EurJOC European Journal of Organic Chemistry

SHORT COMMUNICATION

DOI: 10.1002/ejoc.201403535

Rhodium(I)-Catalyzed Cycloisomerization of Allene–Allenylcyclopropanes

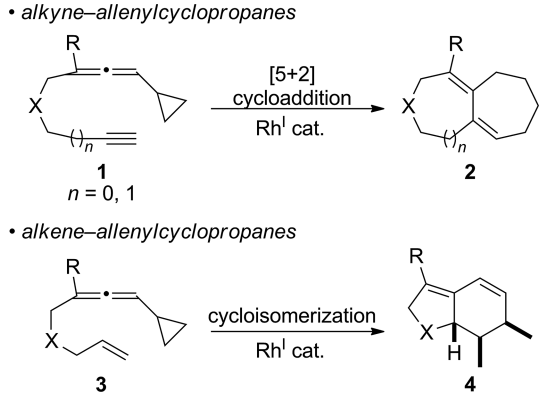
Takamasa Kawamura,[a] Yasuaki Kawaguchi,[a] Katsuya Sugikubo,[a] Fuyuhiko Inagaki,[a] and Chisato Mukai*[a]

Keywords: Allenes / Small ring systems / Rhodium / Cycloisomerization / Cycloaddition

The Rh^I-catalyzed intramolecular [5+2–2]-type cycloisomerization of allene–allenylcyclopropanes was developed. In this reaction, ethylene was liberated from the cyclopropane ring to afford the 1,5,6,7-tetrahydroazulene skeletons.

Introduction

Cyclopropane is one of the most useful and powerful C_3 building blocks[1] in organic reactions owing to its inherent high strain energy (27.5 kcal mol^{-1}).[2] Several types of transition-metal-catalyzed ring cleavages of cyclopropane have already been recorded, and they have been exemplified by [5+2],[3–5] [5+2+1],[6] [5+1+2+1],[7] [3+2],[8] [3+2+1],[9] [3+2+2],[10] and [3+3+1][11] cycloadditions. Recent efforts from our laboratory disclosed that the Rh^I-catalyzed intramolecular [5+2] cycloaddition of alkyne–allene substrates possessing a cyclopropane moiety efficiently produced bicyclo[5.4.0]undecatrienes **2** (n = 0) and bicyclo[5.5.0]dodecatrienes **2** (n = 1).[12] Exchange of the reactive alkyne part of **1** by an alkene group (i.e., compound **3**) significantly changed the reaction pathway, which led to the stereoselective construction of unexpected bicyclo[4.3.0]nona-1(9),2-diene derivatives **4** (Scheme 1).[13] The allyl group of **3** would have initially isomerized into the internal double bond and took part in the ring-closing process. On the basis of these results, our next endeavor focused on the intramolecular reaction between allenylcyclopropane and allene moieties to compare their reactivities with those of the alkyne and alkene π components. This paper describes the unprecedented behavior of cyclopropane acting as a C_1-building block accompanied by liberation of ethylene. Thus, a new type of ring construction mode ([5+2–2]-type ring closure) could be developed by incorporation of cyclopropane into five-membered carbocycles.



Scheme 1. Rh^I-catalyzed cyclization of allenylcyclopropane multiple bonds.

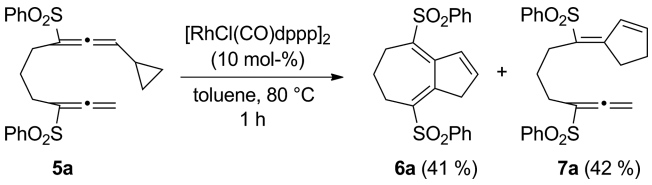
Results and Discussion

The preliminary examination was initiated by using allene–allenylcyclopropane **5a** possessing phenysulfonyl groups on both of the two allenyl moieties. Treatment of **5a** with $[RhCl(CO)dppp]_2$ [10 mol-%, dppp = 1,3-bis(diphenylphosphino)propane], which was effective for the [5+2] cycloaddition of alkyne–allenylcyclopropane **1**, in toluene at 80 °C for 1 h produced 1,5,6,7-tetrahydroazulene derivative **6a** in 41% yield along with cyclopentenylidene derivative **7a** (42% yield, Scheme 2).[14,15] Bicyclic products **2** and **4**, which were predicted on the basis of previous experiments, were never isolated. The formation of **7a** could be easily interpreted by a plausible rhodacyclohexenylidene intermediate, followed by a reductive elimination process (see above). The reaction mechanism for the construction of bicyclo[5.3.0]decatriene skeleton **6a** is not straightforwardly understood. The two-carbon unit of **5a** was clearly lost and some unprecedented stepwise mechanism should have occurred during the formation of **6a**. A suitable catalyst for the conversion of **5a** into **6a** was screened by using $[RhCl(CO)dppm]_2$, $[RhCl(CO)dppe]_2$, $[RhCl(CO)dppb]_2$, $[Rh(CO)(dppp)_2]Cl$,[16] $[Rh(dppp)_2]Cl$,[16] $[RhCl(CO)_2]_2$, $RhCl(PPh_3)_3$, and *trans*-$RhCl(CO)(PPh_3)_2$, but all of them were less effective and furnished poor results [dppm = 1,1-bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenyl-

[a] Division of Pharmaceutical Sciences, Graduate School of Medical Sciences, Kanazawa University,
Kakuma-machi, Kanazawa 920-1192, Japan
E-mail: mukai@p.kanazawa-u.ac.jp
http://www.p.kanazawa-u.ac.jp/~yakuzou/indexen.html

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201403535.

phosphino)ethane, dppb = 1,4-bis(diphenylphosphino)-butane]. Changing the solvent [dioxane, 1,2-dichloroethane (DCE), DMF, CH_3CN, *i*PrOH] and/or reaction temperature (25 °C to reflux) also did not give better results.

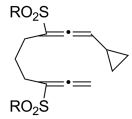
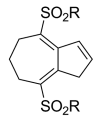
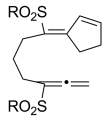
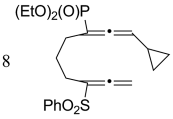
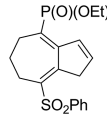
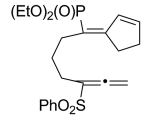
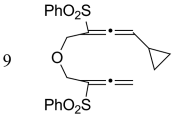
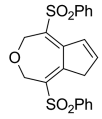
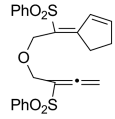
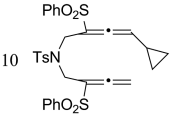
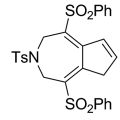
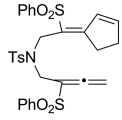
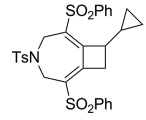
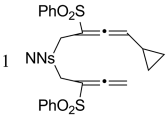
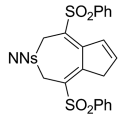
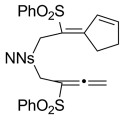
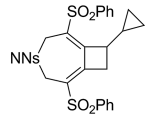


Scheme 2. Rh^I-catalyzed cyclization of allene–allenylcyclopropane **5a**.

Several other bis(phenylsulfonyl) substrates were exposed to the standard conditions {10 mol-% $[RhCl(CO)dppp]_2$ in toluene at 80 °C}. These results are summarized in Table 1. Treatment of the *ortho*-tolylsulfonyl (*o*Ts) derivative **5b** with $[RhCl(CO)dppp]_2$ afforded desired bicyclo[5.3.0] product **6b** in 28% yield together with **7b** in 31% yield (Table 1, entry 1). The reaction of *para*-tolyl (*p*Tol) and $pMeOC_6H_4$ substrates **5c** and **5d** provided results similar to those obtained with **5b** (Table 1, entries 2 and 3). In the case of $pClC_6H_4$ derivative **5e**, bicyclo[5.3.0] product **6e** was obtained in poor yield together with cyclopentenylidene product **7e** (54% yield; Table 1, entry 4). Bulky mesityl (Mes) derivative **5f** produced bicyclic product **6f** in moderate yield (45% yield; Table 1, entry 5). Aliphatic sulfonyl derivatives **5g** and **5h** provided desired products **6g** and **6h**, but their yields were rather low (Table 1, entries 6 and 7). Thus, the consistent formation of the bicyclo[5.3.0]decatriene skeleton from the carbon-tethered bis(phenylsulfonyl) substrates was achieved in low to moderate yields. The diethylphosphonate group on the allenylcyclopropane moiety was found to work in a manner similar to that of the sulfonyl functionality to furnish **6i** in 30% yield (Table 1, entry 8). Application of the Rh^I-catalyzed [5+2–2]-type cycloaddition for the construction of the oxabicyclo[5.3.0] ring systems as well as azabicyclo[5.3.0] ring systems was next investigated. Ether derivative **5j** was exposed to conditions similar to those used for simple carbon tether derivatives **5a**–**i**, and desired oxabicyclo[5.3.0]decatriene derivative **6j** was obtained in 39% yield along with cyclopentenylidene derivative **7j** (28% yield; Table 1, entry 9). The reaction of *N*-tosylamide derivative **5k** also provided corresponding azabicyclo[5.3.0] derivative **6k** in 19% yield. The major product, however, became [2+2] cycloaddition product **8k**, which was obtained in 49% yield alongside cyclopentenylidene derivative **7k** in 21% yield (Table 1, entry 10).[17] *N*-Nosylated (Ns) substrate **5l** behaved similarly to **5k** to furnish three products: bicyclo[5.3.0]decatriene **6l**, cyclopentenylidene **7l**, and bicyclo[5.2.0] derivative **8l** (Table 1, entry 11).

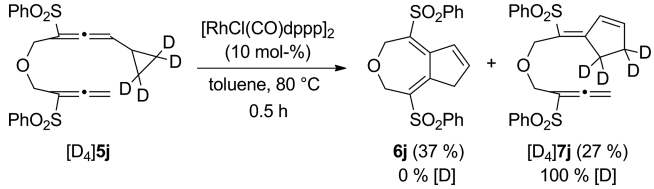
It is postulated that the C_2H_4 component must have been lost during the conversion of **5** into tetrahydroazulene derivatives **6**. We tentatively assumed that the collapse of the cyclopropane ring into ethylene and a C_1 species occurred and the thus-formed C_1 unit would take part in the ring formation reaction. To obtain some information to prove

Table 1. Rh^I-catalyzed cyclization of allene–allenylcyclopropanes **5b**–**l**.[a]

Entry	Substrate	Time [h]	Product, yield [%]	
				
1	**5b** (R = *o*Tol)	1	**6b**, 28	**7b**, 31
2	**5c** (R = *p*Tol)	1	**6c**, 29	**7c**, 26
3	**5d** (R = $pMeOC_6H_4$)	1	**6d**, 35	**7d**, 31
4	**5e** (R = $pClC_6H_4$)	1	**6e**, 11	**7e**, 54
5[b,c]	**5f** (R = Mes)	1	**6f**, 45	**7f**, 41
6	**5g** (R = *n*Bu)	2	**6g**, 28	**7g**, 50
7	**5h** (R = *t*Bu)	3	**6h**, 5	**7h**, 46
8	 **5i**	2.5	 **6i**, 30	 **7i**, 8
9	 **5j**	0.5	 **6j**, 39	 **7j**, 28
10	 **5k**	1	 **6k**, 19	 **7k**, 21  **8k**, 49
11	 **5l**	0.75	 **6l**, 35	 **7l**, 18  **8l**, 30

[a] Reactions were performed by using $[RhCl(CO)dppp]_2$ (10 mol-%) in toluene at 80 °C. [b] Chemical yields were calculated on the basis of ^1H NMR spectroscopy. [c] The [5+2] product was formed in 13% yield.

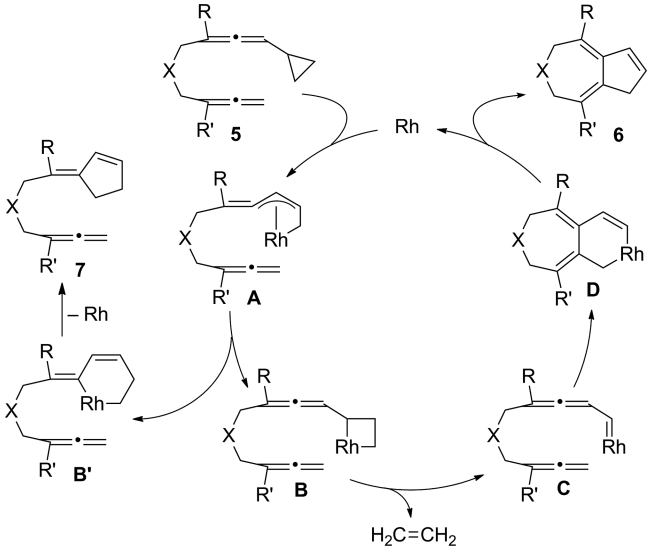
this assumption, a deuterium labeling experiment was performed (Scheme 3). Exposure of tetradeuterated substrate $[D_4]$**5j** to $[RhCl(CO)dppp]_2$ in toluene at 80 °C produced bicyclo[5.3.0] derivative **6j** in 37% yield along with deuterated cyclopentenylidene derivative $[D_4]$**7j** in 27% yield. Deuterated **6j** was not detected, whereas **7j** possessing the tetradeuterated cyclopentenylidene framework was exclu-



Scheme 3. Rh^I-catalyzed cyclization of deuterated substrate $[D_4]$**5j**.

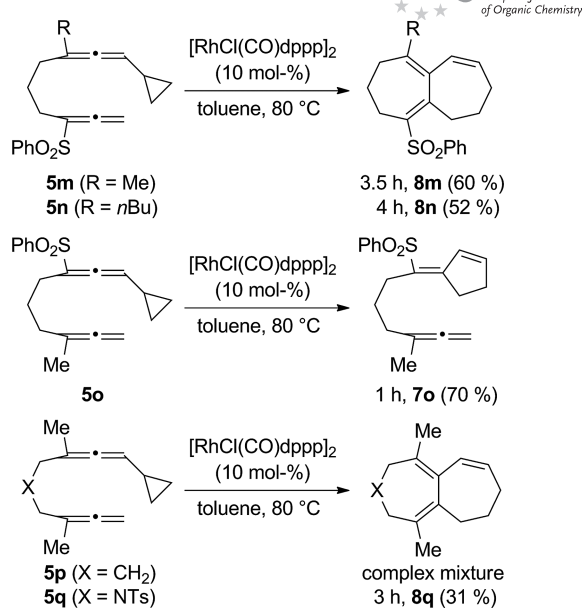
sively formed. These results provided fairly informative clues for understanding the reaction mechanism.

On the basis of the deuteration experiment, the following plausible reaction mechanism might be proposed. Relief of the high strain energy of the cyclopropane ring of substrate **5** would result in a fast reaction with the Rh catalyst to form vinylidene π–allyl complex **A** (Scheme 4). Intermediate **A** could be in equilibrium between rhodacyclobutane **B** and/or rhodacyclohexenylidene **B′**. Intermediate **B** would then liberate ethylene, which would result in the formation of rhodium carbenoid species **C**.[18] This could then undergo a 6π-electrocyclic type ring closure[19] to afford rhodabicyclo[5.4.0] intermediate **D**. Reductive elimination of **D** would finally lead to desired tetrahydroazulene derivative **6**. The production of cyclopentenylidene derivative **7** can be rationalized by the mechanism that involves intermediate **B′** followed by reductive elimination.



Scheme 4. Plausible mechanism for the Rh^{I}-catalyzed cyclization of allene–allenylcyclopropane substrates **5**.

We next examined the Rh^{I}-catalyzed cyclization of allene–allenylcyclopropanes possessing electron-donating groups on the allene moiety. Upon exposure to the standard conditions, **5m** with a methyl group on the allenylcyclopropane produced bicyclo[5.5.0] derivative **8m** in 60% yield (Scheme 5). The corresponding tetrahydroazulene compound, such as **6**, was not obtained at all. Similarly, the selective production of **8n** (52%) from butyl derivative **5n** was observed. The formation of **8m** and **8n** could be interpreted in line with the plausible mechanism proposed for the conversion of **1** into **2**. Substrate **5o**, having the two substituents reversed on the allenyl moieties of **5m**, no longer produced any bicyclic derivatives. Cyclopentenylidene derivative **7o** was instead isolated in 70% yield as the sole isolatable product. *N*-Tosylamide derivative **5q** with two methyl groups on both of the two allene groups provided [5+2] product **8q** in 31% yield, although corresponding carbon-tethered analogue **5p** gave an intractable mixture.



Scheme 5. Rh^{I}-catalyzed miscellaneous reactions of allene–allenylcyclopropanes.

It is too early to conclude definitively, but judging from the results described in Table 1 and Scheme 5, it might tentatively be stated that the ring-closing pattern of allene–allenylcyclopropane **5** clearly depends on the electronic properties of both allenyl functionalities. The formation of bicyclo[5.3.0]deca-1,6,8-triene skeleton **6** requires both electron-deficient groups on both allenyl groups, whereas bicyclo[5.5.0] derivative **8** could be produced if starting substrate **5** has an alkyl substituent on its allenylcyclopropane moiety.

Conclusions

We found that the Rh^{I}-catalyzed intramolecular [5+2–2]-type cycloisomerization of allene–allenylcyclopropane furnished bicyclo[5.3.0]deca-1,6,8-triene skeletons; this was accompanied by the liberation of ethylene from the cyclopropane ring. To the best of our knowledge, this is the first example in which the cyclopropane ring is used as a C_1 building block. This novel transformation was significantly affected by the properties of the substituents on both of the two allenyl moieties. Details of the reaction mechanism are still unclear. Methods to improve the chemical yields and elucidation of the mechanism are currently under investigation.

Supporting Information (see footnote on the first page of this article): Experimental procedures, characterization data, and spectroscopic data.

Acknowledgments

The authors are grateful for financial support by the Ministry of Education, Culture, Sports, Science, and Technology (Japan) through a Grant-in-Aid for Scientific Research.

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Received: November 26, 2014
Published Online: December 22, 2014

