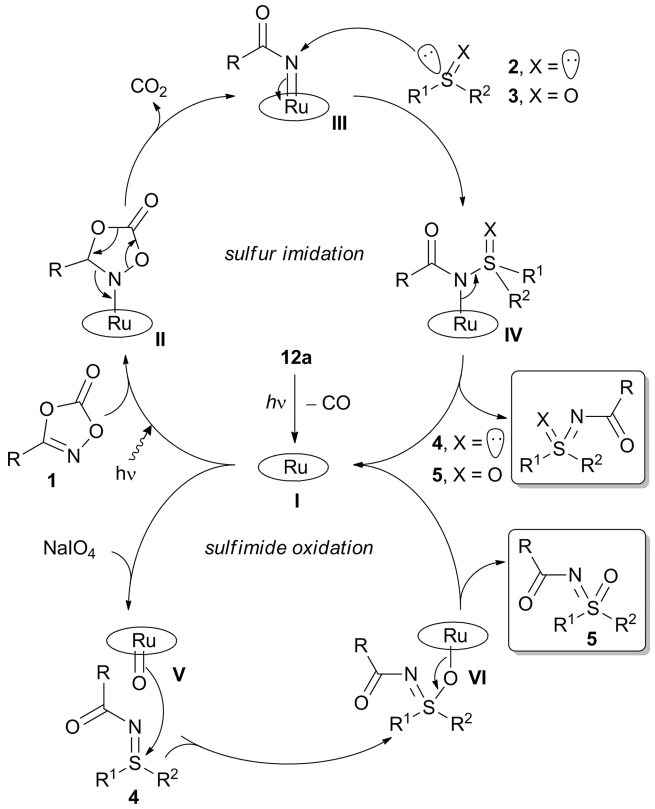


Figure 2. Structures of proposed ruthenium intermediates observed in MS experiments.

Based on the detection of *N*-acyl nitrene-bound ruthenium complex **C**, the following reaction mechanism for the sulfur imidation can be proposed (Scheme 5). Upon light irradiation, ruthenium porphyrin **12a** loses CO, leading to a new complex **I** (which was observed as complex **A** by MS; Figure 2) having an open coordination site. Through one of the heteroatoms, 1,4,2-dioxazol-5-one **1** interacts with **I**, forming ruthenium complex **II**.



Scheme 5. Proposed mechanism for the light-induced ruthenium-catalyzed sulfur imidation/oxidation reactions.

Loss of CO_2 provides rutheno *N*-acyl nitrene complex **III** (which was observed as Na^+ adduct **C** by MS; Figure 2). Interaction of **III** with the sulfur atom of sulfide **2** or sulfoximine **3** allows a *N*-acyl nitrene transfer reaction (via a complex such as **IV**), providing the imidated products **4** or **5**, respectively. Concomitantly, ruthenium complex **I** is regenerated, starting a new catalytic cycle. The subsequent sulfimide oxidation can then either involve an oxo-ruthenium complex such as **V**[18] and proceed via **VI**, or it may be catalyzed by a new ruthenium species generated by degradation of **12a** upon reaction with the oxidant ($NaIO_4$).

Conclusions

We have studied various *N*-acyl nitrene precursors in light-induced ruthenium-catalyzed imidations of sulfides and sulfoxides and found that 3-substituted 1,4,2-dioxazol-5-ones **1** were the most reactive species. In this manner, a wide range of N-substituted sulfimides and sulfoximines has been prepared. Crossover experiments revealed an activity grading, and potentially catalytic intermediates were identified by ESI-MS. The evaluation of all reaction details allowed a mechanistic scheme summarizing the observed proceedings to be proposed. Further studies regarding the use of **1** as *N*-acyl nitrene precursors in reactions with other nucleophiles are ongoing in our laboratories, and the results will be published in due course.

Experimental Section

General Procedure for the Sulfur Imidation: To a solution of sulfide **2** or sulfoxide **3** (0.25 mmol) and 1,4,2-dioxazol-5-one **1** (0.25 mmol) in anhydrous toluene (1 mL) under argon was added Ru(TPP)CO (1.9 mg, 0.0025 mmol). The reaction mixture was irradiated with a 125 W high-pressure mercury lamp at room temperature until full conversion was reached (as analyzed by TLC). The mixture was concentrated under reduced pressure and purified by column chromatography over silica gel (pentane/ethyl acetate) to give the corresponding *N*-acyl sulfimide **4** or sulfoximine **5**.

General Procedure for the "One-Pot" Sulfur Imidation/Oxidation: Upon completion of the imidation step, the mixture was concentrated under reduced pressure to remove toluene and was then dissolved in dichloromethane (2.5 mL). A solution of sodium periodate (107 mg, 0.5 mmol) in water (1.25 mL) was added and vigorous stirring of the reaction mixture was performed by using a magnetic cross-shaped stir bar. After full conversion (one night at room temperature), the mixture was extracted with dichloromethane, dried with sodium sulfate, and concentrated under reduced pressure. The product was then purified by column chromatography over silica gel (pentane/EtOAc) to give the corresponding *N*-acyl sulfoximine **5**.

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