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Highly Selective Skeletal Reorganization of 1,6- and 1,7-Enynes to 1-Vinylcycloalkenes Catalyzed by $[RuCl_2(CO)_3]_2$

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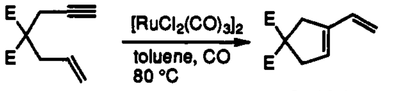
The development of new, efficient methods for the construction of ring systems represents an important ongoing challenge for synthetic organic chemists.[1] One very useful approach is Pd-catalyzed cycloisomerization of enynes[2] studied recently by Trost and co-workers.[3–5] Their results can be classified into two types, one not involving carbon–carbon bond cleavage[3,4] and the other involving carbon–carbon bond cleavage.[5] The latter allows remarkable skeletal reorganization of hept-1-ene-6-ynes to 1-vinylcyclopentenes. While synthetically attractive, this Pd-catalyzed reaction seemed highly selective only in the case of substrates having an electron-withdrawing group on the acetylenic terminal carbon and a cis substituent at the olefinic part. The limitation diminishes the utility of this novel skeletal reorganization reaction.

An issue critical to the synthetic utility of the cycloisomerization (or any isomerization reactions) is whether complete conversion with formation of only one product can be attained, because difficulty in separation of the unreacted starting material from the product is foreseen. We now report a new, synthetically useful ruthenium-catalyzed skeletal reorganization (cyclorearrangement) of 1,6-enynes to 1-vinylcyclopentenes with high chemical yields and high selectivity (>98% isomeric purity in all cases). The new catalytic reaction is also applicable to a 1,7-enyne.

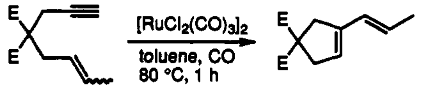


(1)

1 2 96%

The treatment of 1,6-enyne **1** with 4 mol % $[RuCl_2(CO)_3]_2$ in toluene under nitrogen gave a skeletal reorganization product, 3-ethenyl-3-cyclopentene-1,1-dicarboxylic acid diethyl ester (**2**),[6] in 69% isolated yield. Attempts for optimization of the reaction conditions using additives such as phosphines, isonitriles, and amines ended in vain. It was finally found that the presence of CO had a pronounced effect on the yield of **2**. Thus, the reaction of **1** (1 mmol) with $[RuCl_2(CO)_3]_2$ (0.04 mmol) in toluene (5 mL) at 80 °C under an atmosphere of CO was complete within 12 h to give **2** in 96% isolated yield with high selectivity (>99% isomeric purity) (eq 1). Any byproducts could not be detected by GC and NMR. A variety of ruthenium complexes were examined for their ability to catalyze reaction 1. Although $Ru_3(CO)_{12}$, $H_2Ru(CO)(PPh_3)_3$, $RuCl_2(CO)_2(PPh_3)_2$, $[Cp^*RuCl_2]_n$, $CpRuCl(PPh_3)_2$, $[Ru(OAc)(CO)_2]_n$, and $Ru(acac)_3$ were not active, the halide complexes such as $[RuBr_2(CO)_3]_2$ (87%), $[RuCl_2(p\text{-cymene})]_2$ (88%), and $RuCl_3{\cdot}xH_2O$ (84%) exhibited high catalytic activities when the reaction was run under an atmosphere of CO. The latter two did not show any catalytic activities under N_2 or Ar. $[RuCl_2(CO)_3]_2/AgBF_4$ (1:4 molar ratio) did not catalyze the reaction. These results show that the presence of a halide and CO ligands on ruthenium is essential for the reaction to proceed.

It is noteworthy that the present Ru-catalyzed reaction can be applied to enynes having a terminal acetylene moiety, which gave a mixture of products including skeletal reorganization products by Trost's Pd(II) catalyst.[5a] Substitution of a methyl group at the olefinic part enhanced the reactivity. The reactions of **3*E*** and **3*Z*** were complete within 1 h. Of particular note is the exclusive *E* geometry of the newly formed vinyl subunit, irrespective of the geometry of the starting enynes (eq 2).[7]

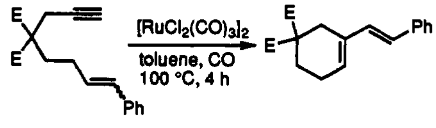


(2)

3*E* (*E*/*Z* = 80/20) **4** 95%
3*Z* (*E*/*Z* = 11/89) **4** 81%

The results obtained for a variety of enynes are summarized in Table 1. In all cases, starting enynes were completely consumed and the isomeric purity was quite high (>98%). No byproducts could be detected in GC.[8] The reaction of phenyl- or trimethylsilyl-substituted enynes gave the corresponding (*E*)-dienes exclusively (entries 1 and 2). The successful reorganization of **9** and **11** indicates that the geminal substitution in the tethers is not necessary (entries 3 and 4). The reaction of 1,6-enynes having an alkyl group at the internal carbon of the olefin moiety also proceeded smoothly (entries 5 and 6). Siloxy substitution at either the propargylic position or the allylic position favored the reaction (entries 7 and 8). The olefinic part can be trisubstituted (entry 9).

In contrast to Trost's system, a 1,7-enyne can be effectively trasnsformed to 1-vinylcyclohexenes.[9] The reaction of an *E*/*Z* mixture of 1,7-enyne **23** afforded only the *E* isomer of 1-vinylcyclohexene **24** in 86% yield when the reaction was run at 100 °C for 4 h (eq 3). This is the first example of skeletal reorganization of 1,7-enynes to vinylcyclohexenes.



(3)

23 (*E*/*Z* = 81/19) **24** 86%

The Trost's Pd(II) catalyst[3–5] seems not applicable to the skeletal reorganization of all the 1,6- and 1,7-enynes described above. To compare our Ru(II) catalyst system with Trost's Pd(II) catalyst system in which only enynes containing ester-

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[1] For recent papers on the transition-metal-mediated cyclization of dienes, enynes, and diynes, see: Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800. Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199. Trost, B. M.; Shi, Y. *J. Am. Chem. Soc.* **1993**, *115*, 9421. Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856. Chatani, N.; Fukumoto, Y.; Ida, T.; Murai, S. *J. Am. Chem. Soc.* **1993**, *115*, 11614.

[2] In these studies, 1,6-enynes were cycloisomerized to cyclopentane derivatives containing a 1,3- or 1,4-diene unit,[3] to bicyclo[4.2.0]cyclooctene derivatives via [2 + 2]cycloaddition,[4] and to 1-vinylcyclopentenes.[5]

[3] Trost, B. M.; Lautens, M. *J. Am. Chem. Soc.* **1985**, *107*, 1781. Trost, B. M.; Lautens, M. *Tetrahedron Lett.* **1985**, *26*, 4887. Trost, B. M.; Chen, S.-F. *J. Am. Chem. Soc.* **1986**, *108*, 6053. Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268. Trost, B. M.; Lautens, M.; Chan, C.; Jebaratnam, D. S.; Mueller, T. *J. Am. Chem. Soc.* **1991**, *113*, 636. Trost, B. M.; Gelling, O. J. *Tetrahedron Lett.* **1993**, *34*, 8233. Wartenberg, F.-H.; Hellendahl, B.; Blechert, S. *Synlett* **1993**, 539. Trost, B. M.; Czeskis, B. A. *Tetrahedron Lett.* **1994**, *35*, 211.

[4] Trost, B. M.; Yanai, M.; Hoogsteen, K. *J. Am. Chem. Soc.* **1993**, *115*, 5294.

[5] (a) Trost, B. M.; Tanoury, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 1636. (b) Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32*, 3647. (c) Trost, B. M.; Trost, M. K. *J. Am. Chem. Soc.* **1991**, *113*, 1850.

[6] All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analyses or high-resolution mass spectra. See the supplementary material.

[7] In contrast to our result, a stereospecific reaction was observed in the case of the Pd(II)-catalyzed reaction of ethoxycarbonyl-substituted enynes. (*Z*)-Enyne gave a diene product which consisted of only the *E* isomer. The *E* substrate gave predominantly the *Z* product. See ref 5a.

[8] Partial polymerization of enynes seems to be a side reaction, thus fortunately preventing the product from contamination with unreacted enynes.

[9] The Pd(II)-catalyzed reaction of 1,7-enynes resulted in [2 + 2]-cycloaddition with formation of bicyclo[4.2.0]octene derivatives, 1-vinylcyclohexenes not being obtained. See ref 4.

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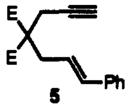
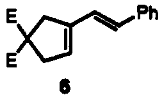
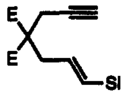
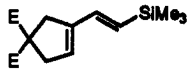
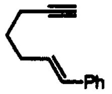
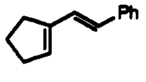
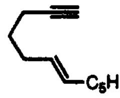
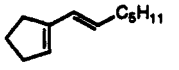
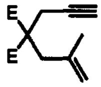
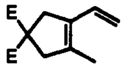
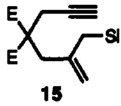
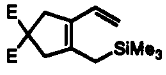
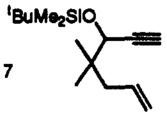
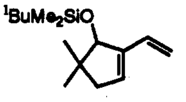
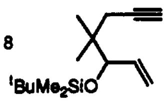
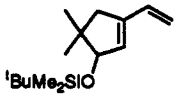
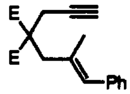
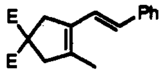
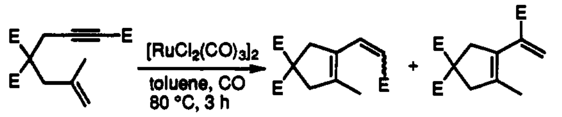
Table 1. $[RuCl_2(CO)_3]_2$-Catalyzed Reaction of Enynes to 1-Vinylcyclopentenes[a]

entry	enyne	product	yield[b] time
1	 **5**	 **6**	97% 1 h
2	 **7**	 **8**	86% 6 h
3	 **9**	 **10**	79% 4 h
4	 **11**	 **12**	83% 2 h
5	 **13**	 **14**	94% 1 h
6	 **15**	 **16**	80% 1 h
7	 **17**	 **18**	90% 1.5 h
8	 **19**	 **20**	90% 2 h
9	 **21**	 **22**	93% 1 h

[a] Reaction conditions: enyne (1 mmol), $[RuCl_2(CO)_3]_2$ (0.04 mmol), toluene (5 mL), 80 °C under CO. [b] Isolated yield based on the enyne.

substituted alkynes are employable substrates,[5] the reaction of an ethoxycarbonyl-substituted enyne **25** was carried out using $[RuCl_2(CO)_3]_2$ catalyst. The reaction of **25** in the presence of $[RuCl_2(CO)_3]_2$ under CO gave **26*Z*** as a major product, along with small amounts of **26*E*** and **27** (eq 4). In contrast, the reaction of **25**[10] with Trost's Pd(II) catalyst gave a 1:1.4 mixture of **27** and a bicyclo[3.2.0]heptene derivative, but **26** was not formed. These results show that the present reaction differs considerably from Trost's reaction.


$[RuCl_2(CO)_3]_2$
toluene, CO
80 °C, 3 h
E = COOEt
25 **26** **27**
90% (**26*Z***:**26*E***:**27** = 83:11:6) (4)

The reaction mechanism is not clear at present and must wait for further study.[11,12] The mechanistic aspect aside, the present reaction provides a new, efficient method of converting enynes to vinylcycloalkenes, which should find wide applications in practical organic synthesis.[15] Interestingly, some other metal halides such as $[RhCl(CO)_2]_2$, $ReCl(CO)_5$, $[IrCl(CO)_2]_n$, $PtCl_2$, and $AuCl_3$ can cause a similar skeletal reorganization and some of these complexes exhibited characteristic substrate specificity. These results will appear in the near future.

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Supplementary Material Available: Lists of spectral data and elemental analyses for the products (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(10) Trost used **25** (E = COOMe) in place of **25** (E = COOEt).

(11) Trost suggested that two paths are operating for the reaction with terminal acetylenes and only one path for the reaction with ester-substituted acetylenes to account for the dueterium labeling pattern.[5a] See also: Trost, B. M.; Hashmi, A. S. K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1085. We examined the reorganization of **1** with ^2H and ^{13}C labeling. Our labeling studies also revealed coexisting of two mechanistic pathways for the $[RuCl_2(CO)_3]_2$-catalyzed reaction of **1**.

(12) There are the following three possibilities for a first step of the reaction mechanism: (i) the formation of a ruthenacyclopentene complex via oxidative cyclization, (ii) a vinyl ruthenium complex via chlororuthenation,[13] and (iii) a slipped, polarized η^1-isomer bearing a positive charge at the β position via the rearrangement of an η^2-alkyne ruthenium complex.[14] A detailed discussion will be presented in the near future.

(13) Holland, P. R.; Howard, B.; Mawby, R. J. *J. Chem. Soc., Dalton Trans.* **1983**, 231.

(14) Pilette, D.; Moreau, S.; Le Bozec, H.; Dixneuf, P. H.; Corrigan, J. F.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1994**, 409.

(15) Fringuelli, F.; Taticchi, A. *Dienes in the Diels-Alder Reaction*; John Wiley & Sons, Inc.: New York, 1990. Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990.