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Skeletal Reorganization of Enynes to 1-Vinylcycloalkenes Catalyzed by $GaCl_3$

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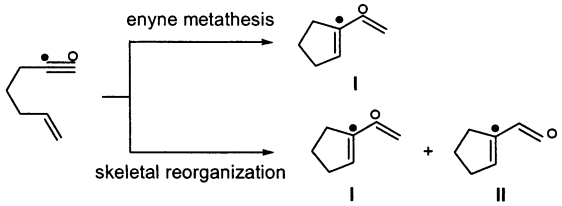
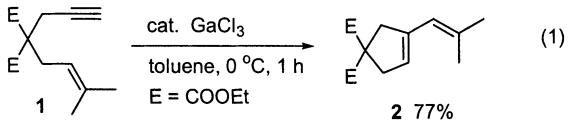
The transformation of enynes into 1-vinylcycloalkenes has been the subject of extensive study, because it provides a powerful method for the construction of a useful ring system by means of a simple operation.[1] The transformation can be classified into two types: enyne metathesis[2−4] and skeletal reorganization,[5−8] while one has not strictly distinguished these two reactions (Scheme 1). Enyne metathesis was first reported by Katz[2] and later further developed by Mori.[3] Enyne metathesis appears to proceed through a carbene mechanism, and type **I** products are obtained selectively, in which the original acetylenic carbons remain connected consecutively (Scheme 1).

Scheme 1. Transformation of Enynes to 1-Vinylcycloalkenes



In contrast, skeletal reorganization of enynes provides two possible isomers, types **I** and **II**. Production of the type **II** product involves the double cleavage of the C−C triple bond and double bond. In many cases, either of the two products is obtained, and the selectivity is dependent on the structure of the substrates and the catalysts used. The first report on the skeletal reorganization of enynes was published by Trost.[5a] When enynes bearing an ester group on the acetylenic carbon were used, **I** was selectively formed. In the case of a terminal alkyne entity, a mixture of types **I** and **II** was obtained. We also found that $[RuCl_2(CO)_3]_2$,[6a] $PtCl_2$,[6b] and $[IrCl(CO)_3]_n$[6c] are even more practical and simple catalysts for the skeletal reorganization of enynes bearing a terminal alkyne to 1-vinylcycloalkenes to the type **I** product. On the other hand, the reaction of enynes bearing a substituent, such as a methyl, phenyl, and ester, on the acetylenic carbon gave **II** as a main product.[6b] Fürstner et al. also reported that the skeletal reorganization of enynes is effectively catalyzed by $PtCl_2$.[7b] Quite recently, Oi et al. reported that platinum(II) cation complexes catalyze the skeletal reorganization of enynes.[8] Most importantly, the reaction mechanism of the skeletal reorganization of enynes is totally different from that of enyne metathesis. Cyclopropyl carbenoids or related complexes have been proposed as key intermediates in the formation of **I** and **II**.[5a,6d,8−10] All catalysts applicable to skeletal reorganization reported thus far involve late transition metal complexes. We wish to report here on the first use of typical element halides, such as $GaCl_3$, as a catalyst for the skeletal reorganization of enynes.

Recently, Yamaguchi et al. reported that $GaCl_3$ is a good activator of alkynes.[11] We also found that the cycloisomerization of ω-acetylenic benzene derivatives is catalyzed by $GaCl_3$.[12] These results prompted us to examine the possibility that $GaCl_3$ might function as the catalyst for the reaction of enynes. The reaction of 1,6-enyne **1** with a catalytic amount of $GaCl_3$ (1 M in a methylcyclohexane solution) in toluene at 0 °C was complete within 1 h, giving 1-vinylcyclopentene **2** as the product in 77% yield (eq 1). It should be noted that **1** is not a suitable substrate for the transformation of enynes to 1-vinylcyclopentenes reported thus far.[5−9]



(1)

Substantial structural variations can be accommodated, as can be seen from Table 1. Disubstituted enynes were found to serve as good substrates (entries 1 and 2). The $GaCl_3$ catalytic system was applicable to the formation of 1-vinylcyclohexenes (entries 2, 5, and 6). Sulfoneamide functionalities in the tether did not alter the course of the reaction (entries 5−7). It should be noted that the skeletal reorganization of enynes, which contain a monosubstituent at the olefinic terminal carbon, proceeds in a stereospecific manner (entries 3−6).[5a] This is in sharp contrast to previously reported results on the Ru(II)- and Pt(II)-catalyzed reaction of enynes, where trans isomers were obtained irrespective of the geometry of the starting materials.[6a,b] The reaction of the 1,7-enyne **13** is important, in that it provides for a better understanding of the reaction mechanism. Thus, the reaction of 1,7-enyne **13** at 40 °C resulted in an intramolecular [2 + 2] cycloaddition[13] to give a tricyclic compound **14**, which contains a cyclobutene ring. This indicates the possible participation of cyclobutene in the skeletal reorganization of enynes.

A proposed reaction mechanism is shown in Scheme 2. The reaction mechanism involves the production of a cyclobutene intermediate, as in **20**, which subsequently undergoes ring opening in a conrotatory manner, which explains the retention of the geometry of the olefinic portion. The electrophilic addition of $GaCl_3$ to an acetylene gives the vinyl-gallium species **16**,[12] which is stabilized by the olefinic portion, as in **17**.[14] The dotted triangle and positive charge represent a three-center two-electron bond and consist of one bonding and one positive charge. After the formation of the cyclopentane ring, the newly formed carbocation is stabilized by the Ga-substituted olefinic portion, as in **18**. The formation of the second C−C bond results in the production of the cyclobutane ring, generating **19**, which is followed by the elimination of $GaCl_3$ to afford the cyclobutene intermediate **20**. The ring opening of **20** would give 1-vinylcyclopentene **21**.[15] The direct conversion of **19** to **21**, which bypasses the formation of **20**, is an alternative route.

In summary, a typical metal halide, $GaCl_3$, also shows a high catalytic activity for the skeletal reorganization of enynes to 1-vinylcycloalkenes. The process is simple and provides a diverse

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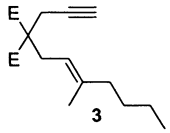
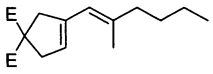
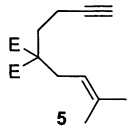
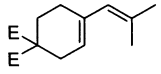
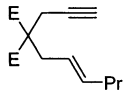
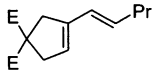
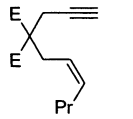
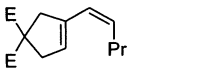
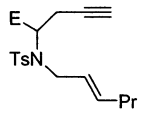
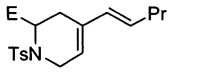
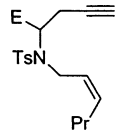
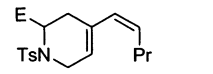
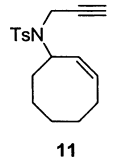
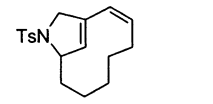
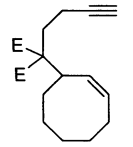
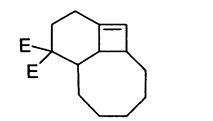
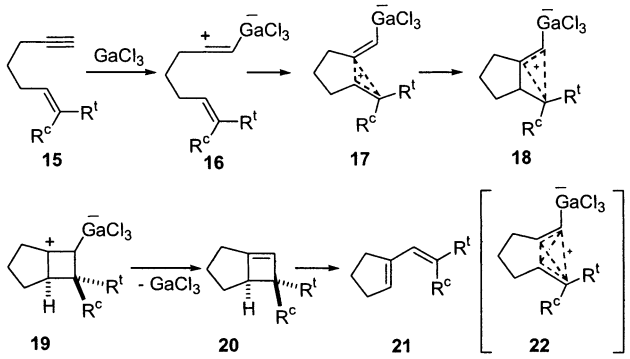
Table 1. Skeletal Reorganization of Enynes Catalyzed by $GaCl_3$[a]

entry	enynes	conditions	products
1	 **3**	0 °C 30 min[b]	 **4** 81%
2	 **5**	40 °C 30 min	 **6** 66%
3[c]	 **7E** (*E*/*Z* = 91/9)	40 °C 30 min	 **8E** 77% (*E*/*Z* = 91/9)
4	 **7Z** (*E*/*Z* = 10/90)	60 °C 30 min	 **8Z** 86% (*E*/*Z* = 11/89)
5	 **9E** (*E*/*Z* = 88/12)	60 °C 2 h	 **10E** 69% (*E*/*Z* = 93/7)
6	 **9Z** (*E*/*Z* = 11/89)	40 °C 2 h	 **10Z** 87% (*E*/*Z* = 5/95)
7	 **11**	60 °C 3 h	 **12** 72%
8	 **13**	40 °C 2 h	 **14** 79%

[a] Reaction conditions: enyne (0.5 mmol), $GaCl_3$ (0.05 mmol, 1.0 M in methylcyclohexane), and toluene (2.5 mL) under N_2. [b] Solvent: methylcyclohexane. [c] A small amount (4% yield) of a six-membered byproduct was also formed.

range of enynes in good to high yields. The $GaCl_3$-catalyzed system offers several advantages: (1) enynes bearing two substituents at the olefinic terminal carbon undergo an efficient skeletal reorganization, and (2) enynes that are monosubstituted at the terminal olefinic carbon undergo a stereospecific skeletal reorganization with respect to the geometry of the olefin moiety. The mechanistic difference between $GaCl_3$ and late transition metal complexes will be described later in a full article.

Scheme 2. A Proposed Reaction Mechanism



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Supporting Information Available: Lists of spectral data and elemental analyses for all of the new compounds (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Echavarren proposed the olefin-stabilized vinyl cation similar to **17** which is formed by the reaction of 1,6-enyne with Pt(II) complex as transition structure. See ref 9.

(15) A delocalized cation **22** can represent the forms **17** and **18**. Fürstner proposed a similar intermediate. See ref 7b.

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