ORGANIC
LETTERS

2005
Vol. 7, No. 8
1445−1447

$W(CO)_5(L)$-Catalyzed Formal Cope Rearrangement of Allenyl Silyl Enol Ethers

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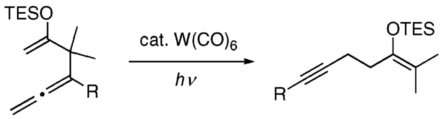
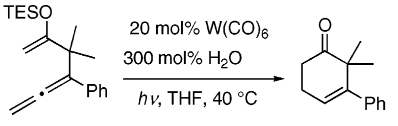
Received December 22, 2004

ABSTRACT



On treatment of 5-siloxyhexa-1,2,5-trienes with a catalytic amount of $W(CO)_6$ under photoirradiation, formal Cope rearrangement proceeded to give 2-siloxyhex-1-en-5-ynes in good yield. The electrophilic activation of the allenyl moiety by $W(CO)_5$ triggers the intramolecular attack of the silyl enol ether in a 6-*endo* manner to produce a cyclohexenyl tungsten species. Carbon–carbon bond cleavage occurs by electron donation from the anionic $W(CO)_5$ into the silyloxonium moiety to afford the products with regeneration of the $W(CO)_5(L)$.

Low-valent carbonyl complexes of group 6 metals such as $M(CO)_5(L)$ ($M = Cr, Mo, W$; $L = THF, Et_3N$, etc.) have emerged as useful catalysts for the electrophilic activation of unsaturated carbon−carbon bonds, and a variety of new reactions have been developed recently.[1] In the course of our studies on $W(CO)_5(L)$-catalyzed cyclization reactions of silyl enol ethers,[2] we found that $W(CO)_5$ can activate the allenyl moiety effectively, and the *endo*-selective cyclization of allenyl silyl enol ethers was found to proceed smoothly,[2f] where 5-siloxyhexa-1,2,5-triene **1a** gave six-membered β,γ-unsaturated ketone **2a** in 68% yield by carrying out the reaction using a catalytic amount of $W(CO)_6$ (0.2 equiv) under photoirradiation in the presence of H_2O (3.0 equiv) (eq 1).[3]



1a **2a** (1)

During these studies, we found that the reaction of the same substrate **1a** in the absence of H_2O under similar conditions proceeded by a different pathway to give a formal Cope rearrangement product, 2-siloxyhex-1-en-5-yne **3a**, in good yield. While there has been an abundant study of thermal or transition-metal-catalyzed Cope rearrangements of hexa-1,5-dienes,[4] that of hex-1-en-5-ynes or hexa-1,2,5-trienes has not been studied extensively despite their synthetic potential.[5−8] In this paper is described a novel $W(CO)_5(L)$-catalyzed formal Cope rearrangement of 5-siloxyhexa-1,2,5-trienes leading to 2-siloxyhex-1-en-5-yne derivatives.

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(1) For selected examples of catalytic reactions using low-valent group 6 metals, see: (a) Alcazar, E.; Pletcher, J. M.; McDonald, F. E. *Org. Lett.* **2004**, *6*, 3877. (b) Ohe, K.; Yokoi, T.; Miki, K.; Nishino, F.; Uemura, S. *J. Am. Chem. Soc.* **2002**, *124*, 526. (c) Sangu, K.; Fuchibe, K.; Akiyama, T. *Org. Lett.* **2004**, *6*, 353 and references therein.

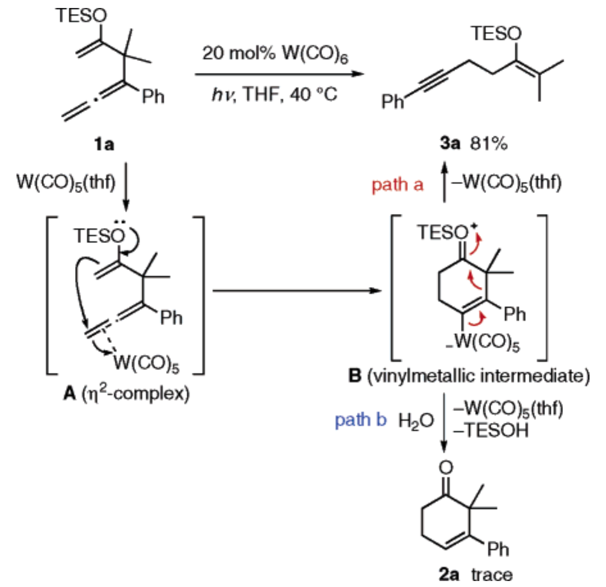
(2) (a) Maeyama, K.; Iwasawa, N. *J. Am. Chem. Soc.* **1998**, *120*, 1928. (b) Iwasawa, N.; Maeyama, K.; Kusama, H. *Org. Lett.* **2001**, *3*, 3871. (c) Miura, T.; Iwasawa, N. *J. Am. Chem. Soc.* **2002**, *124*, 518. (d) Kusama, H.; Yamabe, H.; Iwasawa, N. *Org. Lett.* **2002**, *4*, 2569. (e) Iwasawa, N.; Miura, T.; Kiyota, K.; Kusama, H.; Lee, K.; Lee, P. H. *Org. Lett.* **2002**, *4*, 4463. (f) Miura, T.; Kiyota, K.; Kusama, H.; Lee, K.; Kim, H.; Kim, S.; Lee, P. H.; Iwasawa, N. *Org. Lett.* **2003**, *5*, 1725. (g) Miura, T.; Murata, H.; Kiyota, K.; Kusama, H.; Iwasawa, N. *J. Mol. Cat. A* **2004**, *213*, 59.

(3) The reaction using an equimolar amount of $W(CO)_6$ was reported in ref 2f. After further examinations, we found the catalytic conditions shown in eq 1.

10.1021/ol0473694 CCC: $30.25

When 5-siloxyhexa-1,2,5-triene **1a** was treated with a catalytic amount of $W(CO)_6$ (0.2 equiv) in THF at 40 °C under photoirradiation for 1 day in the absence of H_2O, the cyclized product **2a** was obtained in a trace amount and 2-siloxyhex-1-en-5-yne **3a**, a formal Cope rearranged product, was obtained in 81% yield (Scheme 1).

Scheme 1

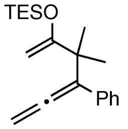
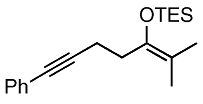
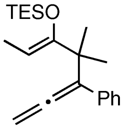
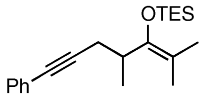
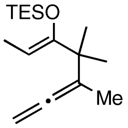
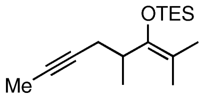
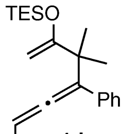
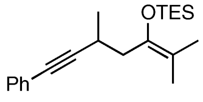
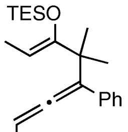
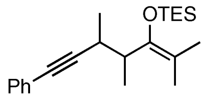


No reaction occurred when the substrate **1a** was irradiated at ambient temperature in the absence of $W(CO)_6$,[9] and thus, activation of the substrate **1a** by $W(CO)_5(L)$ is essential for this transformation.[10] The reaction pathway is proposed as follows: Coordination of $W(CO)_5$, generated *in situ* from $W(CO)_6$ under photoirradiation, onto the allenyl moiety gives the allene−$W(CO)_5$ η^2-complex **A**. Then, intramolecular attack of the silyl enol ether occurs on the distal carbon of the electrophilic allene moiety to give the vinylmetallic intermediate **B**. Electron donation from the $W(CO)_5$ anion into the silyloxonium moiety induces the carbon−carbon bond cleavage to give 2-siloxyhex-1-en-5-yne **3a** with regeneration of $W(CO)_5(L)$ (path a). Six-membered β,γ-unsaturated ketone **2a** is obtained by the protonation of the carbon−tungsten bond with a trace amount of H_2O present in the reaction mixture (path b).

Examinations of several reaction conditions revealed that the reaction time was greatly diminished from 1 day to 2 h by changing the reaction solvent from THF to toluene. Furthermore, by the addition of a catalytic amount of DABCO (0.1 equiv), the reaction proceeded cleanly to give the product **3a** in 90% yield as a sole product.[11]

Under these optimized conditions, reactions of a variety of 2-siloxyhex-1-en-5-ynes were carried out, and the results are summarized in Table 1.

Table 1. Formal Cope Rearrangement of 5-Siloxyhexa-1,2,5-trienes **1** with a Catalytic Amount of $W(CO)_6$ in Toluene[a]

entry	substrate	product	yield/%
1	 **1a**	 **3a**	90
2	 **1b**	 **3b**	68
3	 **1c**	 **3c**	61
4	 **1d**	 **3d**	86
5[b]	 **1e**	 **3e**	47[c]

[a] The reaction was carried out with **1** and DABCO (0.1 equiv) in toluene (0.1 M) in the presence of $W(CO)_6$ (0.2 equiv) at 40 °C under photoirradiation, unless otherwise noted. [b] The reaction was carried out in toluene (1.0 M). [c] *syn*:*anti*=1:1

The catalytic process worked well either with substrates containing a trisubstituted silyl enol ether moiety or a

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(4) For reviews on the Cope rearrangement reaction, see: (a) Hill, R. K. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 785−826. (b) Lutz, R. P. *Chem. Rev.* **1984**, *84*, 205. (c) Overman, L. E. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 579.

(5) For the first example, see: Black, D. K.; Landor, S. R. *J. Chem. Soc.* **1965**, 6784.

(6) For reviews dealing with the acetylenic or allenic Cope rearrangement, see: (a) Viola, A.; Collins, J. J.; Filipp, N. *Tetrahedron* **1981**, *37*, 3765. (b) Huntsman, W. D. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; J. Wiley and Sons: Chichester, 1980; Part 2, pp 582−643.

(7) For recent representative examples, see; (a) Owens, K. A.; Berson, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 5973. (b) Black, K. A.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 5622. (c) Hopf, H.; Wolff, J. *Eur. J. Org. Chem.* **2001**, 4009 and references therein.

(8) Metal-free Cope rearrangements of hexa-1,2,5-trienes normally require high reaction temperature (>250 °C).

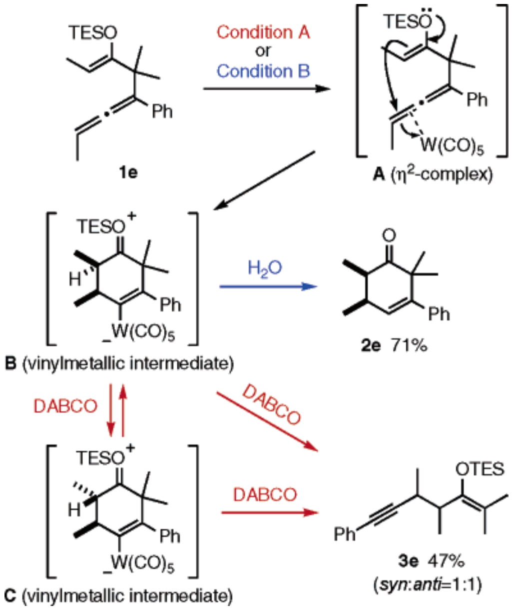
(9) When the substrate **1a** was heated at 250 °C in the absence of the catalyst, a thermal Cope rearrangement gradually proceeded to give a 3:1 mixture of **1a** and **3a** after 4 h.

(10) For an example of the transition-metal-catalyzed cycloisomerizations of allenynes, see: Cadran, N.; Cariou, K.; Hervé, G.; Aubert, C.; Fensterbank, L.; Malacria, M.; Marco-Contelles, J. *J. Am. Chem. Soc.* **2004**, *126*, 3408 and references therein.

(11) No additive (71%). Other amines: Et_3N (62%), *i*-Pr_2NEt (62%), *n*-Bu_3N (72%), and DBU (66%).

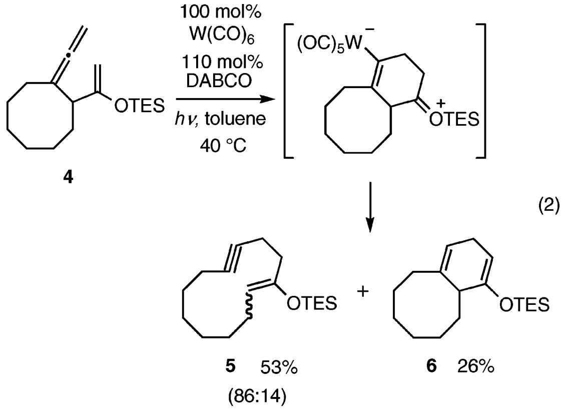
trisubstituted allene moiety to give the corresponding products **3b**−**d** in good yield (entries 2−4). In the case of substrate **1e** possessing both of these trisubstituted moieties, the reaction gave the product **3e** in moderate yield as a 1:1 mixture of *syn* and *anti* isomers (entry 5). It was noted that the reaction in the presence of H_2O gave the cyclized product **2e** in 71% yield stereoselectively (Scheme 2). Thus, isomerization probably occurred at the vinylmetallic intermediate **B** and/or **C** by DABCO.

Scheme 2



Condition A: $W(CO)_6$ (0.2 equiv) and DABCO (0.1 equiv) in toluene (1.0 M) under photoirradiation at 40 °C. Condition B: $W(CO)_6$ (0.2 equiv) and H_2O (3.0 equiv) in THF (1.0 M) under photoirradiation at 40 °C.

Next we examined a ring-expansion reaction by formal Cope rearrangement of a cyclic 5-siloxyhexa-1,2,5-triene.[12] When cyclooctane derivative **4** was irradiated in the presence of $W(CO)_6$ (1.0 equiv) and DABCO (1.1 equiv) in toluene, the reaction proceeded as expected to give the ring-expanded 12-membered cyclic product **5**[13] in 53% yield as an 86:14 mixture of *E* and *Z* isomers[14] together with a 26% yield of silyl enol ether **6** (eq 2).



In summary, we have developed a formal Cope rearrangement of 5-siloxyhexa-1,2,5-trienes catalyzed by $W(CO)_5(L)$. We can prepare two types of synthetically useful compounds, that is, 6-*endo* cyclization products or the Cope rearrangement products, from the same starting materials *via* the same intermediates simply by changing reaction conditions. Further studies to expand the utility of this reaction are in progress in our laboratory.

Acknowledgment. This research was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. We also thank Central Glass Co., Ltd. for a generous gift of TfOH. T. M. was a recipient of a Research Fellowship of the Japan Society for the Promotion of Science for Young Scientists.

Supporting Information Available: Experimental details and spectral data for new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] For an example of a ring-expansion reaction by thermal allenyl Cope rearrangement of hepta-1,2,6-triene, see: Vedejs, E.; Cammers-Goodwin, A. *J. Org. Chem.* **1994**, *59*, 7541.

[13] For some examples of synthesis of cyclic alkynes, see: (a) Gordon, D. M.; Danishefsky, S. J.; Schulte, G. K. *J. Org. Chem.* **1992**, *57*, 7052. (b) Sugai, M.; Tanino, K.; Kuwajima, I. *Synlett* **1997**, 461. (c) Young, D. G. J.; Burlison, J. A.; Peters, U. *J. Org. Chem.* **2003**, *68*, 3494.

[14] The geometry of **5** was not determined.