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Rh(III)-Catalyzed C−H Activation with Allenes To Synthesize Conjugated Olefins

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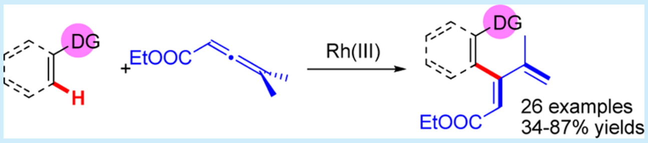
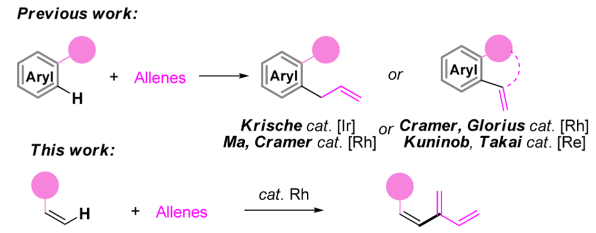
Supporting Information

ABSTRACT: Rh^{III}-catalyzed C−H activation with allenes produces highly unsaturated conjugated olefins. The reaction is applicable to both olefin and arene C(sp^2)−H and is compatible with a variety of functional groups. The products can be further transformed into other important skeletons through Diels−Alder reaction and intramolecular transesterification.



Allenes are highly valuable synthetic precursors in preparative organic chemistry. Development of new reactions by using allenes has been intensively studied in synthetic organic chemistry.[1] Among them, several examples of transition metal catalyzed C−H with allenes were reported (Scheme 1),[2,3] for directed C−H activation has advantages over traditional protocols based on substrate preactivation.[4] In 2009, the Krische group reported an Ir-catalyzed benzamide directed C−H with allenes for synthesis of allylarenes.[2a] In 2010, the Cramer group reported imine directed C−H tandem cyclization with allenes. Almost at the same time,[2b] Kuninobu and Takai showed that Re could also be utilized in a similar reaction procedure.[2c] Recently, Glorius's,[3a] Ma's,[3b,d] and Cramer's[3c] group reported Rh^{III}-catalyzed C−H activation with allenes for the synthesis of allylarenes and heteroaromatic compounds. Despite these impressive advances, little has been shown to produce an oxidative Heck-type product (conjugated diene) by using simple C−H and allenes.[6] Herein we report an example of Rh^{III}-catalyzed C−H activation with allenes to produce highly unsaturated conjugated olefins, while conjugated olefins were a very useful building block to the constrained cyclic skeleton.[5,6]

Scheme 1. C−H Functionalized with Allenes



Rh^{III}-catalyzed processes proved to be an efficient strategy in C−H functionalization reactions.[7] Examples such as alkenes,[8] alkynes,[9] imines,[10] arenes,[11] an electrophilic amination reagent,[12] an electrophilic halogen reagent,[13] diazo compounds,[14] etc.[15] were reported. The applications of allenes in Rh^{III}-catalyzed C−H activation have been reported recently. Despite these impressive advances, the development of new types of reactions between C−H and allenes is still highly desirable.[6]

At the outset of this project, we initially examined the Rh(III)-catalyzed coupling reaction of phenyl dimethylcarbamate with ethyl 4-methylpenta-2,3-dienoate (**2a**) under the conditions previously reported for C−H activation oxidative Heck reaction ([RhCp*Cl$_2$]$_2$/AgSbF$_6$/Cu(OAc)$_2$/THP/110 °C). However, no desired product was observed (without shown in Table 1). To our delight, the application of **1a** as the substrate resulted in the formation of conjugated olefins **3a** in 65% yield. We believed that lowering the reaction temperature would cause a better yield of the reaction. Next, after reducing the reaction temperature, an 83% yield of the desired product was obtained under 80 °C, a much higher yield obtained at 60 °C (86%, entry 3). Under 40 °C, the yield was slightly lower. A survey of solvents showed that THF, toluene, *t*-amyl-OH, and dioxane could also give considerable yields (entries 5−8). Compared to Cu(OAc)$_2$, Ag$_2$CO$_3$ was also an excellent oxidation agent for this reaction (75%, entry 9). Comparative tests showed that [RuCl$_2$(*p*-cymene)]$_2$ and Pd(OAc)$_2$ were not effective catalysts for this reaction (entries 10, 11). In the absence of [RhCp*Cl$_2$]$_2$ the reaction did not take place (entry 12).

With these optimal conditions in hand, different enolate derivatives were investigated (Table 2). Both electron-withdrawing and -donating enolate substrates were tested, and all of them exhibited good reactivities, such as 4-OMe, 3-CF$_3$, and 4-OBn. Various halogen substituents showed good compatibility, which made additional functionalization possible at these positions (**3e**−**3h**). A naphthyl-substituted enolate derivative smoothly survived the process (**3i**), which was confirmed by X-

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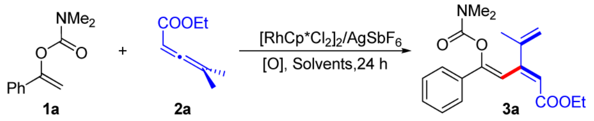
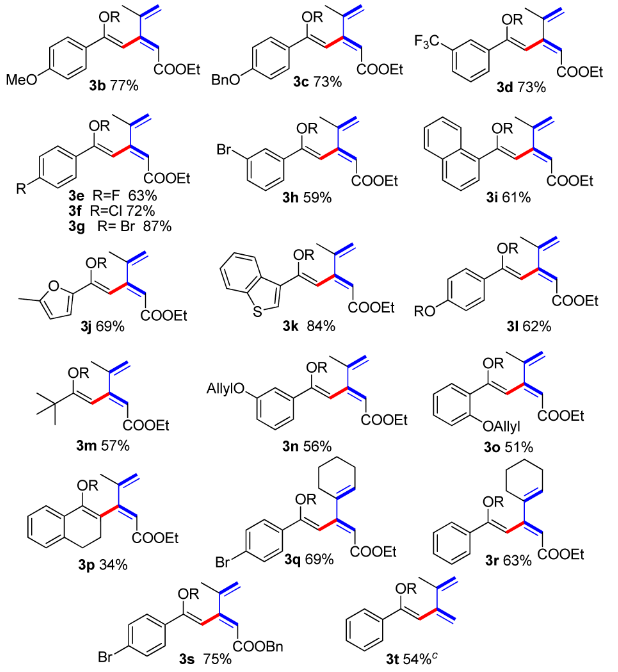
Table 1. Optimization of the Reaction Conditions[a]



entry	[O]	solvent	*T* (°C)	yield (%)
1	$Cu(OAc)_2$	THP	110	65
2	$Cu(OAc)_2$	THP	80	83
3	**$Cu(OAc)_2$**	**THP**	**60**	**86**
4	$Cu(OAc)_2$	THP	40	75
5	$Cu(OAc)_2$	THF	60	81
6	$Cu(OAc)_2$	toluene	60	36
7	$Cu(OAc)_2$	*t*-AmylOH	60	77
8	$Cu(OAc)_2$	dioxane	60	72
9	Ag_2CO_3	THP	60	75
10[b]	$Cu(OAc)_2$	THP	60	<5
11[c]	$Cu(OAc)_2$	THP	60	<2
12[d]	$Cu(OAc)_2$	THP	60	0

[a] Conditions: **1a** (0.2 mmol), **2a** (2 equiv), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), Oxidant (2 equiv), solvent (0.5 mL), 24 h, under Ar, isolated yields (average of two runs). [b] $[RuCl_2(p\text{-cymene})]_2$ instead of $[RhCp^*Cl_2]_2$. [c] $Pd(OAc)_2$ instead of $[RhCp^*Cl_2]_2$. [d] Without use $[RhCp^*Cl_2]_2$. THP = Tetrahydropyran.

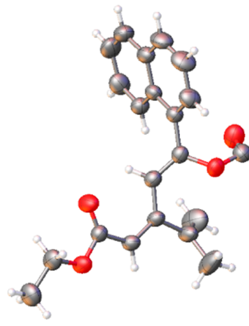
Table 2. The Scope of Substrates[a,b]



[a] Conditions: **1** (0.2 mmol), **2** (2 equiv), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2$ (2 equiv), THP, 60 °C, 24 h, Ar. [b] Isolated yields. [c] 2 equiv Ag_2CO_3 instead of $Cu(OAc)_2$, under 40 °C for 12h. R = $CON(Me)_2$.

ray analysis of the product (Scheme 2).[16] The very good compatibility of a heterocyclic ring structure, such as furan and thiophene (**3j**, **3k**), was achieved. It was noteworthy that an allylic ether substituted enolate was compatible with this reaction (**3n**, **3o**), while previous reports showed that allyl ether can react with arene C−H bonds under the Rh(III)-catalyst. A cyclic enol ester could also be transformed but with a much lower yield (**3p**, 34%).

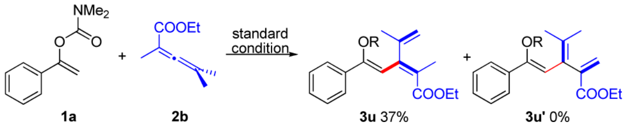
Scheme 2. Crystal Structure of the Product 3i



Other substituted allenes were also examined. Moderate yields were obtained for electron-withdrawing allenes (**3q**−**3s**). Intriguingly, when 1,1-dimethylallene was treated with **1a** under a lower temperature (40 °C) by use of Ag_2CO_3 as an oxidant, the corresponding product **3t** was obtained in 54% yield. Unfortunately, monosubstituted allenes exhibited poor reactivities in this reaction.

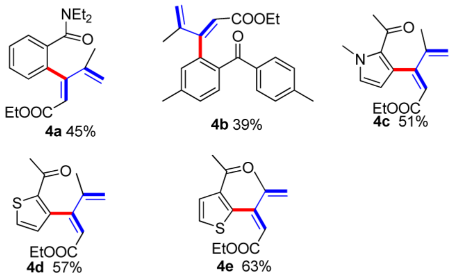
It was interesting to find that, when **1a** was reacted with tera-substituted allene **2b**, highly regioselective C−H elimination of the allene was observed. Only 37% of **3u** was observed, but without product **3u′** (Scheme 3).

Scheme 3. Regioselectivity C−H Elimination of Allene (R = $CONMe_2$)



To further explore the scope of the process, arenes' C−H bonds were tested. We were delighted to find that both aromatic and heteroaromatic substrates could be successfully transformed when an amide and ketone were used as directing groups under 120 °C (Table 3). The amide could be converted in a moderate yield (**4a**). Aromatic and heteroaromatic ketones exhibited good compatibility (**4b**−**e**).

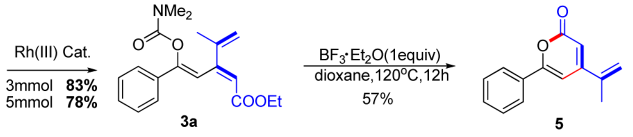
Table 3. C−H Functionalization of Arenes[a]



[a] Conditions: **1** (0.2 mmol), **2** (2 equiv), $[RhCp^*Cl_2]_2$ (2.5 mol %), $AgSbF_6$ (10 mol %), $Cu(OAc)_2$ (2 equiv), dioxane, 120 °C, 24 h, Ar.

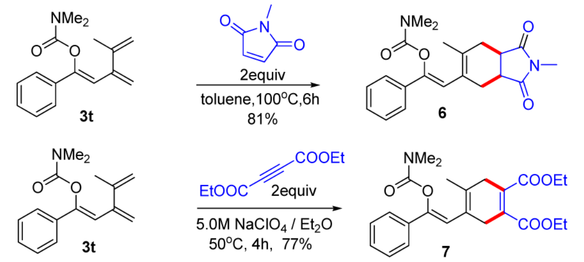
In a scaled-up experiment (3 mmol scale, Scheme 4), we found that the yield of **3a** remained satisfactory (83%). A larger scale reaction (5 mmol scale) was performed, and a 78% yield of **3a** was obtained. Thus the reaction was synthetically useful because conjugated olefins could be readily converted to diverse cyclic skeletons. A 2*H*-pyran-2-one derivative (**5**) could be obtained when **3a** was treated with $BF_3{\cdot}OEt_2$ under refluxing

Scheme 4. Intramolecular Transesterification



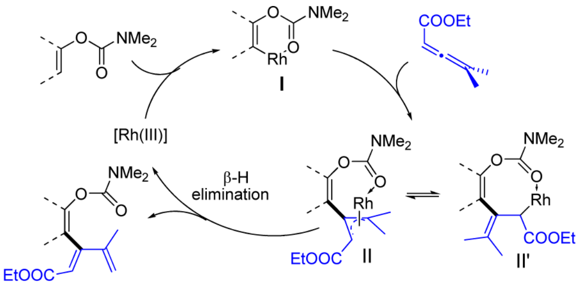
1,4-dioxane (Scheme 4). Furthermore, we were convinced that the reaction of **3t** with dienophiles would be useful for the synthesis of six-membered carbocycles[17] (Scheme 5). First, **3t** was treated with 2 equiv of *N*-methylmaleimide to afford **6** in 81% yield. Along the same line, the use of diethyl acetylenedicarboxylate provided the product **7** in 77% yield.

Scheme 5. Diels−Alder Reaction with 3t



We propose that the mechanism of the reaction is as follows (Scheme 6): First, the Rh(III) catalyst reacted with the substrate through a C−H activation step to generate an intermediate (**I**). Second, Rh(III) in **I** was coordinated with allene followed by insertion of the moiety into the C−Rh(III) bond to produce complex **II** or **II′**. Finally, *β*-H elimination occurred to generate the target product. The Rh(III) complex then went back into the catalytic cycle.

Scheme 6. Proposed Mechanistic Pathway



In conclusion, an example of Rh(III) catalyzed C−H activation with allenes to produce highly unsaturated conjuncted olefins was reported. This reaction features high regioselectivity, mild reaction conditions, and excellent functional group tolerance. Furthermore, we had demonstrated that the unsaturated conjugated olefins could be transformed into other important skeletons through Diels−Alder reaction and intramolecular transesterification. This transformation provided a new method to synthesize conjunction olefins. Further exploration of the synthetic utilities of this chemistry and in-depth mechanistic study are currently in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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