Rh(II)-catalyzed skeletal reorganization of enynes involving selective cleavage of C–C triple bonds†

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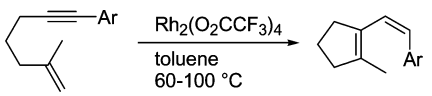
Treatment of enynes with a catalytic amount of Rh(II) complex results in skeletal reorganization to give *cis*-configured 1-vinylcycloalkenes, the formation of which occurs *via* double cleavage of both C–C double and C–C triple bonds.

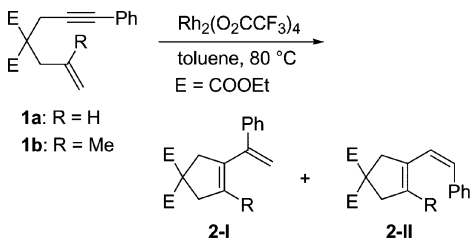
Recently, skeletal reorganization of enynes, leading to 1-vinylcycloalkenes, and related cycloisomerization reactions catalyzed by electrophilic metal complexes have been extensively studied.[1] These reactions are initiated by interactions between alkynes and electrophilic metals.[2] Interestingly, two possible isomers, type **I** and type **II**, form in the skeletal reorganization of enynes (Scheme 1).[3] When enynes having a substituent either at a terminal alkyne carbon or a terminal alkene carbon are used, one can determine which type of products form.

The formation of type **II** isomers involves double cleavage of both C–C triple and C–C double bonds, a phenomenon that is mechanistically interesting.[4,5] However, the number of reports describing the formation of type **II** products is limited. A mixture of type **I** and **II** products was usually obtained even when type **II** was formed[3] and the selective formation of type **II** products is rare.[3f] During the examination of catalysts that can catalyze the skeletal reorganization of enynes, we found that $Rh_2(O_2CCF_3)_4$ is active in the skeletal reorganization of enynes, especially enynes with an aryl group at the alkyne carbon. We wish to focus on selective formation of *cis*-configured type **II** products, which involves double cleavage of both C–C triple and C–C double bonds (eqn (1)).



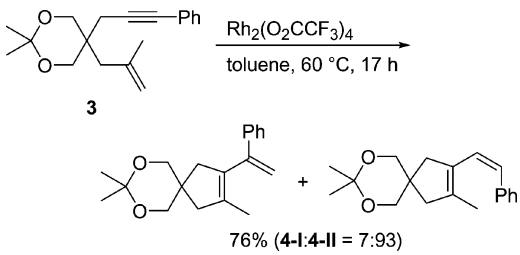
(1)

First, we examined the reaction of enyne **1a**, which has a phenyl group at the alkyne carbon and a malonate moiety in the tether, and that selectively gave the type **I** product **2a-I** (eqn (2)). Interestingly, substitution of a methyl group at the internal alkene carbon, as in **1b**, increased the product yield and gave a mixture of type **I** and **II** products in a nearly 1 : 1 ratio. Surprisingly, the type **II** product had a *cis* configuration.[6] This is the first example of exclusive formation of *cis*-configured type **II** products as a result of skeletal reorganization of enynes.[7]



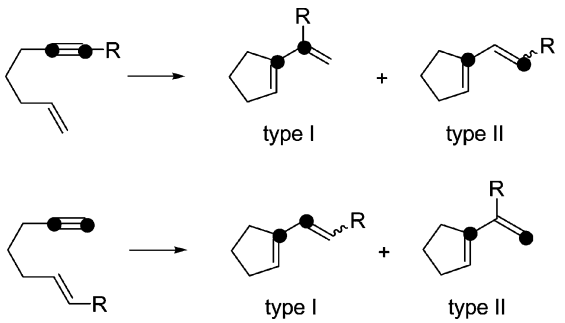
(2)

It is noteworthy that substituting the malonate moiety in the tether with a ketal moiety, as in **3**, led to the selective formation of type **II** isomers. This result demonstrates that the structure of the tether had a significant effect on the product distribution.



(3)

Based on the results in eqn (3), as expected, enynes **5**, **7**, **9**, and **11** also led to the selective formation of type **II** products. It was also found that enynes with an electron-withdrawing group, such as a CF_3 group on the phenyl ring, as in **13**, selectively gave the type **II**, as with product **14**, even if they have a malonate tether (compare with **1b** in eqn (2)). In addition, use of a sterically hindered aryl group, as in **17**, also selectively gave the type **II** product **18** in high yield. The electronic and steric natures of a substituent on the phenyl ring also affect the product distribution. In the case of 1,7-enyne **19**, the type **II** product was exclusively formed, even



Scheme 1 Type **I** *vs.* type **II**.

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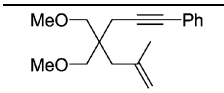
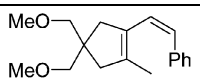
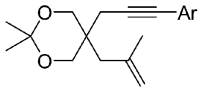
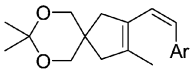
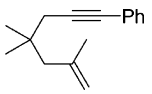
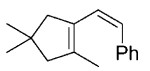
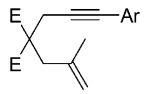
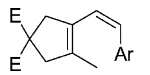
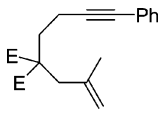
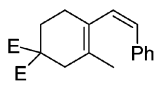
Table 1 Skeletal reorganization of enynes involving selective cleavage of C–C triple bonds[a]

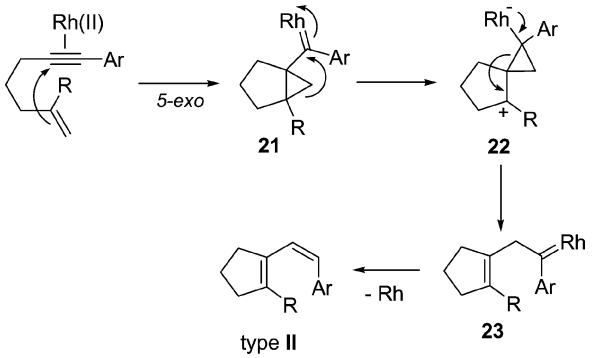
Enyne	Type **II** product	Yield (%)[b]
		73 (>98%) 5 h
5	**6**	
		
Ar = 1-Naphthyl (**7**)	**8**	76 (>98%)[c]
Ar = 4-$CF_3C_6H_4$ (**9**)	**10**	72 (95%) 3 h[d]
		67 (>98%) 4 h
11	**12**	
		
Ar = 4-$CF_3C_6H_4$ (**13**)	**14**	76 (91%)
Ar = 4-$MeOOCC_6H_4$ (**15**)	**16**	93 (87%)
Ar = 2-MeC_6H_4 (**17**)	**18**	94 (>98%)
		76 (>98%)[e]
19	**20**	

[a] Reaction conditions: enyne (0.5 mmol), $Rh_2(O_2CCF_3)_4$ (0.01 mmol), toluene (2.5 mL) at 80 °C for 20 h. [b] Type **II** selectivity is shown in parentheses. [c] $Rh_2(O_2CCF_3)_4$ (0.02 mmol) was used. [d] The reaction was carried out at 60 °C. [e] The reaction was carried out at 100 °C using $Rh_2(OOCCF_3)_4$ (0.04 mmol).

though **19** has a malonate tether, showing that chain length is also important, see Table 1 for results.

The proposed mechanism for the formation of type **II** is depicted in Scheme 2. Generation of metal–carbene complex **21** *via* the 5-*exo* pathway has already been proposed based on trapping of the metal–carbene intermediates[8] as well as DFT calculations.[9] Ring opening of **21** gives a spiro intermediate **22**. The presence of a methyl group (R = Me) on the alkene carbon facilitates formation of type **II** isomers because the methyl group stabilizes the tertiary cation in **22**.[10] Ring-opening of **22** gives the carbene complex **23**, which undergoes 1,2-H shift to give *cis*-configured type **II** isomers.[11]

In summary, we have demonstrated that a Rh(II) complex shows high catalytic activity for skeletal reorganization of 1,6- and 1,7-enynes and for selective formation of *cis*-configured type **II** products. Although the substrate scope is limited, this is the first example of the selective formation of *cis*-configured type **II** products. The reaction involves double cleavage of both C–C double and triple bonds. The origin of this selectivity, especially the role of the tether is not fully understood. Elucidation of the reaction mechanism is the subject of current investigations.



Scheme 2 Proposed reaction mechanism of the formation of type **II** products.

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