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RHODIUM(I)-CATALYZED ISOMERIZATION OF SILOXYCYCLOPROPANES LEADING TO ENOL SILYL ETHERS AND ALLYL SILYL ETHERS

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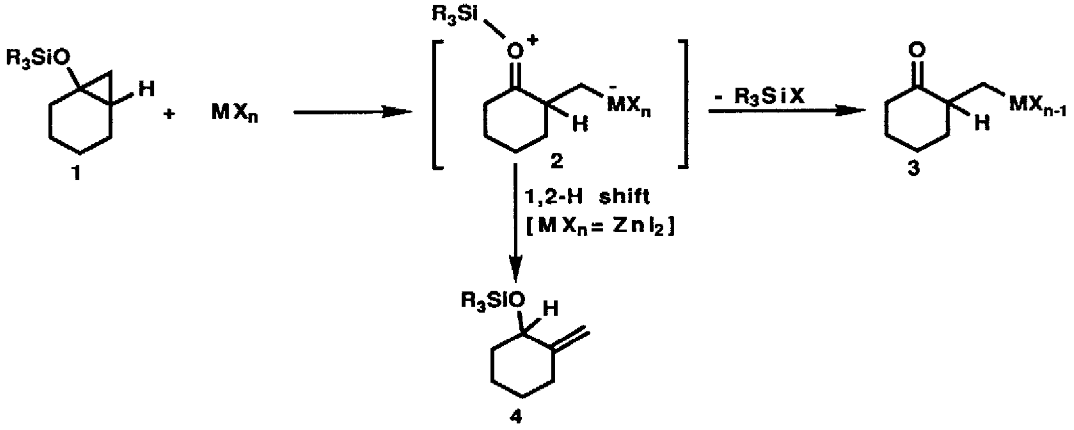
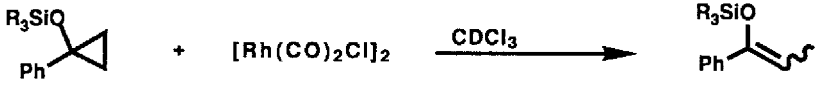
Summary: *The isomerization of siloxycyclopropanes to enol silyl ethers and allyl silyl ethers was accomplished by using* $[Rh(CO)_2Cl]_2$ *as a catalyst. Regiochemistry with respect to the newly formed double bond of the product was highly dependent on the substitution pattern of cyclopropane ring.*

In our continuous studies concerning siloxycyclopropane **1**,[1] we have revealed that two major reaction courses are available for metal-induced cleavages of **1**: (i) formation of β-metallo ketone **3**[2] and (ii) isomerization to allylic ether **4**.[3] Both processes are accounted for by assuming the electrophilic ring opening of **1** by metal ion to give an ionic intermediate **2**, followed by desilylation and 1,2-hydrogen shift, respectively. Although the transition-metal promoted ring opening of strained cyclopropanes has become of considerable interest in recent years,[4] examples of the reaction have been confined to cyclopropanes without electron donating substituents. Particularly intrigued by the possibility of the ring opening of siloxycyclopropane **1** with transition-metal complexes, we have examined the reaction of **1** with rhodium complexes.[5] Herein we report the Rh(I)-catalyzed isomerization of **1** to allyl silyl ether **4** and enol silyl ether **5**.



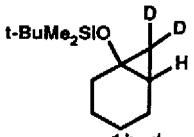
We first attempted the stoichiometric reaction of 1-phenyl-1-(trimethylsiloxy)cyclopropane (**1a**) with $[Rh(CO)_2Cl]_2$. The reaction did not afford any isolable rhodium complexes containing a fragment arising from **1a**, but isomerization of **1a** leading to 1-phenyl-1-(trimethylsiloxy)propene (**5a**) took place. For example, treatment of **1a** (0.2 mmol) with $[Rh(CO)_2Cl]_2$ (0.1 mmol) in $CDCl_3$ at 55°C for 12 h gave **5a** (46%), together with hydrolyzed propiophenone (51%). Although the reaction also proceeded with a catalytic amount of rhodium complex, hydrolysis to propiophenone became more serious. This undesirable side reaction was circumvented by using t-$BuMe_2Si$ derivative **1b** in place of **1a**. Thus, the catalytic isomerization of **1b** to enol silyl ether **5b** was well performed by using 2.5~5 mol% of $[Rh(CO)_2Cl]_2$.[6]



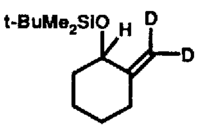
1a: $R_3Si=Me_3Si$ 0.2mmol	0.1mmol	55°C, 12h	**5a** 46% [E/Z=79/21]
1b: R_3Si=t-$BuMe_2Si$ 0.2mmol	0.05mmol	62°C, 6h	**5b** 91% [E/Z=51/49]

Isomerization of various siloxycyclopropanes **1** was usually carried out in sealed tubes without solvent (Table I). 2-Alkyl substituted siloxycyclopropanes **1e** and **1f** underwent regioselective ring opening to give enol silyl ethers **5e** and **5f**, respectively. The latter reaction also afforded allyl silyl ether **4f** as a minor product. With the exception of the bicyclic siloxycyclopropane **1g**, which gave small amounts of ring-expanded products **7g** and **8g**,[7] the ring opening took place regioselectively between the peripheral and the siloxy carbons. Interestingly, isomerization of **1h** bearing a six-membered ring led only to allyl silyl ether **4h** with no other double bond isomers detectable.[8]

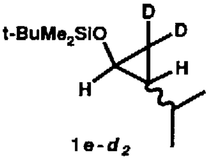
In order to obtain further insight into the mechanism, the Rh-catalyzed isomerization of **1h**-d_2 was carried out. The isotopic composition of isomerized allylic ethers was determined by GC-MS to be 90% d_2, 10% d_1, 0% d_0. The location of two deuteriums in d_2 product was exocyclic methylene carbon as depicted in **4h**-d_2 (^1H NMR). A similar experiment with **1e**-d_2 afforded **5e**-d_2 with ~100% d_2 content. When isomerization of **1h**-d_2 was carried out in the presence of 2-methyl-1-(siloxy)cyclohexene **5h**, no contamination with d_0 product **4h** was observed, while **5h** remained unreacted. We concluded, accordingly, that allylic ether **4h** was not formed by the second isomerization from initially formed enol silyl ether **5h**.[9]



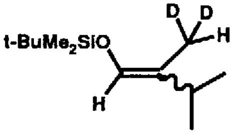
1h-d_2



4h-d_2



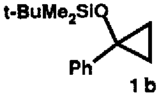
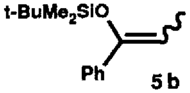
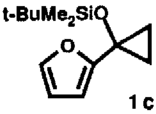
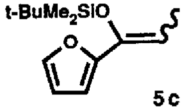
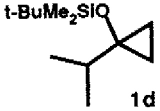
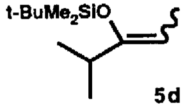
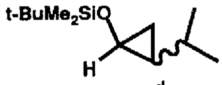
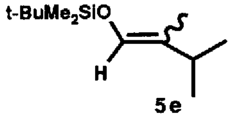
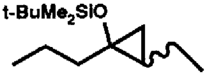
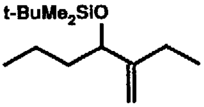
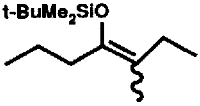
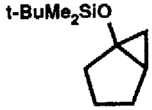
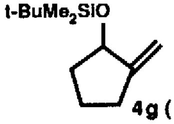
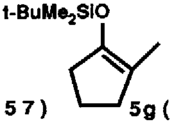
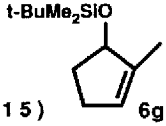
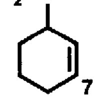
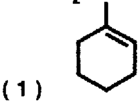
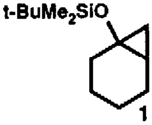
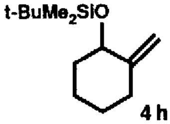
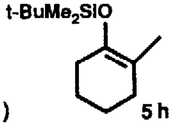
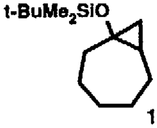
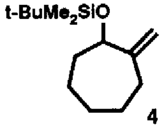
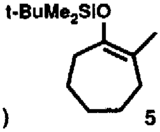
1e-d_2



5e-d_2

The above results lend support to the following pathway (Scheme I). The first step is probably an oxidative addition leading to rhodacyclobutane **9** across the peripheral bond of cyclopropane adjacent to siloxy

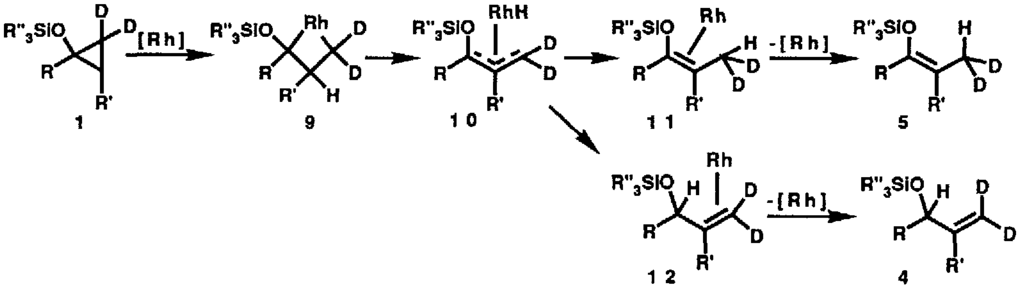
Table I. Rh(I)-Catalyzed Isomerization of Siloxycyclopropanes 1[a]

entry	substrate	temp(°C), time(h)	product (E/Z, yield(%))[b]
1	 1b	70, 6	 5b (52/48, 90)
2[c]	 1c	62, 27	 5c (80/20, 70)
3	 1d	90, 27	 5d (70/30, 63)
4	 1e[d]	90, 27	 5e (58/42, 71)
5	 1f[e]	120, 45	 4f (3)  5f (65/35, 55)
6	 1g	90, 72	 4g (57)  5g (15)  6g (7)  7g (1)  8g (7)
7	 1h	90, 40	 4h (69)  5h (-)
8[f]	 1i	100, 42	 4i (21)  5i (27)

a) Conducted in sealed tubes with 5mol% of $[Rh(CO)_2Cl]_2$. b) Determined by GC and/or ^1H NMR. c) $CHCl_3$ reflux. d) E/Z=64/36. e) E/Z=64/36. f) Starting material 1i was recovered (38%).

group.[10] β-Hydrogen abstraction from **9** gives π-allyl rhodium hydride **10**. Reductive elimination from **10** at C_1 and C_3 carbons produces π-complexes **12** and **11**, respectively. The selectivity of **5** and **4** would be concerned with the relative kinetic stability of these π-complexes,[11] although we have not probed for direct evidence on this point.

Scheme I



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References and Notes

(1) For a review, see: Murai, S.; Ryu, I.; Sonoda, N. *J. Organomet. Chem.* **1983**, *250*, 121.

(2) For a recent work, see: Ryu, I.; Suzuki, H.; Ogawa, A.; Kambe, N.; Sonoda, N. *Tetrahedron Lett.* **1988**, *29*, 6137.

(3) Some siloxycyclopropanes **1** underwent ZnI_2-promoted isomerization to allyl silyl ethers **4**, see: (a) Ryu, I.; Aya, T.; Otani, S.; Sonoda, N. *J. Organomet. Chem.* **1987**, *321*, 279. (b) Murai, S.; Aya, T.; Renge, T.; Ryu, I.; Sonoda, N. *J. Org. Chem.* **1974**, *39*, 859. (c) Ryu, I.; Murai, S.; Otani, S.; Sonoda, N. *Tetrahedron Lett.* **1977**, 1975. (d) Ryu, I.; Murai, S.; Sonoda, N. *Ibid.* **1977**, 4611; **1978**, 856. (e) Bartels, K.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 251.

(4) For reviews, see: (a) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245. (b) Sarel, S. *Acc. Chem. Res.* **1977**, *11*, 204. (c) Bishop III, K. C. *Chem. Rev.* **1976**, *76*, 461.

(5) For Rh(I) catalyzed isomerization of highly strained compounds, see: (a) Gassman, P. G.; Bonser, S. M.; M, -Majerski, K. *J. Am. Chem. Soc.* **1989**, *111*, 2652. (b) Wiberg, K. B.; Bishop III, K. C. *Tetrahedron Lett.* **1973**, 2727. (c) Chum, S.; Roth, J. A. *J. Catal.* **1975**, *39*, 198. (h) Katz, T. J.; Cerefice, S. A. *J. Am. Chem. Soc.* **1971**, *93*, 1049. (d) Hidai, M.; Orisaku, M.; Uchida, Y. *Chem. Lett.* **1980**, 753.

(6) Wilkinson's catalyst ($(PPh_3)_3RhCl$) was virtually inactive under comparable conditions.

(7) The formation of endo olefin **6g** seems rather queer in light of the mechanism shown in Scheme I. For the pathway to **6g** the possibility of the acid-catalyzed isomerization from **4g** remains unexcluded.0

(8) The reaction sequence is formally identical with previously reported isomerization by ZnI_2, see: ref 3.

(9) Metal catalyzed isomerization of allyl silyl ether to enol silyl ether has been known, see: Suzuki, H.; Koyama, Y.; Moro-oka, Y.; Ikawa, T. *Tetrahedron Lett.* **1979**, 1415.

(10) Formation of rhodacyclobutanes is well precedented, see: (a) McQuillin, F. J.; Powell, K. C. *J. Chem. Soc., Dalton Trans.* **1972**, 2129. (b) Roundhill, D. M.; Lawson, D. N.; Wilkinson, G. *J. Chem. Soc. (A)*, **1968**, 845. (c) Johnson, T. H.; Baldwin, T. *J. Org. Chem.* **1980**, *45*, 140. (d) Perina, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1984**, *106*, 7272.

(11) Judging from the absence of positional scrambling for deuterium in d_2 product, an equilibrium among **10**, **11**, and **12** would be excluded.

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