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Synthetic Methods

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Light-Induced Ruthenium-Catalyzed Nitrene Transfer Reactions: A Photochemical Approach towards N-Acyl Sulfimides and Sulfoximines**

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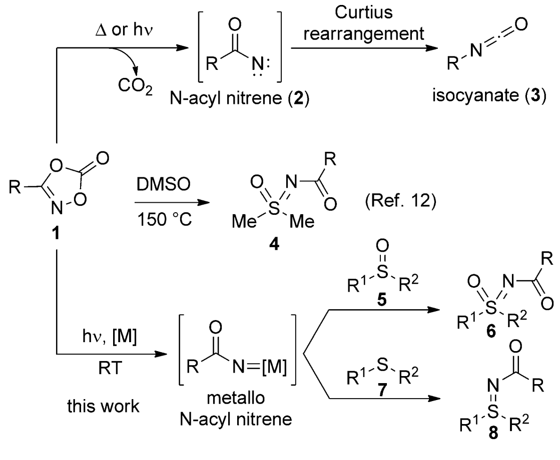
Abstract: *1,4,2-Dioxazol-5-ones are five-membered heterocycles known to decarboxylate under thermal or photochemical conditions, thus yielding N-acyl nitrenes. Described herein is a light-induced ruthenium-catalyzed N-acyl nitrene transfer to sulfides and sulfoxides by decarboxylation of 1,4,2-dioxazol-5-ones at room temperature, thus providing direct access to N-acyl sulfimides and sulfoximines under mild reaction conditions. In addition, a one-pot sulfur imidation/oxidation sequence catalyzed by a single ruthenium complex is reported.*



Scheme 1. Reactivity of 1,4,2-dioxazol-5-ones (**1**).

Over the last fifty years, various methods for the synthesis of sulfimides and sulfoximines have been reported.[1,2] Some of those products showed relevant biological properties in crop protection[3] and medicinal chemistry.[4] Our interest has been focused on the application of such sulfur reagents in asymmetric catalysis.[5] For most synthetic approaches towards sulfimides and sulfoximines, sulfur imidations of sulfides and sulfoxides, respectively, are key transformations, and consequently several protocols have been developed.[6–13] However, only few such methods give direct access to N-acylated derivatives, which are synthetically valuable because of the ease of subsequent N functionalization. An early example stems from Swern and co-workers, who prepared N-acyl sulfimides by reaction of sulfides with *N*-bromoacetamides and subsequent treatment of the resulting *N*-acetylimino sulfonium bromides with base.[7] Other methods involve the use of imidation reagents such as *N*-phenyliodonio carboxamide tosylates,[8] *N*,*O*-bis(trifluoroacetyl)hydroxylamine in combination with a catalytic amount of a copper(II) salt,[9] nitridomanganese(V) complexes with trifluoroacetic anhydride,[10] and trifluoroacetamide in the presence of a catalytic amount of a rhodium(II) complex.[11] Mechanistically, they appear to proceed via N-acyl nitrenes or the corresponding (metal)nitrenoids.

An interesting alternative N-acyl nitrene formation was reported by Sauer and Mayer, who studied the reactivity of 3-substituted-1,4,2-dioxazol-5-ones (**1**; Scheme 1).[12] They found that these heterocycles decarboxylated under thermal or photochemical conditions, thus generating highly reactive N-acyl nitrenes (**2**), which rearranged to the isocyanates **3**. An important stimulus for our research was the observation that the N-acyl sulfoximines **4** were formed when the reactions were performed in DMSO at 150 °C. Although the yields of **4** were mostly moderate, we hypothesized that improvements were possible by applying a combination of photoinitiation and metal catalysis.[14] Herein we report on the success of this approach and the development of sulfoxide and sulfide imidations which proceed by the photolysis of **1** in the presence of a ruthenium catalyst, thus providing the N-acyl sulfoximines **6** and N-acyl sulfimides **8** at room temperature.

The study was initiated by a catalyst screening with 3-phenyl-1,4,2-dioxazol-5-one (**1a**) and methylphenylsulfoxide (**5a**) as starting materials. The results are summarized in Table 1. By applying slightly modified reaction conditions, relative to those described by He and co-workers,[14] using [Ru(TPP)CO][15] in toluene at 50 °C for 18 hours, success was achieved. The desired *N*-benzoyl sulfoximine **6aa** was indeed formed, albeit in only low yield (37 %). The major product was *N*,*N*′-diphenyl urea (**9a**), which resulted from a hydrolytic process of the intermediate phenyl isocyanate (**3a**). Photochemical activation of the catalysis allowed lowering of the reaction temperature (from 50 °C to RT) and shortening of the reaction time (from 18 h to 6 h), but unfortunately, also under those reaction conditions, the undesired **9a** remained the major product (Table 1, entry 2). Realizing that water played a prominent role in the formation of **9a**, the catalysis was next performed under inert conditions using dry toluene as the solvent. To our delight, **6aa** was now the exclusive product, and was isolated in 99 % yield after 4 hours at

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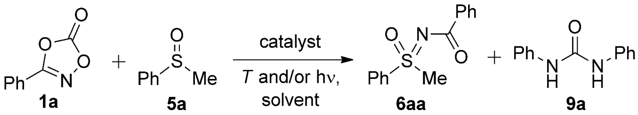
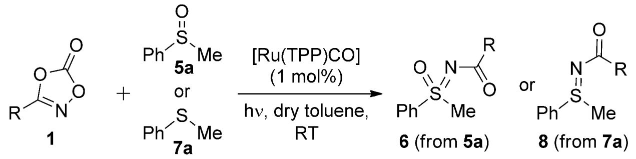
Table 1: Optimization of the reaction conditions.



Entry	Catalyst	Solv.[a]	T	t [h]	$h\nu$	Yield [%]	
						6aa	**9a**
1	[Ru(TPP)CO]	tol[b]	50°C	18	–	37	61
2	[Ru(TPP)CO]	tol[b]	RT	6	+	45	54
3	[Ru(TPP)CO]	tol	RT	4	+	99	0
4	–	tol	RT	4	+	0	0
5[c]	[Ru(TPP)CO]	tol	RT	18	–	0	0
6	[Ru(TPP)CO]	tol	50°C	18	–	42	9
7[c]	[Ru(TPP)CO]	tol	50°C	18	–	3	11
8	[Ru(TMP)CO]	tol	RT	4	+	2	0
9	[Ru(F_{20}-TPP)CO]	tol	RT	4	+	9	0
10	[$Rh_2(OAc)_4$]	tol	RT	4	+	0	0
11	[$Rh_2(OAc)_4$]	CH_2Cl_2	RT	4	+	0	0
12	[$RuCl_2$(*p*-Cym)]$_2$	tol[d]	RT	4	+	5	0
13	[$RuCl_2$(*p*-Cym)]$_2$	CH_2Cl_2	RT	4	+	31	0
14	[Ru(TPP)CO]	CH_2Cl_2	RT	4	+	21	75
15	[Ru(TPP)CO]	THF	RT	6	+	0	0
16	[Ru(TPP)CO]	MeCN[d]	RT	6	+	0	0

[a] Unless noted otherwise, dry solvents were used; tol = toluene. [b] Non-distilled solvent. [c] The reaction was carried out in the dark. [d] The catalyst was poorly soluble in this solvent.

Table 2: Imidations of **5a** and **7a** with various 1,4,2-dioxazol-5-ones (**1**).[a]



Entry	1	R	6 Yield [%]	8 Yield [%]
1	**1a**	Ph	99 (**6aa**)	99 (**8aa**)
2	**1b**	Me	95 (**6ba**)	98 (**8ba**)
3	**1c**	Bn	7 (**6ca**)[b]	86 (**8ca**)
4	**1d**	*t*Bu	0 (**6da**)[c]	0 (**8da**)[c]
5	**1e**	CF_3	0 (**6ea**)[c]	54 (**8ea**)
6	**1f**[d]	*p*MeOC_6H_4	35 (**6fa**)	99 (**8fa**)
7	**1g**[e]	*p*$NO_2C_6H_4$	62 (**6ga**)	72 (**8ga**)

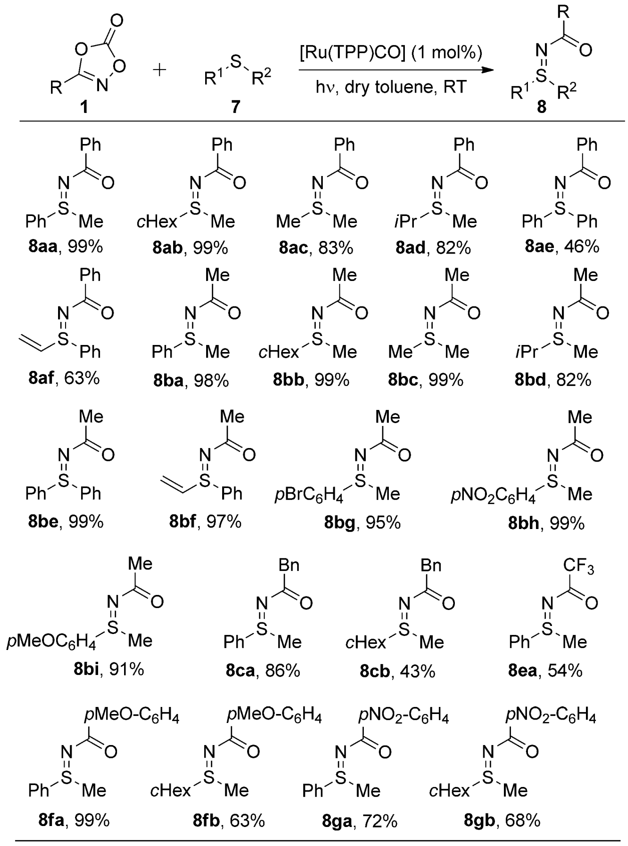
[a] Reaction were conducted until full consumption of **1**. [b] The sulfoximine was obtained in a mixture with the corresponding urea. [c] Decomposition of **1** was observed. [d] Use of 3 mL of toluene instead of 1 mL. [e] Use of 2 mL of toluene instead of 1 mL.

ambient temperature (Table 1, entry 3). Additional experiments revealed that the presence of both [Ru(TPP)CO] and light were essential for promoting the reaction at room temperature (Table 1, entries 4 and 5). Under thermal conditions using dry toluene as the solvent, **6aa** was obtained in 42% yield (Table 1, entry 6). Performing the reaction in the dark at 50°C led to **6aa** in only 3% yield (Table 1, entry 7), thus highlighting the importance of the photochemical activation in this process. We assume that the light provides the essential energy for the formation of a reactive rutheno N-acyl nitrene intermediate without reaching the higher level of energy required for the Curtius rearrangement which leads to isocyanates.[16] Other ruthenium porphyrin catalysts such as [Ru(TMP)CO] and [Ru(F_{20}TPP)CO], as well as [$RuCl_2$(*p*-Cym)]$_2$ and [$Rh_2(OAc)_4$] were less efficient or ineffective (Table 1, entries 8–13).[15,17] In terms of solvents, toluene proved to be superior over CH_2Cl_2, THF, or acetonitrile (Table 1, entry 3 versus entries 14–16).

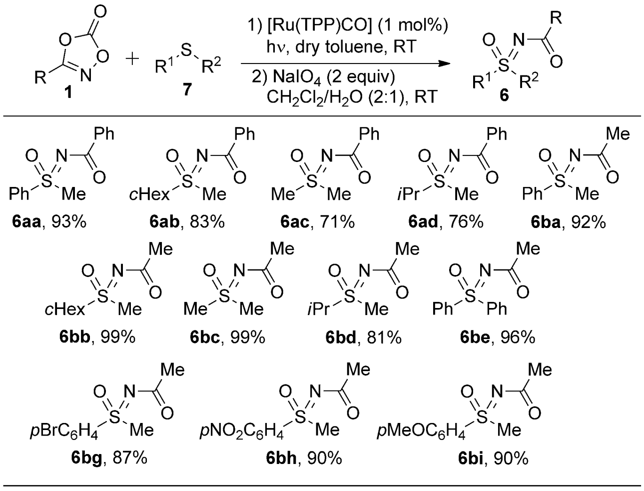
An initial test reaction showed that **1a** reacted equally well with the sulfide **7a**, just as it did with the sulfoxide **5a**, under the photocatalytic conditions with [Ru(TPP)CO] to give **8aa** in 99% yield (Table 2, entry 1). Hence, the subsequent evaluation of the substrate scope involved both of these starting materials, which were explored in their reactivity with a range of 1,4,2-dioxazol-5-ones (**1**). With the exception of the 3-*tert*-butyl-substituted derivative **1d** (Table 2, entry 4), which proved to be unstable under the reaction conditions, all the 1,4,2-dioxazol-5-ones **1** showed a pronounced N-acyl nitrene transfer ability, thus providing the corresponding N-acylated sulfoximines **6** and sulfimides **8** in yields of up to 99%. In general, **5a** was less reactive than sulfide **7a**, as examplified by the comparison of the respective iminations providing the N-acyl sulfoximine **6ca** and N-acyl sulfimide **8ca.** Whereas the former was only obtained in a very low quantity [<7%, as an inseparable mixture with *N,N'*-dibenzylurea (**9c**)], the latter was isolated in 86% yield (Table 2, entry 3). The conversions of **5a** and **7a** with 3-trifluoromethyl-substituted 1,4,2-dioxazol-5-one (**1e**; Table 2, entry 5) were limited by the sensitivity of the iminating agent towards traces of water, and an undesired deoxygenation of **5a**, thus forming sulfide **7a**. As a result, **5a** could not be iminated, and the sulfimide **8ea** was obtained from **7a** in only moderate yield (54%).

Encouraged by the high reactivity and pronounced selectivity in the imidations of **7a** with various 1,4,2-dioxazol-5-ones (**1**), respective transformations of diversely substituted sulfides were investigated next. The results are shown in Scheme 2. In general, the positive data obtained in the conversions of **7a** were reflected in this study. Thus, sulfides with an alkyl/alkyl substitution pattern reacted equally well with **1a**, thus providing the corresponding products (**8ab**, **8ac**, and **8ad**) in yields ranging from 82 to 99%. Only the imidations of diphenylsulfide (**7e**) and phenylvinyl sulfide (**7f**) with **1a** proved more difficult, thus leading to the corresponding sulfimides (**8ae** and **8af**) in yields of 46 and 63%, respectively. Further improvements were observed when **1b** was used as imidating agent, thus providing sulfimides **8ba–bi**. Now, the yields were generally high (82–99%) irrespective of the substitution pattern of the sulfide. Noteworthy also is that sulfides with bromo, nitro, and methoxy substituents in the *para* position of the *S*-aryl group reacted well, thus providing the corresponding N-acyl sulfimides **8bg–bi** in high yields. As expected from the initial study with **7a** (Table 2), the other 1,4,2-dioxazol-5-ones (**1c**, **1e–1g**) could be used to deliver the N-acylated sulfimides **8ca–gb** in moderate to high yields (43–99%).

Motivated by the positive results of the aforementioned photochemically-induced ruthenium-catalyzed imidation of sulfides (Scheme 2), we wondered about the possibility to



Scheme 2. Scope of the sulfide imidation.



Scheme 3. Scope of the one-pot imidation/oxidation reaction.

directly prepare the corresponding synthetically highly appreciated N-protected sulfoximines by introducing a subsequent one-pot metal-catalyzed sulfimide oxidation.[18] We hypothesized that this second step could then take advantage of the ruthenium complex already present in the medium. In fact, [Ru(TPP)CO] was known to react with an oxidant to give [Ru(TPP)O_2], which was capable of oxidizing sulfides.[19,20] To evaluate the potential of the oxidation step following this strategy, **8aa** was treated with a mixture of 1 mol% of [Ru(TPP)CO] and 2 equivalents of $NaIO_4$. In the first attempt, toluene was chosen as solvent because it proved essential for the first step (imide formation). Unfortunately, however, even after 72 hours the yield of **6aa** was only 9% (in combination with traces of methyl phenyl sulfone detected by NMR spectroscopy; 79% of **8aa** were re-isolated). To increase the solubility of the oxidant in the reaction mixture, water was added (toluene/water = 2:1), and to our delight, under the biphasic conditions the yield of **6aa** increased to 77% (with traces of sulfone; 20% of re-isolated **8aa**). Finally, the best reaction conditions were obtained with a 2:1 mixture of CH_2Cl_2 and water for the ruthenium-catalyzed oxidation of **8aa** with $NaIO_4$, thus affording **6aa** in 99% yield after only 4 hours at room temperature. This result paved the path for the intended one-pot imidation/oxidation protocol leading to N-acyl sulfoximines starting from sulfides (Scheme 3). All substitution patterns (dialkyl, alkyl/aryl, and diaryl) on the sufide were well tolerated, and the desired products **6** were obtained in good to excellent yields (71–99%).

To the best of our knowledge, this direct catalytic imidation/oxidation sequence has no precedence in the literature. With a single metal complex two very distinct substrate oxidations are achieved. While the first step requires a mild photochemical activation of 3-substituted 1,4,2-dioxazol-5-ones, the second makes use of a simple inorganic oxidant under phase-transfer catalysis. Overall, a variety of sulfides can directly be converted in one pot into synthetically valuable N-protected sulfoximines. Mechanistic investigations and further attempts to expand the substrate scope are currently ongoing in our laboratories.

Experimental Section

General procedure for the sequential one-pot imidation/oxidation: [Ru(TPP)CO] (1.9 mg, 0.0025 mmol) was added to a solution of sulfide **7** (0.25 mmol) and 1,4,2-dioxazol-5-one **1** (0.25 mmol) in dry toluene (1 mL) under argon. 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 to remove toluene and 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 rigorous stirring of the reaction mixture was performed using a magnetic cross-shaped stir bar. After full conversion (one night at room temperature), the mixture was extracted with dichloromethane, dried over sodium sulfate, and concentrated under reduced pressure. The product was then purified by column chromatography over silica gel (pentane/AcOEt) to give the corresponding N-acyl sulfoximine **6**.

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Communications

Synthetic Methods

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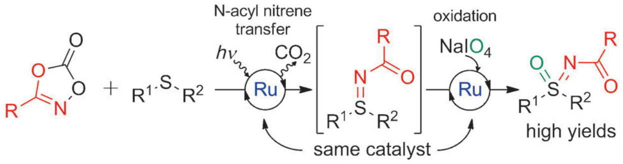
Light-Induced Ruthenium-Catalyzed Nitrene Transfer Reactions: A Photochemical Approach towards N-Acyl Sulfimides and Sulfoximines



Double duty: A one-pot sulfur imidation/oxidation sequence using a single ruthenium complex for both steps was developed (see scheme). Photochemical decarboxylations of 1,4,2-dioxazol-5-ones provide N-acyl nitrenes, which imidate sulfides at ambient temperature. The subsequent oxidation then occurs under mild phase-transfer catalysis conditions. In this manner, N-acyl sulfimides and sulfoximines can be obtained in high yields starting from sulfides.