Ruthenium Catalysis

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Ruthenium-Catalyzed Oxidative Transformations of Terminal Alkynes to Ketenes By Using Tethered Sulfoxides: Access to β-Lactams and Cyclobutanones**

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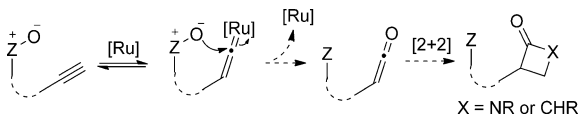
Abstract: *The oxidation of in situ generated Ru vinylidenes to ketenes is realized with tethered sulfoxides. The result is a Ru-catalyzed oxidative transformation of terminal alkynes to highly valuable ketenes. Moreover, the ketenes generated here were shown to undergo characteristic ketene [2+2] cycloaddition reactions with tethered alkenes and external imines, yielding synthetically versatile bicyclic cyclobutanones and β-lactams, respectively.*

Ruthenium vinylidenes[1] are versatile intermediates in organic synthesis. Owing to their ready accessibility from terminal alkynes, ruthenium vinylidenes have served as an entry into a diverse range of efficient transformations,[2] in which the carbene center reacts with various nucleophiles. To date, the oxidation[3] of in situ-generated Ru vinylidenes to synthetically useful ketenes[4] (Scheme 1), thereby realizing



Scheme 1. Ru-catalyzed oxidation of a terminal alkyne to a ketene and subsequent [2+2] cycloaddition reactions.

the Ru-catalyzed oxidative transformation of a terminal alkyne into a ketene, has had limited success. An exception is the excellent work by Liu and co-workers[5] using tethered epoxides or nitrones as the oxidants, which were, however, confined in conformationally rigid systems. Recently, Lee reported that a Rh complex could catalyze this transformation with either internal or external oxidants;[6] however, the generated ketenes were trapped only by heteronucleophiles, leading to the formation of esters, amides, and acids.[7] Herein, we disclose a Ru-catalyzed oxidation of terminal alkynes into ketenes with flexibly tethered sulfoxides[6,8] as internal oxidants under mild reaction conditions. Most importantly, besides being trapped by heteronucleophiles, these oxidatively generated ketenes were shown to undergo the characteristic ketene [2+2] cycloaddition[9] with tethered alkenes and external imines.[7] This offers strong evidence for the intermediacy of a ketene and yields synthetically versatile and strained cyclobutanones and β-lactams,[10] respectively, in mostly good yields.

At the outset, we chose the enynyl aryl sulfoxide **1a** as the substrate and anticipated that if its terminal alkyne could be converted into a ketene moiety (as in **B**) an intramolecular [2+2] cycloaddition with the tethered C=C bond would afford the bicyclic cyclobutanone **2a** (Table 1).[11] The substrate was readily prepared from chloroacetone in four steps and was obtained as a mixture of diastereoisomers (d.r. 1.1:1, see the Supporting Information, SI). This mixture was treated with various ruthenium catalysts under different conditions. Whereas Ru^{III} catalysts such as $RuCl_3$ (entry 1) and $[Ru(acac)_3]$ (entry 2) did not promote the reaction at all, a Ru^{II} catalyst, $[Ru(CO)_3]Cl_2$, did catalyze the reaction albeit **2a** was formed in only 20% yield (entry 3). $[CpRu(PPh_3)_2]Cl$, a typical catalyst for the generation of ruthenium vinylidenes,[12] was ineffective in the absence of a chloride scavenger (entry 4).[13] However, when $NaPF_6$ (10 mol%) was added, the desired bicyclic cyclobutanone **2a** was formed in 36% yield (entry 5). A nearly equal amount of a bicyclic aldehyde side product, i.e., **3a**, was isolated as a single diastereoisomer (for a proposed mechanism, see SI).

To our surprise, no reaction occurred when the bulkier $[Cp^*Ru(PPh_3)_2]Cl$ was employed (entry 6). The fact that **3a** was formed in a large amount in entry 5 suggested that the generation of ruthenium vinylidenes was not efficient. The phosphine ligand **L1**, an AZARPHOS in which the pyridine nitrogen atom is sterically shielded from coordinating to Ru,[14] is known to facilitate the Ru-catalyzed anti-Markovnikov hydration of terminal alkynes[15] by accelerating the isomerization of the terminal alkyne to the corresponding Ru vinylidene.[16] Indeed, when 10 mol% of **L1** was added, the yield of **2a** increased to 81% and the formation of **3a** (4% yield) was significantly suppressed (entry 7). An even better result was attained with the synthetically more accessible AZARPHOS **L2** (entry 8).[14] Lowering the ligand loading to 5 mol%,[17] however, decreased the yield (entry 9). Little improvement was achieved when the chloride scavenger was changed to $AgNTf_2$ (entry 10), but $NaBAr^F_4$ (entry 11) proved to be superior, and the bicyclic cyclobutanone **2a** was formed in 90% NMR yield. Acid side products were observed in the above reactions and confirmed by a reaction in the presence of 10 equiv of H_2O (see SI for details); however, when the reaction was run in the presence of 4 Å MS, **2a** was isolated in excellent yield(entry 12). A lower yield was detected when the reaction was run at a much higher

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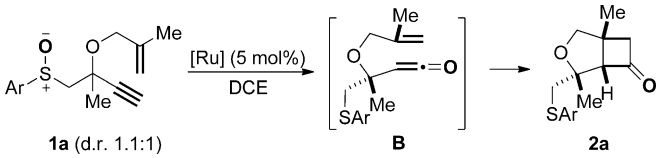
Table 1: Initial reaction discovery and optimization.[a]



1a (d.r. 1.1:1) **B** **2a**

Entry	Catalyst	Ligand (mol%)	T [°C], t [h]	**2a**[b], **3a** [%][c]
1	$RuCl_3$	none	80, 24	0, <1
2	$[Ru(acac)_3]$	none	80, 24	0, 0
3	$[Ru(CO)_3]Cl_2$	none	80, 24	20, <1
4	$[CpRu(PPh_3)_2]Cl$	none	60, 2	0, 0
5	$[CpRu(PPh_3)_2]Cl$, $NaPF_6$ (10 mol%)	none	40, 2.5	36, 37
6	$[Cp^*Ru(PPh_3)_2]Cl$, $NaPF_6$ (10 mol%)	none	80, 24	0, 0
7	$[CpRu(PPh_3)_2]Cl$, $NaPF_6$ (10 mol%)	**L1** (10)	60, 2	81, 4
8	$[CpRu(PPh_3)_2]Cl$, $NaPF_6$ (10 mol%)	**L2** (10)	60, 4	86, <2
9	$[CpRu(PPh_3)_2]Cl$, $NaPF_6$ (10 mol%)	**L2** (5)	60, 4	72, 8
10	$[CpRu(PPh_3)_2]Cl$, $AgNTf_2$ (5 mol%)	**L2** (10)	60, 1	87, 2
11	$[CpRu(PPh_3)_2]Cl$, $NaBAr^F_4$ (10 mol%)	**L2** (10)	60, 1.5	90, <1
12[d]	**$[CpRu(PPh_3)_2]Cl$, $NaBAr^F_4$ (10 mol%)**	**L2 (10)**	**60, 1.5**	**93 (94)**[e], **<1**
13[d,f]	$[CpRu(PPh_3)_2]Cl$, $NaBAr^F_4$ (10 mol%)	**L2** (10)	60, 1.5	80, <1
14[d]	$[CpRu(\mathbf{L2})_2(MeCN)]^+PF_6^-$	–	60, 16	82, <2
15[d]	$[CpRu(\mathbf{L2})(PPh_3)(MeCN)]^+PF_6^-$	–	60, 6.5	81, 6
16[d,g]	$[CpRu(PPh_3)_2]Cl$, $NaBAr^F_4$ (10 mol%)	**L2** (10)	60, 1.5	86 (87[e]), <1

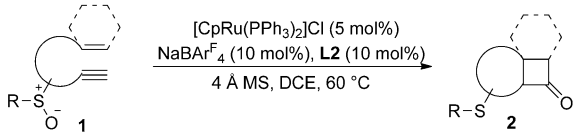
[a] Initial [**1a**] = 0.05 M. Ar = 2,6-dimethylphenyl. [b] d.r. ca. 1.2:1 to 1.3:1. The structure of the major isomer is shown. [c] Estimated by ^{1}H NMR spectroscopy using diethyl phthalate as the internal reference. [d] 4 Å MS used. [e] Yield of the isolated product. [f] Initial [**1a**] = 0.5 M. [g] Ar = Ph. d.r. ca. 1.7:1. acac: acetylacetone.

3a **L1** **L2**

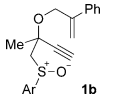
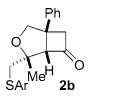
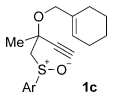
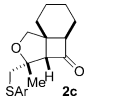
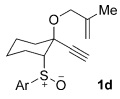
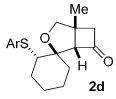
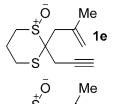
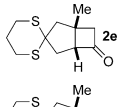
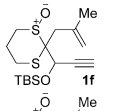
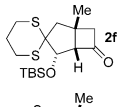
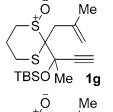
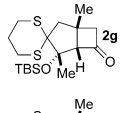
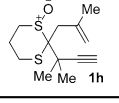
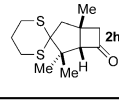
initial concentration of **1a** ([**1a**] = 0.5 M instead of 0.05 M, entry 13). To gain insight into the real catalytic species in the reaction, we prepared $[CpRu(\mathbf{L2})_2(MeCN)]^+PF_6^-$ and $[CpRu(\mathbf{L2})(PPh_3)(MeCN)]^+PF_6$ according to the reported procedures.[14,15] Interestingly, both catalyzed the reaction with good efficiency,[17] though with the former catalyst less side product **3a** was detected (entries 14 and 15). It should be pointed out that both diastereomers of **1a** participated smoothly in this Ru-catalyzed reaction, although slightly different reaction rates were observed by NMR monitoring (see SI for details), and the diastereomeric ratio of the products remained constant at 1.2:1 to 1.3:1 in all these cases. The relative stereochemistry of the major isomer (structure shown) was established by NOESY experiments and is consistent with literature reports.[11] Finally, our use of the sterically hindered 2,6-dimethylphenyl group instead of a simple phenyl as the aryl group in **1a** was intended to attenuate the potential cyclization of the sulfide of **B** to its ketene moiety. Indeed, when the phenyl counterpart was used, the corresponding bicyclic cyclobutanone was formed in a lower NMR yield (86%) and isolated in 87% yield (entry 16). Notably, a slightly improved d.r. (1.7:1) was observed in this case.

With the optimized conditions (see Table 1, entry 12), we then examined the substrate scope (Table 2) by varying the alkene unit of **1a**. Whereas the removal of the alkenyl methyl group in **1a** resulted in a much lower yield (data not shown), its replacement with a phenyl group was possible, and the cyclobutanone **2b** was isolated in 82% yield as a mixture of diastereomers (entry 1). A substrate containing a trisubstituted alkene in the form of a cyclohexene afforded the product **2c**, although the reaction worked better when it was performed at a higher reaction temperature and with **L1** as the added ligand (entry 2). The product **2c** with an angular 4,5,6-fused skeleton was isolated in a moderate yield (64%). The enynyl sulfoxide **1d** (entry 3) also underwent the reaction

Table 2: Scope of the [2+2] cycloaddition reactions involving oxidatively generated ketenes.[a,b]



1 **2**

	Substrate Structure	d.r.	t [h]	Product Structure	Yield [%]	d.r.
1	 **1b**	1.5:1	3	 **2b**	82	1.2:1
2[c,d]	 **1c**	1.1:1	1	 **2c**	64	1.2:1
3[c,d]	 **1d**	1.2:1	3	 **2d**	65	1.4:1
4	 **1e**	1.2:1	24	 **2e**	62	–
5	 **1f**	2.1:2.1:1.9:1	4	 **2f**	87	7.1:1
6	 **1g**	3.4:3.1:1.1:1	24	 **2g**	70	–
7	 **1h**	7:1	1.5	 **2h**	91	–

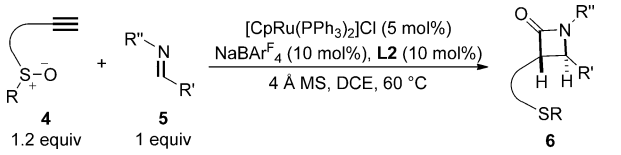
[a] Initial [**1**] = 0.05 M. Reactions were run in oven-dried vials in the presence of 4 Å MS. [b] The structure of the major diastereomer, if applicable, is shown; the relative stereochemistry was established by NOESY experiments (see the Supporting Information). In entries 1 and 5, both isomers were isolated in pure form and fully characterized. [c] Reactions were run at 80°C. [d] **L1** was used.

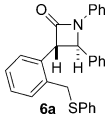
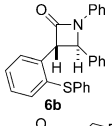
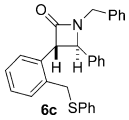
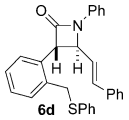
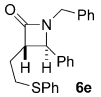
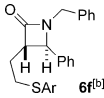
under the slightly modified conditions, yielding the tricyclic cyclobutanone **2d** with a 1-oxaspiro[4.5]decane moiety.

An apparent problem associated with tethered oxidants is their limited utility in either the oxidized or reduced form in an overall synthetic sequence apart from the oxidation step. To address this issue in the context of ketene chemistry, we speculated that a 1,3-dithiane moiety might also be suitable for delivering an oxygen intramolecularly to a Ru vinylidene. Importantly, 1,3-dithianes are widely used as synthetic equivalents for acyl anions and as protected ketones in organic synthesis.[18] We reasoned that this moiety could simplify the synthesis of substrates and be removed later to release a synthetically useful carbonyl group. The sulfoxide **1e** is easily accessible from the corresponding enynyl 1,3-dithiane, which in turn was prepared through a one-pot double alkylation from the parent 1,3-dithiane. Compound **1e** was subjected to our optimized conditions and the desired cyclobutanone **2e** was formed in a satisfactory yield (entry 4). The enynyl 1,3-dithiane substrates with one or two substitutes at the propargylic position (i.e., **1f**–**1h**, entries 5–7) also underwent the reaction smoothly. In addition to higher efficiencies, these reactions exhibited good to excellent diastereoselectivities and **2f** was obtained in a diastereomeric ratio of 7.1:1, whereas **2g** was isolated as a single diastereomer. Notably, these are the first examples of a metal-catalyzed 1,6-enyne isomerization that delivers bicyclic cyclobutanones. Additionally, the products **2e**–**2h** exhibit a 5,4-fused bicyclic skeleton with two well-differentiated ketone groups, enabling their further selective modification.

The Staudinger ketene–imine cycloaddition is a classical transformation[19] and provides rapid access to valuable β-lactams.[9] Much to our delight, when *N*-benzylideneaniline was present in the reaction mixture, the Ru catalysis smoothly transformed 1-ethynyl-2-(phenylsulfinylmethyl)benzene (**4a**) to the β-lactam **6a** in 95% yield and with excellent diastereoselectivity (Table 3, entry 1). Its *trans* structure is assigned based on the characteristic coupling constant of the lactam ring hydrogens (2.6 Hz; for *trans* ca. 2.0 Hz, for *cis* ca. 5.0 Hz) and corroborated by NOESY experiments of **6d** (see below). A similarly efficient reaction was realized with 1-ethynyl-2-(phenylsulfinyl)benzene as the substrate (entry 2). The reacting partner imine was also varied: an *N*-benzylimine (entry 3) and an α,β-unsaturated *N*-phenylimine (entry 4) all resulted in excellent yields of the *trans* isomer. Besides phenyl sulfoxides possessing arylacetylene moieties, substrates with aliphatic terminal alkynes were also investigated. A substrate having a phenyl sulfoxide provided the desired β-lactam **6e** in only 34% yield (entry 5); however, when the phenyl group was replaced with a 2,6-dimethylphenyl, the yield was drastically improved (entry 6). Considering the high yields obtained in entries 1–4, in which phenyl sulfoxide tethered arylacetylene substrates were used, the benefit of the significantly bulkier phenyl group in this case appeared to be mostly applicable to aliphatic alkyne substrates, which is consistent with our previous observation (Table 1, entry 16). This phenomenon could be readily understood by appreciating the fact that an aliphatic ketene is more electrophilic than an aryl ketene and hence the former is more prone to be intramolecularly attacked by the nascent sulfide moiety unless it is sterically impeded. Because β-lactams are of high synthetic utility, we performed a 5 mmol-scale reaction (entry 7) in order to establish the applicability of this Ru catalysis upon scale-up. Hence, with a lower catalyst loading (2 mol% instead of 5 mol%), 4 mol% of **L2**, and 4 mol% of $NaBAr^F_4$, 1.87 g of **6f** was isolated after 8 h reaction. This corresponds to a yield of 93%, which is higher than that achieved at a smaller scale during the scope study (entry 6).

Table 3: Formation of β-lactams.[a]

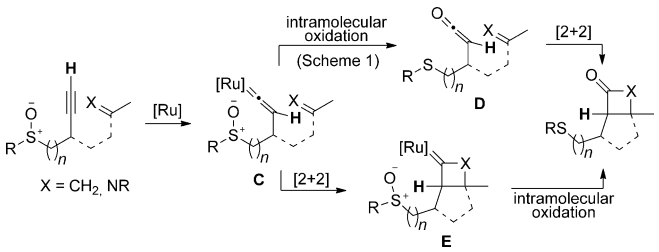


	Product	*t* [h]	Yield [%]	d.r.
1	 **6a**	2	95	>100:1
2	 **6b**	3	93	>80:1
3	 **6c**	2	95	>100:1
4	 **6d**	2	94	>20:1
5	 **6e**	3.5	34	>20:1
6		4	84	>20:1
7[c]	**6f**[b]	**8**	**93 (1.87 g)**	>20:1

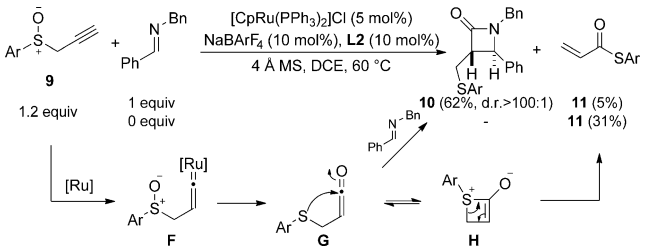
[a] [**6**] = 0.05 M. Reactions were run in oven-dried vials in the presence of 4 Å MS. The *trans* products were assigned based on the coupling constant of the lactam ring hydrogens and the NOESY spectrum of **7d**. [b] Ar = 2,6-dimethylphenyl. [c] Gram-scale reaction: $[CpRu(PPh_3)_2]Cl$ (2 mol%), $NaBAr^F_4$ (4 mol%), **L2** (4 mol%).

Because the [2+2] cycloaddition reactions affording cyclobutanones and β-lactams are characteristic ketene chemistry, the results presented so far are consistent with a mechanism involving a key ketene intermediate (i.e., **D**, Scheme 2, the top route), although the participation of a Ru-complexed ketene could not be ruled out. An alternative mechanism entailing an initial [2+2] cycloaddition[20] involving the Ru vinylidene complex **C**, followed by an intramolecular oxidation of the nascent Ru carbene **E**[21] could also account for the reaction outcomes[22] (Scheme 2, the bottom route).

Several studies were performed to offer further insight into the reaction mechanism: firstly, the intermediacy of the Ru vinylidene **C** was corroborated by the deuterium-labeling

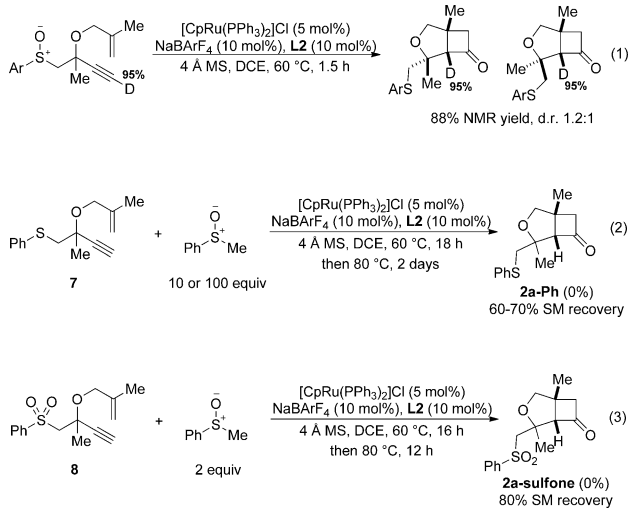


Scheme 2. The proposed reaction mechanism (top route) and an alternative (bottom route).



Scheme 3. Ru-catalyzed reaction of propargyl sulfoxide **9** and the proposed mechanism. Ar: 2,6-$Me_2C_6H_3$.

study shown in Equation (1); secondly, the cyclobutanone product **2a-Ph** was not formed when the enynyl sulfide **7** along with an excess of phenyl methyl sulfoxide was subjected to the optimized reaction conditions [Eq. (2)]. To ascertain that the tethered sulfide moiety in **7** was not responsible for the lack of reactivity, it was oxidized to a sulfone (**8**), and again no desired reaction occurred [Eq. (3)].



These results argue against the Ru carbene route, because the intermolecular oxidation of Ru carbenes to carbonyl groups has been documented.[21a] A counter-argument might be that the intramolecular oxidation of Ru carbene by a tethered sulfoxide could be much more facile. This, however, cannot explain the finding that the formation of the diastereoisomer of **2a** with an *exo* sulfide is nearly as facile as that of the *endo* isomer (see Table 1, entry 12); the *exo* isomer of the Ru carbene precursor of type **E** would have difficulty in the intramolecular oxidation step due to spatial constraints and, as a result, the intermolecular oxidation should at least be able to compete when a similar sulfoxide is present in excess, as in Equation (2). Lastly, when we examined the propargyl sulfoxide **9** as the ketene precursor for the Staudinger ketene–imine cycloaddition, the desired β-lactam **10** was formed in a reasonable yield of 62% (Scheme 3). In addition, we detected the formation of the thioester **11** in 5% yield. In the absence of the imine reacting partner, **11** was isolated in 31% yield. In the proposed mechanism for its formation (see Scheme 3), the intermediacy of the sulfide ketene **G** confers a straightforward rationale for the migration of the arylthio group. The proposed intramolecular attack of the tethered sulfide at the ketene is in line with the observed decrease of the reaction efficiency with aliphatic alkyne substrates when the aryl group on sulfur becomes less hindered (i.e., from 2,6-$Me_2C_6H_3$ to Ph).

In summary, we have developed an efficient ruthenium-catalyzed transformation of terminal alkynes into synthetically versatile ketenes through an intramolecular oxidation of Ru vinylidene intermediates. Sulfoxides derived from thioethers or synthetically versatile 1,3-dithianes are suitable mild oxidants when appropriately tethered. The ketenes generated in this manner are shown to undergo the characteristic Staudinger ketene [2+2] cycloaddition reaction with tethered alkenes and external imines, thereby affording synthetically versatile bicyclic cyclobutanones and β-lactams, respectively. The extension of this Ru catalysis by using external oxidants is currently pursued.

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