Ring Expansion

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Rhodium-Catalyzed Ring Expansion of Cyclopropanes to Seven-membered Rings by 1,5 C–C Bond Migration**

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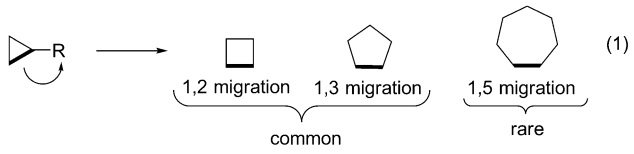
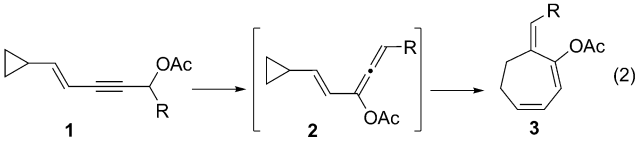
Selective cleavage and subsequent elaboration of carbon–carbon σ bonds into complex molecules represents a fundamental challenge in chemistry. The C–C σ bonds of cyclopropanes are activated owing to ring strain, and the ring expansion of cyclopropanes is an attractive route to other ring systems because of the well-documented stereoselective methods for cyclopropanation.[1] Indeed, ring expansion of cyclopropanes to four- or five-membered rings by 1,2 or 1,3 migration is routinely practiced in organic synthesis [Eq. (1)].[2] In contrast, ring expansion of cyclopropanes to seven-membered rings by 1,5 C–C bond migration has not



(1)

been developed as a general method, in spite of the prevalence of cycloheptane skeletons in natural products and pharmaceutical agents.[3] The 1,5 migration of a cyclopropane C–C bond has been mainly studied in bicyclo[4.1.0]heptadienes and a few other conformationally constrained bicyclic compounds under thermal conditions.[4] In fact, it was reported that simple 1,3-dienylcyclopropanes underwent 1,3 C–C bond migration to form vinylcyclopentenes in the presence of Ni or Pd catalysts.[5]

The most well-known example of the direct expansion of three-membered rings to seven-membered rings is the [3,3]-sigmatropic Cope rearrangement of divinylcyclopropanes to 1,4-cycloheptadienes.[6] Although this process requires the double activation of cyclopropanes by two vinyl groups, it is still one of the most important methods for the preparation of seven-membered rings. Methods that can promote ring expansion of cyclopropanes to seven-membered rings with complementary functionalities would be highly desirable. We herein describe the synthesis of functionalized alkylidene cycloheptadiene **3** by a Rh^I-catalyzed tandem isomerization of the monoactivated cyclopropane **1** via an allene intermediate **2** [Eq. (2)].



(2)

Based on the high reactivity of allenes with respect to transition metals,[7] we hypothesized that a 1,5 migration of a cyclopropane C–C bond in intermediate **2** may become favored over a 1,3 migration, which would generate an allenyl cyclopentene without the participation of the allene. We recently discovered that the $[\{Rh(CO)_2Cl\}_2]$ catalyst was able to promote 1,3 acyloxy migration of propargyl esters to form allenes;[8] this transformation was previously realized mainly by π-acidic metal-based catalysts such as silver,[9,10] copper,[9–11] platinum,[11,12] and gold[10,13] in various cascade reactions.[14,15] Given this novel reactivity of $[\{Rh(CO)_2Cl\}_2]$ for the promotion of 1,3 acyloxy migration and its well-known capability to undergo oxidative addition and reductive elimination, we envisioned that alkylidene cycloheptadiene **3** could be prepared directly from readily available cyclopropane **1**[16] in the presence of the $[\{Rh(CO)_2Cl\}_2]$ catalyst.[17] The acyloxy substituent on propargyl ester **1** not only eases the preparation of allene **2** but also differentiates the three double bonds in product **3**.

To test the proposed transformation in Equation (2), substrate **1a** was prepared in four steps from commercially available cyclopropanecarboxaldehyde.[16] Treatment of cyclopropane **1a** with 3 mol% of $[\{Rh(CO)_2Cl\}_2]$ at 60°C provided a significant amount of product **3a** (Table 1, entry 1) after 12 hours and some starting materials were also recovered. Complete conversion was realized after increasing the catalyst loading to 5 mol% (Table 1, entry 2). Under these reaction conditions, however, a small amount of eight-membered-ring product **4a** was also observed. Product **4a** was isolated in 22% yield when the catalyst loading was increased to 10 mol% (Table 1, entry 3). We speculated that increasing the CO pressure would provide more CO-insertion product **4a**. Surprisingly, a complex mixture was observed with more CO (Table 1, entries 4 and 5). No reaction occurred in the presence of several other rhodium catalysts (Table 1, entries 6–8). Changing the solvent from DCE to dioxane led

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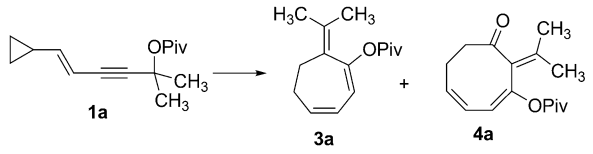
Table 1: Screening of catalysts and reaction conditions.



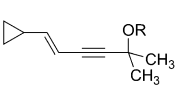
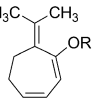
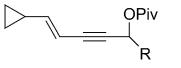
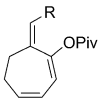
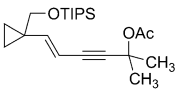
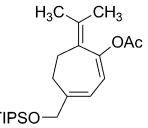
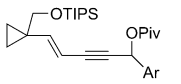
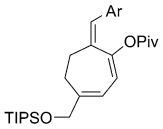
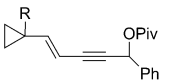
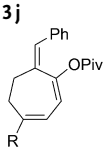
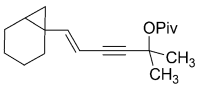
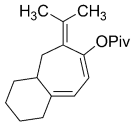
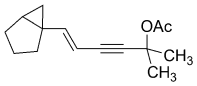
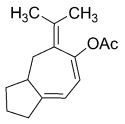
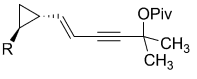
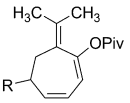
Entry	Catalyst	Conditions	Yield [%]
1	$[\{Rh(CO)_2Cl\}_2]$ (3 mol%)	60°C, DCE, 12 h	**3a**, 72[a]
2	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%)	60°C, DCE, 12 h	**3a**, 82[b]
3	$[\{Rh(CO)_2Cl\}_2]$ (10 mol%)	60°C, DCE, 12 h	**3a**, 70[b] **4a**, 22[b]
4	$[\{Rh(CO)_2Cl\}_2]$ (10 mol%)	60°C, DCE, CO (1 atm), 12 h	complex mixture
5	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%)	60°C, DCE, CO (5 atm), 12 h	complex mixture
6	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%)	60°C, DCE, 3 h	NR
7	$[Rh(PPh_3)_3Cl]$ (5 mol%)	60°C, DCE, 3 h	NR
8	$[Rh(cod)_2]BF_4$ (5 mol%)	60°C, DCE, 3 h	NR
9	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%)	60°C, dioxane, 6 h	**3a**, >95[a]
10	$[\{Rh(CO)_2Cl\}_2]$ (5 mol%)	100°C, dioxane, 2.5 h	**3a**, >95[a]
11	$[AuCl(PPh_3)]$ (5 mol%) AgOTf (5 mol%)	RT, MeCN, 20 h	0
12	$PtCl_2$ (10 mol%)	80°C, DCE, 20 h	0
13	$HNTf_2$ (10 mol%)	RT, CH_2Cl_2, 20 h	0

[a] Yields were determined by ^{1}H NMR spectroscopy using CH_2Br_2 as internal standard. [b] Yields of the isolated product. cod = cyclooctadiene, DCE = dichloroethane, NR = No reaction, Piv = pivaloyl.

to quantitative production of seven-membered-ring **3a** without any eight-membered-ring **4a**, as determined by ^{1}H NMR analysis of the crude product (Table 1, entry 9). The reaction time was shortened from 6 hours to 2.5 hours at higher temperature (Table 1, entry 10). Moreover, π-acidic metal-based catalysts such has Au^I and Pt^{II} or Brønsted acid catalyst did not provide any desired product **3a** (Table 1, entries 11–13).

We then set out to examine the scope of this tandem isomerization process (Table 2). The reaction worked well when the ester was changed from pivalate to acetate (Table 2, entry 2). The *gem*-dimethyl group on the propargyl ester could be replaced by other alkyl or aryl groups (Table 2, entries 3–5). However, a stereoselectivity issue arises for the exocyclic olefins in these cases. For propargyl ester **3c** with a phenyl substituent, we observed a 14:1 *Z*/*E* selectivity[16] (Table 2, entry 3), which is much higher than the selectivity that was obtained in the [5+1] cycloaddition of acyloxy-substituted allenyl cyclopropanes with CO.[8] Lower selectivity was generally observed for substrates with alkyl groups (Table 2, entries 4 and 5). The 1,1-disubstituted cyclopropane **1f** could provide product **3f**, which has an additional substituent on the seven-membered ring (Table 2, entry 6). The *Z*/*E* selectivity for the *exo* cyclic olefins varied slightly with electron-rich or electron-poor aryl substituents (Table 2, entries 7–9).[18] An aryl group with one *ortho* substituent significantly lowered the *Z*/*E* selectivity (Table 2, entry 10). Various functional groups, such as acetate, free alcohol, and even aldehyde, were tolerated under the reaction conditions (Table 2, entries 11–13). Ring expansion of cyclopropanes **1n** and **1o** led to 6,7 and 5,7 fused bicyclic systems respectively

Table 2: Scope of the Rh^I-catalyzed ring expansion.[a]

Entry	Substrates	Products	Yield [%][b]	*Z*/*E*[c]
				
1	**1a**, R = Piv	**3a**	83	–
2	**1b**, R = Ac	**3b**	83	–
				
3	**1c**, R = Ph	**3c**	76	14:1
4	**1d**, R = *n*Bu	**3d**	82	1:1
5	**1e**, R = *i*Pr	**3e**	93	2:1
				
6	**1f**	**3f**	92	–
				
7	**1g**, Ar = Ph	**3g**	87	7:1
8	**1h**, Ar = 4-$MeOC_6H_4$	**3h**	87	9:1
9	**1i**, Ar = 4-$CF_3C_6H_4$	**3i**	70	8:1
10	**1j**, Ar = 2,4-$Cl_2C_6H_3$	**3j**	83	3:1
				
11	**1k**, R = CH_2OAc	**3k**	95	8:1
12	**1l**, R = CH_2OH	**3l**	81	7:1
13	**1m**, R = CHO	**3m**	66	5:1
				
14	**1n**	**3n**	91	–
				
15	**1o**	**3o**	85	–
				
16	**1p**, R = Ph (92% *ee*)	**3p** (91% *ee*)	68	–
17	**1q**, R = CH_2OTIPS	**3q**	99	–
18	**1r**, R = CH_2OAc	**3r**	92	–

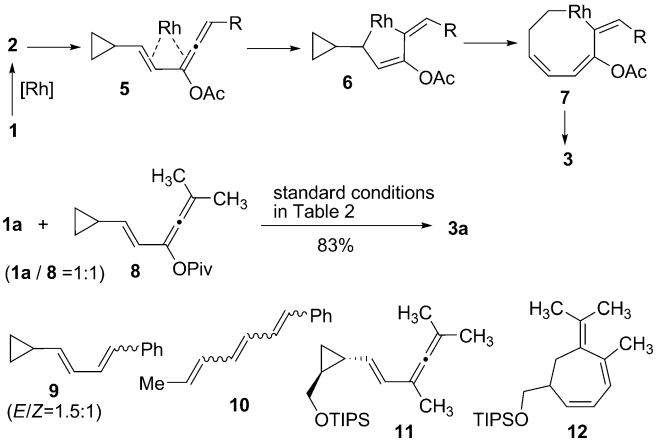
[a] Reaction conditions: $[\{Rh(CO)_2Cl\}_2]$ (5 mol%), 100°C, dioxane, 2-3 h. [b] Yields of the isolated products. [c] Estimated by ^{1}H NMR spectroscopy. TIPS = triisopropylsilyl.

(Table 2, entries 14 and 15); these fused bicyclic systems are widely present in bioactive natural products.[19]

For unsymmetrically substituted cyclopropanes, the cleavage of different cyclopropane C–C σ bonds will lead to

isomeric products. Our group[8,20] and other groups[21] have found that the regioselectivity for the cleavage of C–C σ bonds in cyclopropanes depends on the stereochemistry of the cyclopropane ring. Only one regioisomer was obtained for aryl- or alkyl-substituted *trans* cyclopropanes (Table 2, entries 16–18). Interestingly, the corresponding *cis* cyclopropanes with either aryl or alkyl substituents provided a mixture of seven-membered rings with low regioselectivity under identical reaction conditions.[16] The chirality in substrate **1p** was successfully transferred to the seven-membered-ring product **3p** (Table 2, entry 16). This paved the way for the preparation of optically pure seven-membered rings from chiral cyclopropanes.

The mechanism for the ring expansion of cyclopropane **1** to alkylidene cycloheptadiene **3** is proposed in Scheme 1. A Rh^I-catalyzed 1,3 acyloxy migration may occur first and generate allene intermediate **2**. Formation of η^4-(vinylallene)rhodium complex **5** can initiate an oxidative cyclization to yield alkylidene metallacyclopentene **6**. This transformation has been documented in the rhodium-catalyzed [4+1] cycloaddition of vinylallenes with CO,[22] and also the corresponding alkylidene metallacyclopentene complexes were isolated and characterized in the absence of CO.[23,24] Alkylidene metallacyclooctadiene **7** can be obtained by the cleavage of the strained cyclopropane ring in complex **6**. Reductive elimination of metallacycle **7** then yields the desired seven-membered-ring **3**.[25] The isolation of the eight-membered-ring product **4a** supports the involvement of metallacycle **7**, which may undergo carbonylation to form an eight-membered ring.



Scheme 1. Proposed mechanism and related evidence.

When propargyl ester **1a** was treated with catalyst $AgSbF_6$,[14] an inseparable mixture of allene **8** and enyne **1a** was obtained (ratio = 1:1). Submitting this mixture to the standard reaction conditions provided the desired product **3a** in 83% yield, thus suggesting that the acyloxy-substituted allene is a plausible intermediate in the ring-expansion reaction.

To gain further insights about the metal-catalyzed 1,5 C–C bond migration, we then prepared 1,3-dienyl cyclopropane **9** and treated it with Rh^I catalyst. In the absence of CO, triene **10** was isolated in 77% yield under the standard reaction conditions in Table 2.[26] No reaction occurred in the presence of CO.[27] This confirmed the importance of the allene group in intermediate **2** for the net 1,5 C–C bond migration.

We also prepared allene **11** by treating propargyl ester **1q** with excess methyl cuprate reagents.[28] Under our standard reaction conditions in Table 2, seven-membered-ring product **12** could be obtained in 62% yield from allene **11**, thus indicating that the acyloxy substituent in intermediate **2** is not required for the ring expansion. However, the acyloxy substituent is important for differentiating the three double bonds in product **3** for selective functionalization.[16]

In summary, we developed a novel method for the preparation of highly functionalized seven-membered rings directly from substituted cyclopropanes through a 1,5 C–C migration. This method may provide efficient access to mono- and polycyclic bioactive sesquiterpenoids that contain isopropylidene cycloheptanones.[29] The π-acidic rhodium catalyst is essential for the conversion of readily available cyclopropanes with propargyl ester group to alkylidene cycloheptadienes with three well-differentiated double bonds. Further studies to understand the details of the 1,5 C–C bond migration and apply this tandem isomerization reaction to the synthesis of bioactive compounds are currently in progress.

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