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Communications

A New Cycloisomerization Reaction: Formation of Eight-Membered-Ring Compounds from 3-Sila 1,7-Enynes

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Summary: An intramolecular cycloisomerization occurred upon adding a tertiary amine N-oxide to alkyne−cobalt complexes, derived from 3-sila 1,7-enynes and dicobalt octacarbonyl. As a result, eight-membered cyclic dienylsilanes were obtained by a regioselective insertion of the alkynyl group into the C(1)−H bond.

The Pauson−Khand reaction[1] is a potent method for the preparation of cyclopentenone derivatives from alkenes, alkynes, and carbon monoxide. This reaction usually is performed by heating a mixture of an alkene and an alkyne−cobalt complex. A variety of modifications have been reported; tertiary amine *N*-oxides,[2] DMSO,[2d] and silica gel[3] effectively promote the reaction.

During our initial study concerning the intramolecular Pauson−Khand reaction of silicon-tethered 1,7-enyne **1**, we observed the unexpected formation of eight-membered cyclic dienylsilanes **2** instead of cyclopentenone derivative **3** (Scheme 1).[4] A characteristic of this cycloisomerization reaction[5] is that a new C−C bond was formed between the C(1) and the C(8) of the 1,7-enyne to give a 1,3-cyclooctadiene skeleton. Some cycloisomerization reactions of 1,7-enynes have been reported, which can be classified into three categories on the basis of the structure of the products: the cycloisomerizations to (1) 1,2-dimethylenecyclohexanes,[6] (2) 1-methylene-2-vinylcyclohexanes,[6b,7] and (3) 1-vinylcyclohexenes.[8] However, no cycloisomerization reaction of 1,7-enynes giving 1,3-cyclooctadienes has been reported so far. Although an eight-membered ring is a common structural element in both natural and un-

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(1) For recent reviews on the Pauson−Khand reaction, see: (a) Schore, N. E. *Org. React.* **1991**, *40*, 1. (b) Schore, N. E. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, U.K., 1991; Vol. 5, p 1037. (c) Schore, N. E. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, U.K., 1995; Vol. 12, p 703.

(2) (a) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Tetrahedron Lett.* **1990**, *31*, 5289. (b) Jeong, N.; Chung, Y. K.; Lee, B. Y.; Lee, S. H.; Yoo, S.-E. *Synlett* **1991**, 204. (c) Krafft, M. E.; Romero, R. H.; Scott, I. L. *J. Org. Chem.* **1992**, *57*, 5277. (d) Chung, Y. K.; Lee, B. Y.; Jeong, N.; Hudecek, M.; Pauson, P. L. *Organometallics* **1993**, *12*, 220. (e) Jeong, N.; Lee, B. Y.; Lee, S. M.; Chung, Y. K.; Lee, S.-G. *Tetrahedron Lett.* **1993**, *34*, 4023. (f) Krafft, M. E.; Scott, I. L.; Romero, R. H.; Feibelmann, S.; Van Pelt, C. E. *J. Am. Chem. Soc.* **1993**, *115*, 7199.

(3) Smit, W. A.; Buhanjuk, S. M.; Simonyan, S. O.; Shashkov, A. S.; Struchkov, Y. T.; Yanovsky, A. I.; Caple, R.; Gybin, A. S.; Anderson, L. G.; Whiteford, J. A. *Tetrahedron Lett.* **1991**, *32*, 2105 and references therein.

(4) In the reaction of alkynes with electron-deficient alkenes under the Pauson−Khand conditions, the corresponding dienyl products have been obtained: Khand, I. U.; Pauson, P. L. *J. Chem. Soc., Chem. Commun.* **1974**, 379.

(5) For a recent review, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 259.

(6) (a) Trost, B. M.; Tour, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 5268. (b) Trost, B. M.; Gelling, O. J. *Tetrahedron Lett.* **1993**, *34*, 8233. (c) Trost, B. M.; Tanoury, G. J.; Lautens, M.; Chan, C.; MacPherson, D. T. *J. Am. Chem. Soc.* **1994**, *116*, 4255. (d) Trost, B. M.; Romero, D. L.; Rise, F. *J. Am. Chem. Soc.* **1994**, *116*, 4268.

(7) Trost, B. M.; Czeskis, B. A. *Tetrahedron Lett.* **1994**, *35*, 211.

(8) (a) Katz, T. J.; Sivavec, T. M. *J. Am. Chem. Soc.* **1985**, *107*, 737. (b) Chatani, N.; Morimoto, T.; Muto, T.; Murai, S. *J. Am. Chem. Soc.* **1994**, *116*, 6049. (c) Kinoshita, A.; Mori, M. *Synlett* **1994**, 1020. (d) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901.

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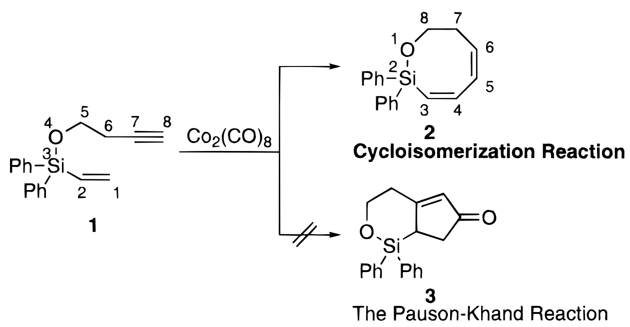
Scheme 1



natural compounds, its synthesis is rather difficult because of its high degree of ring strain and transannular interaction.[9] In this paper, we report a novel cycloisomerization reaction of 1,7-enynes, providing a conceptually new method for the construction of eight-membered rings.

As mentioned above, it was found that the alkyne–cobalt complex, prepared from 1,7-enyne **1** and dicobalt octacarbonyl in CH_2Cl_2 at room temperature, reacted with *N*-methylmorpholine *N*-oxide monohydrate (NMO•H_2O) (abbreviated as the *N*-oxide condition) to give eight-membered cyclic dienylsilane **2** in 46% yield.[10] Neither a carbonylated nor a regio- and/or stereoisomeric product could be detected by capillary GC-MS analysis of the crude reaction mixture. It is noteworthy that the cycloisomerization mode is quite different from that of 1,7-enynes that do not contain silicon; they underwent the Pauson–Khand reaction to produce bicyclo[4.3.0]nonenone derivatives on treatment with amine *N*-oxides[2a,c,e,f] or upon heating.[11]

The stereochemistry of the diene moiety of product **2** was determined on the basis of the ^{1}H NMR coupling constants of the olefinic protons.[12] The coupling constants (J_{3-4} = 14.8 Hz, J_{5-6} = 11.5 Hz) clearly indicate that **2** has (3*Z*,5*Z*)-stereochemistry. Furthermore, the stereochemistry was established by an X-ray crystallographic analysis[13] of the epoxyvinylsilane **4**, prepared by the epoxidation of **2** with *m*-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2 (86% yield). This epoxyvinylsilane **4** has (5*R**,6*S**)-stereochemistry as shown in Figure 1. If we take into account that the epoxidation of alkenes by *m*CPBA proceeds by *syn*-addition, the stereochemistry of the original dienylsilane **2** must be 3*Z*,5*Z*.

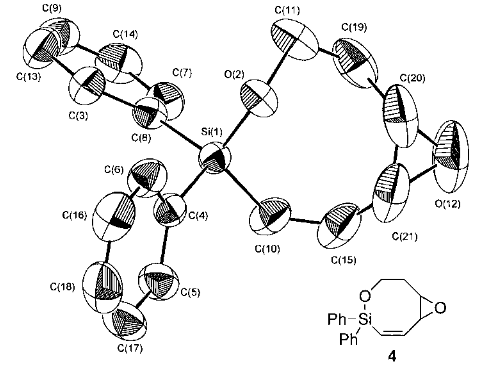
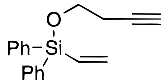
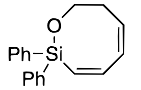
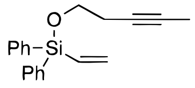
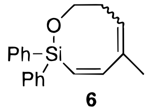
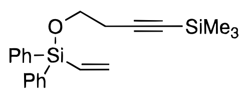
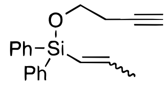
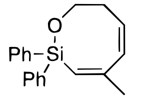
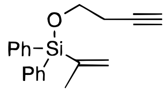
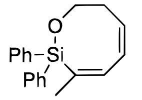
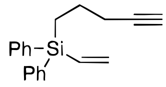
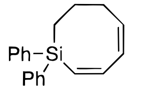
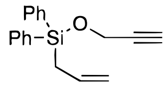


Figure 1. ORTEP view of **4**.

Table 1. Cycloisomerization Reaction of 1,7-Enynes

Entry	1,7-Enyne	Time/h	Product	Yield/%[a]
1	 **1**	1	 **2**	46
2	 **5**	2	 **6** *E*/*Z* = 3:2[c]	30[b]
3	 **7**	4	———	0
4	 **8** *E*/*Z* = 1:4	3	 **9**	24
5	 **10**	2	 **11**	24
6	 **12**	4	 **13**	22[b]
7	 **15**	1	———	0

[a]Isolated yields. [b]GC yields. [c]Stereoisomer ratios were determined by GC.

The results for the cycloisomerization of a variety of 1,7-enynes under the *N*-oxide condition are summarized in Table 1. First, we examined the effect of a substituent on the alkyne terminus (entries 1–3). A bulky substituent at the alkyne terminus such as a trimethylsilyl group retarded the cycloisomerization reaction, and a considerable amount of the decomplexed enyne was recovered. In the reaction of methyl-substituted 1,7-enyne **5**, the (3*Z*,5*E*)-isomer was obtained as a major product in addition to the (3*Z*,5*Z*)-isomer. 1,7-Enynes, which have a methyl group at the alkenyl moiety, also underwent cycloisomerization (entries 4 and 5). 1,7-Enyne **12** gave the expected product **13** (entry 6), and the intramolecularly carbosilylated product **14** (Chart 1), which resulted from the insertion of the alkynyl

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(9) Petasis, N. A.; Patane, M. A. *Tetrahedron* **1992**, *48*, 5757.

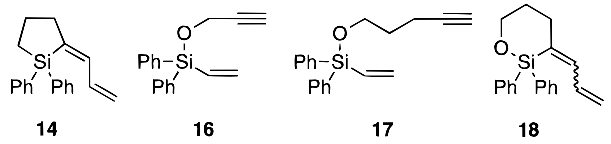
(10) General procedure for the cycloisomerization of enynes: To a solution of $Co_2(CO)_8$ (171 mg, 0.50 mmol) in CH_2Cl_2 (4 mL) was added a solution of enyne **1** (149 mg, 0.50 mmol) in CH_2Cl_2 (4 mL), and the solution was stirred at room temperature for 1 h. After the solution had been diluted with CH_2Cl_2 (40 mL), NMO•H_2O (0.68 g, 5.0 mmol) was added in one portion, and the reaction mixture was stirred at room temperature for 1 h. A purple precipitate formed. The resulting mixture was concentrated and filtered through a short silica gel plug (eluent: 5/1 hexane/ethyl acetate), and the eluent was concentrated. Purification of the crude product by PTLC (eluent: 30/1 hexane/ethyl acetate) gave **2** (63 mg, 46%).

(11) (a) Schore, N. E.; Croudace, M. C. *J. Org. Chem.* **1981**, *46*, 5436. (b) Brown, S. W.; Pauson, P. L. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1205. (c) Castro, J.; Sörensen, H.; Riera, A.; Morin, C.; Moyano, A.; Pericàs, M. A.; Greene, A. E. *J. Am. Chem. Soc.* **1990**, *112*, 9388. (d) Castro, J.; Moyano, A.; Pericàs, M. A.; Riera, A.; Greene, A. E. *Tetrahedron: Asym.* **1994**, *5*, 307.

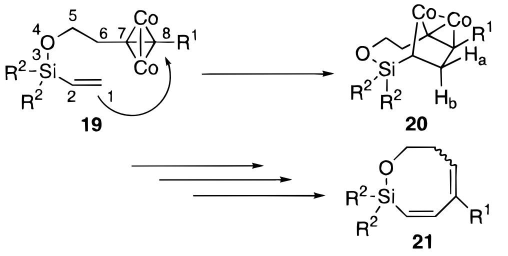
(12) **2**: ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.52 (dt, 2H, J = 5.6, 8.6 Hz), 3.91 (t, 2H, J = 5.6 Hz), 5.73 (dt, 1H, J = 8.6, 11.5 Hz), 5.98 (d, 1H, J = 14.8 Hz), 6.31 (dd, 1H, J = 4.4, 11.5 Hz), 6.84 (dd, 1H, J = 4.4, 14.8 Hz), 7.32–7.63 (m, 10H).

(13) X-ray crystal data for **4**: Triclinic; $P\bar{1}$; colorless crystal; a = 9.415(1), b = 11.909(2), c = 7.697(1) Å; α = 96.56(1), β = 113.02(1), γ = 89.57(1)°; Z = 2; R = 0.043; GOF = 0.30. For full details, see the Supporting Information.

Chart 1



Scheme 2



moiety into the Si−C(2) bond, was a byproduct in 8% yield. In all cases, no six-membered ring product was detected by ^{1}H NMR and capillary GC-MS analysis, although the yields of the cycloisomerized products were not high.

In the reaction of allyl(propargyloxy)silane **15**, no cycloisomerized product was detected (entry 7). In this case, only decomposition of the starting material occurred. Moreover, under the *N*-oxide condition, a one carbon-shorter analog, 1,6-enyne **16**, and a one-carbon-longer analog, 1,8-enyne **17**, did not cycloisomerize to the corresponding seven-membered[14] and nine-membered products, respectively. However, a small amount (4%, E/Z = 1:9) of an intramolecular carbosilylated product **18** was isolated from the reaction mixture of **17** (Chart 1). These results reveal that this cycloisomerization reaction is peculiar to 3-sila 1,7-enynes.

Although the reaction mechanism, especially concerning the regio- and stereoselectivities, and the reason for the lack of incorporation of CO are not clear at present, we consider that metallacycle **20** is a key intermediate in the present cycloisomerization (Scheme 2). The insertion of the vinylsilane part into the C(8)−Co bond of alkyne−cobalt complex **19** occurs in such a manner as to make a bond between the Co atom and the α-carbon (C(2)) of the vinylsilyl group. The regioselectivity would be determined by the stabilization of the α-carbanion by the silyl group, which is well-known.[15] Metallacycle **20** would be converted to **21** by successive β-hydrogen (H_a) abstraction, reductive elimination, and elimination of the cobalt moiety.

In conclusion, we have found a new cycloisomerization reaction of 3-sila 1,7-enynes to give eight-membered cyclic dienylsilanes. Further studies are in progress to explore mechanistic aspects responsible for the regio- and stereoselectivities, as well as to develop a catalytic system.

Supporting Information Available: Text giving experimental procedures and spectral data for synthesized compounds, tables of crystal data, atomic positional and isotropic and anisotropic thermal parameters, bond lengths, and bond angles for compound **4**, and NMR spectra (18 pages). Ordering information is given on any current masthead page.

OM9606294

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[14] The Pd-catalyzed cycloisomerization reaction of 1,6-enynes to cycloheptadiene derivatives has been reported: Trost, B. M.; Trost, M. K. *Tetrahedron Lett.* **1991**, *32*, 3647.

[15] (a) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 10, 21. (b) Takeuchi, R.; Ishii, N.; Sugiura, M.; Sato, N. *J. Org. Chem.* **1992**, *57*, 4189.