Formation of 2-[1-(Trimethylsilyl)alkylidene]-4-cyclopentene-1,3-dione from Lewis Acid-Catalyzed Reaction of Cyclobutenedione Monoacetal with Alkynylsilane: Novel Cationic 1,2-Silyl Migrative Ring Opening and Subsequent 5-*Exo-Trig* Ring Closure

Yoshihiko Yamamoto,† Masashi Noda, Masatomi Ohno, and Shoji Eguchi*

Institute of Applied Organic Chemistry, Faculty of Engineering, Nagoya University, Chikusa, Nagoya 464-01, Japan

Received August 9, 1996⊗

An ethoxycarbenium ion intermediate, which was produced by the catalytic action of a Lewis acid on a cyclobutenedione monoacetal, reacted with phenyl(trimethylsilyl)acetylene to give a normal electrophilic substitution product. In sharp contrast, the same catalytic reaction with bis-(trimethylsilyl)acetylene afforded a 2-methylene-4-cyclopentene-1,3-dione derivative as a ring expansion product instead of an alkynylation product. Butyl(trimethylsilyl)acetylene showed reactivity between the aforementioned compounds as a result of the formation of both types of products. In the reactions of such alkyl-substituted silylacetylenes, both *E*- and *Z*-isomers of 2-(1-silylalkylidene)cyclopentenediones were obtained in ratios dependent on the reaction temperature and the amount of Lewis acid. This rearrangement resulted from unprecedented cationic 1,2-silyl migration on the alkynylsilane and subsequent ring expansion promoted by the formed vinyl cation intermediate. A detailed mechanism of the novel ring-expansion route is discussed with the aid of PM3 calculations, especially for the reclosure step, which is explained by a 5-*exo-trig* cyclization rather than a pentadienyl cation electrocyclization.

2-Alkylidene-4-cyclopentene-1,3-dione, an attractive building block for synthesis of cyclopentanoids,[1] is accessible from ring-expansion routes starting from squaric acid. Liebeskind and co-workers have developed palladium- and mercury-catalyzed rearrangement of 4-alkynyl-4-hydroxycyclobutenones to a variety of 2-alkylidene-4-cyclopentene-1,3-dione derivatives.[2] We have also found a similar type of reaction to furnish 2-(iodomethylene)-4-cyclopentene-1,3-diones, in which ionic rearrangement of a hypoiodite intermediate is believed to be involved.[3] These reactions are based on 1,2-acyl migration at the ring-expansion step. On the other hand, Liebeskind demonstrated an alternative [4 + 1] cycloaddition route using the reaction of cobaltacyclopentenedione with terminal acetylenes.[4] Moore *et al.* also reported a limited thermal rearrangement route involving a (2-alkynylethenyl)ketene.[5]

In the course of our search for electrophilic addition reactions of cyclobutenedione monoacetal with alkynylsilanes, we found a novel rearrangement to 2-[1-(trimethylsilyl)alkylidene]-4-cyclopentene-1,3-dione. It was induced by cationic 1,2-silyl migration after addition of the monoacetal to the alkynylsilane and followed by the formed vinyl cation-induced ring opening and reclosure. Recently, the 1,2-silyl migration has been documented from a synthetic point of view as a key step for ring construction. The [3 + 2] cycloaddition of allenylsilanes leading to various 5-membered carbo- and heterocyclic compounds as developed by Danheiser involved the 1,2-silicon shift of an intermediate vinyl cation to accomplish the subsequent annulation.[6] A similar 1,2-silyl migrative [3 + 2] cycloaddition reaction of allylsilane was first reported by Knölker.[7] In this case, a normal Sakurai reaction product was also formed as a result of competitive desilylation; therefore, a sterically hindered silyl group has to be used to suppress a nucleophilic attack on the silicon atom.[8] In addition to these [3 + 2] cycloadditions, [2 + 1] cycloaddition of 2-selenovinylsilanes with α,β-unsaturated ketones and aldehydes was recently demonstrated by Yamazaki.[9] This cyclopropanation showed that a cationic 1,2-silicon shift was assisted by the adjacent selenyl group. Thus, the 1,2-silyl migration is favored when a cyclization pathway is advanced by the migration and a competing desilylation pathway is suppressed by steric bulkiness of the silyl group. In our case, this migration was observed for the first time as a key step for ring expansion based on

† Research Fellow of the Japan Society for the Promotion of Science.

⊗ Abstract published in *Advance ACS Abstracts,* February 15, 1997.

(1) (a) Kikuchi, H.; Tsukitani, Y.; Iguchi, K.; Yamada, Y. *Tetrahedron Lett.* **1982**, *23*, 25. (b) Iguchi, K.; Kaneta, S.; Mori, K.; Yamada, Y.; Honda, A.; Mori, Y. *Tetrahedron Lett.* **1985**, *26*, 5787. (c) Baker, B. J.; Okuda, R. K.; Yu, P. T. K.; Scheuer, P. J. *J. Am. Chem.Soc.* **1985**, *107*, 2976.

(2) (a) Liebeskind, L. S.; Mitchell, D.; Foster, B. S. *J. Am. Chem. Soc.* **1987**, *109*, 7908. (b) Mitchell, D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 291. (c) Liebeskind, L. S.; Bombrun, A. *J. Org. Chem.* **1994**, *59*, 1149.

(3) Yamamoto, Y.; Ohno, M.; Eguchi, S. *Tetrahedron Lett.* **1995**, *36*, 5539.

(4) Liebeskind, L. S.; Chidambaram, R. *J. Am. Chem. Soc.* **1987**, *109*, 5025.

(5) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975.

(6) (a) Danheiser, R. L.; Carini, D. J.; Basak, A. *J. Am. Chem. Soc.* **1981**, *103*, 1604. (b) Danheiser, R. L.; Carini, D. J.; Fink, D. M.; Basak, A. *Tetrahedron* **1983**, *39*, 935. (c) Danheiser, R. L.; Stoner, E. J.; Koyama, H.; Yamashita, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4407. (d) Danheiser, R. L.; Fink, D. M. *Tetrahedron Lett.* **1985**, *25*, 2513. (e) Danheiser, R. L.; Kwasigroch, C. A.; Tasi, Y.-M. *J. Am. Chem. Soc.* **1985**, *107*, 7233. (f) Danheiser, R. L.; Becker, D. A. *Heterocycles* **1987**, *25*, 277. (g) Becker, D. A.; Danheiser, R. L. *J. Am. Chem. Soc.* **1988**, *111*, 389.

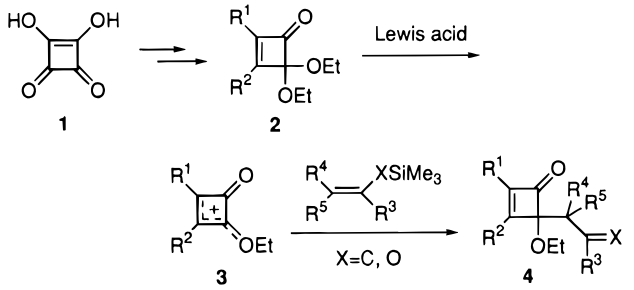
(7) Knölker, H.-J.; Jones, P. G.; Pannek, J.-B. *Synlett* **1990**, 429.

(8) Knölker, H.-J.; Wanzl, G. *Synlett* **1995**, 378 and references cited therein. For an allylstannane case, see: Herndon, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 3165.

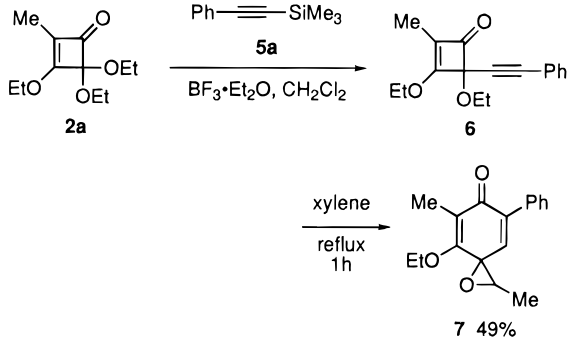
(9) (a) Yamazaki, S.; Tanaka, M.; Yamaguchi, A.; Yamabe, S. *J. Am. Chem. Soc.* **1995**, *60*, 6546. (b) Yamazaki, S.; Tanaka, M.; Inoue, T.; Morimoto, N.; Kumagai, H.; Yamamoto, K. *J. Org. Chem.* **1995**, *60*, 6546.

S0022-3263(96)01552-6 CCC: $14.00

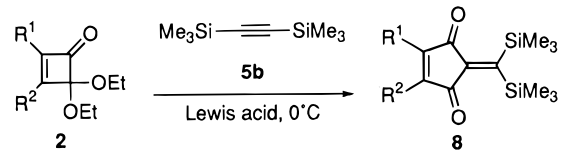
Scheme 1



Scheme 2



Scheme 3



alkynylsilanes. We report here the above cationic rearrangement in relation to the silyl-migration aptitude of various alkynylsilanes and a two-step process of ring opening and reclosure. The present method is of interest as an alternative formal [4 + 1] cycloaddition route to 2-alkylidene-4-cyclopentene-1,3-dione.[2,4]

Results

We previously reported that catalytic action of a Lewis acid on monoacetal **2** available from squaric acid (**1**)[10−12] produced an ethoxycarbenium ion species **3**, which subsequently reacted with allylsilane, silyl enol ether, and silyl ketene acetal regioselectivity to afford the desired substitution products **4** (Scheme 1).[13,14]

This type of electrophilic reaction using silylacetylenes has now been studied. First examined was the phenyl-substituted case. Thus, (phenylethynyl)trimethylsilane (**5a**) (3 equiv) was allowed to react with monoacetal **2a** in the presence of $Et_2O{\cdot}BF_3$ (1.2 equiv) at 0 °C for 24 h, and the expected 4-(phenylethynyl)-4-ethoxycyclobutenone **6** was obtained in 29% yield after standard workup and chromatographic separation (Scheme 2). The yield was increased up to 81% by using more excess of **5a** (5 equiv), but not improved by shorter reaction time (1 h) and higher (room) temperature. The structural determination was based on the spectral inspection: MS peak at *m*/*z* 270 (M^+), IR absorption at 2224 cm^{-1} due to an alkynyl group and at 1769 and 1626 cm^{-1} due to an enone group, and ^1H NMR signals of two ethoxy groups and a phenyl group at δ 7.29−7.36 and 7.44−7.50. The obtained adduct **6** was transformed to an oxaspiro[2.5]-heptadienone **7** according to the known process.[5]

In sharp contrast, the reaction of **2a** with bis(trimethylsilyl)acetylene (**5b**) gave no alkynylation product such as **6** under the same conditions. Instead, a less polar product (TLC analysis) was separated by chromatography and analyzed by spectroscopy. The mass spectrum (M^+, *m*/*z* 310) and the elemental analysis supported not a desilylated but a deacetalized product. The IR spectrum showed no alkynyl absorption but a carbonyl absorption at 1682 cm^{-1}, which was no longer ascribable to a four-membered cyclic ketone. The ^1H NMR spectrum revealed the presence of two different trimethylsilyl groups together with only one ethoxy group. More importantly, the ^{13}C NMR spectrum consisted of all sp^2-carbon signals (δ 134.8, 150.2, 167.0, 174.8, 188.3, and 191.0 ppm) except signals due to substituents. These data allowed us to assign the structure as 2-[bis(trimethylsilyl)methylene]-4-ethoxy-5-methyl-4-cyclopentene-1,3-dione (**8a**) (Scheme 3). Table 1 shows optimization of the reaction conditions. While increasing the amount of $Et_2O{\cdot}BF_3$ and silylacetylene **5b** improved the yield from 13% to 50% (Table 1, entries a−d), choice of the catalyst was critical; $TiCl_4$ (Table 1, entry e) and, more efficiently, $SnCl_4$ raised the yield up to 85% (Table 1, entry f). Under these catalytic conditions, phenyl- and phenylethynyl-substituted monoacetals **2b** and **2c** gave

Table 1. Synthesis of Cyclopentenediones 8a−e from Acetals 2a−e

entry	2	R^1	R^2	Lewis acid (equiv)	acetylene (equiv)	time (h)	8 yield (%)
a	**2a**	Me	OEt	$BF_3{\cdot}OEt_2$ (1.2)	3	24	**8a** (13)[a]
b	**2a**	Me	OEt	$BF_3{\cdot}OEt_2$ (2)	3	24	**8a** (36)[a]
c	**2a**	Me	OEt	$BF_3{\cdot}OEt_2$ (2)	6	24	**8a** (37)[a]
d	**2a**	Me	OEt	$BF_3{\cdot}OEt_2$ (3)	6	24	**8a** (50)[a]
e	**2a**	Me	OEt	$TiCl_4$ (1.2)	3	1	**8a** (41)
f	**2a**	Me	OEt	$SnCl_4$ (1.2)	3	1	**8a** (85)
g	**2b**	Ph	OEt	$SnCl_4$ (1.2)	3	3	**8b** (63)
h	**2c**	PhC≡C	OEt	$SnCl_4$ (1.2)	3	1	**8c** (35)
i	**2d**	Me	Me	$SnCl_4$ (1.2)	3	1	**8d** (57)
j	**2e**	Me	Ph	$SnCl_4$ (1.2)	3	18	**8e** (19)[a]

[a] Deacetalized cyclobutene-1,2-diones were recovered in 66% (entry a), 49% (entry b), 32% (entry c), 30% (entry d), and 35% (entry j) yields, respectively.

(10) West, R. *Oxocarbons*; Academic Press: New York, 1980.
(11) For recent examples of synthetic application, see: (a) Koo, S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1995**, *117*, 3389. (b) Sun, L.; Liebeskind, L. S. *J. Org. Chem.* **1995**, *60*, 8194. (c) Turnbull, P.; Moore, H. W. *J. Org. Chem.* **1995**, *60*, 644. (d) Lee, K. H.; Moore, H. W. *J. Org. Chem.* **1995**, *60*, 735. (e) Turnbull, P.; Moore, H. W. *J. Org. Chem.* **1995**, *60*, 3274. (f) Xiong, Y.; Xia, H.; Moore, H. W. *J. Org. Chem.* **1995**, *60*, 6460. (g) Santora, V. J.; Moore, H. W. *J. Am. Chem. Soc.* **1995**, *117*, 8486. (h) Taing, M.; Moore, H. W. *J. Org. Chem.* **1996**, *61*, 329. (i) Paquette, L. A.; Morwick, T. *J. Am. Chem. Soc.* **1995**, *117*, 1451. (j) Paquette, L. A.; Doyon, J. *J. Am. Chem. Soc.* **1995**, *117*, 6799. (k) Wilson, P. D.; Friedrich, D.; Paquette, L. A. *J. Chem. Soc., Chem. Commun.* **1995**, 1351. (l) Morwick, T.; Doyon, J.; Paquette, L. A. *Tetrahedron Lett.* **1995**, *36*, 2369. (m) Yamamoto, Y.; Ohno, M.; Eguchi, S. *J. Am. Chem. Soc.* **1995**, *117*, 9653. (n) Varea, T.; Grancha, A.; Asensio, G. *Tetrahedron* **1995**, *51*, 12373. (o) Paquette, L. A.; Morwick, T. M.; Negri, J. T. *Tetrahedron* **1996**, *52*, 3075. (p) Schmidt, A. H.; Thiel, S. H.; Gaschler, O. *J. Chem. Soc., Perkin Trans. 1* **1996**, 495.
(12) For review of synthetic application, see: (a) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053. (b) Moore, H. W.; Yerxa, B. R. *Chemtracts: Org. Chem.* **1992**, *5*, 273.
(13) (a) Yamamoto, Y.; Ohno, M.; Eguchi, S. *Chem. Lett.* **1995**, 525. (b) Yamamoto, Y.; Ohno, M.; Eguchi, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1353.
(14) For other examples of the reaction of squaric acid derivatives with unsaturated organosilanes, see: (a) Ohno, M.; Yamamoto, Y.; Eguchi, S. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2272. (b) Ohno, M.; Yamamoto, Y.; Shirasaki, Y.; Eguchi, S. *J. Chem. Soc., Perkin Trans. 1* **1993**, 263. (c) Ohno, M.; Yamamoto, Y.; Eguchi, S. *Tetrahedron Lett.* **1993**, *34*, 4807. (d) Yamamoto, Y.; Ohno, M.; Eguchi, S. *Tetrahedron* **1994**, *50*, 7783. (e) Yamamoto, Y.; Nunokawa, K.; Ohno, M.; Eguchi, S. *Synlett* **1993**, 781. (f) Yamamoto, Y.; Nunokawa, K.; Okamoto, K.; Ohno, M.; Eguchi, S. *Synthesis* **1995**, 571.

Scheme 4

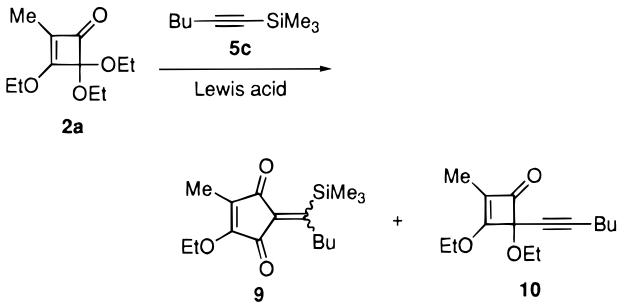


Table 2. Reaction of Monoacetal 2a and Alkynylsilane 5c

entry	Lewis acid (equiv)	T (°C)	time (h)	**9** yield (%) [*E*/*Z*][a]	**10** yield (%)
a	$BF_3{\cdot}OEt_2$ (1.2)	0	24	19 [81/19]	15
b	$BF_3{\cdot}OEt_2$ (1.2)	5	24	23 [56/44]	19
c	$BF_3{\cdot}OEt_2$ (1.2)	10	24	24 [41/59]	18
d	$BF_3{\cdot}OEt_2$ (2.0)	0	24	32 [28/72]	25
e	$BF_3{\cdot}OEt_2$ (2.0)	10	24	31 [30/70]	21
f	$BF_3{\cdot}OEt_2$ (2.0)	20	24	29 [29/71]	11
g	$SnCl_4$ (1.2)	0	1	49 [39/61]	13

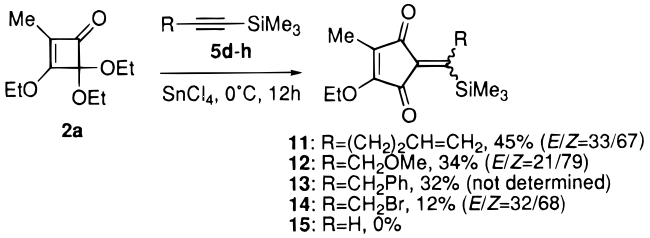
[a] The *E*/*Z* ratio of **9** was determined by the ^{1}H-NMR spectrum.

the corresponding cyclopentenediones **8b** and **8c** (Table 1, entries g and f), respectively, in moderate yields. The reaction of dimethyl-substituted monoacetal **2d** affirmed the above structural assignment (Table 1, entry i); the ^{1}H NMR spectrum of the anticipated symmetrical product **8d** exhibited only two singlet signals due to C_4- and C_5-methyl groups and double trimethylsilyl groups, and the ^{13}C NMR spectrum revealed only two sp^3-carbon signals and four sp^2-carbon signals. The reaction of 3-phenyl-substituted **2e** resulted in low yield even after prolonged reaction time, probably because of the steric effect of a phenyl group at C_3 (Table 1, entry i).

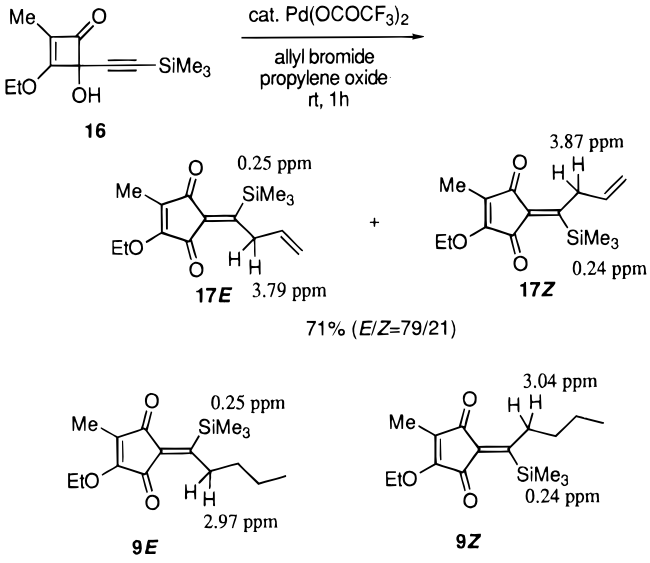
The above results showed the difference in rearrangement aptitude between phenyl(trimethylsilyl)acetylene (**5a**) and bis(trimethylsilyl)acetylene (**5b**). Obviously, a substituent of the acetylene influenced the switching of the reaction course. This fact prompted us to investigate the reaction with various alkyl-substituted silylacetylenes. Typically, the acetal **2a** was reacted with butyl-substituted silylacetylene **5c** (3 equiv) in the presence of $Et_2O{\cdot}BF_3$ (1.2 equiv) at 0 °C for 24 h. In this case, the reactivity was shown to be between **5a** and **5b**; a ring-expansion product **9** with *E*/*Z* ratio of 81/19 and an alkynylation product **10** were obtained in 19% and 15% yields, respectively (Scheme 4, Table 2). The stereoisomerism of the exo-olefin was influenced by the reaction temperature and amount of $Et_2O{\cdot}BF_3$; from 0 to 10 °C with 1.2 equiv of the catalyst, the population of the *Z*-isomer was gradually increased (Table 2, entries a−c). The *E*/*Z* ratio was inversed and reached an almost constant ratio *ca.* 3/7 at 0−20 °C with 2 equiv of the catalyst (Table 2, entries d−f). Nearly the same reaction was attained by use of 1.2 equiv of $SnCl_4$ (Table 2, entry g), where the best yield (49%) was recorded for the ring-expansion product **9** as in the case with **5b** (cf. Table 1).

In this manner, the reaction of **2a** with 3-butenyl-substituted silylacetylene **5d** afforded the corresponding product **11** in a comparable yield and *E*/*Z* ratio (Scheme 5). Similarly, the reaction with methoxymethyl- and benzyl-substituted silylacetylenes **5e** and **5f** gave cyclo-

Scheme 5



Scheme 6



pentenediones **12** and **13**,[15] respectively, in fair yields, but the reactions with bromomethyl-substituted silylacetylene **5g** and unsubstituted silylacetylene **5h** resulted in a low yield, or worse, no product was isolable. In these cases, the alkynylation byproducts were uncharacterized because they could not be obtained in sufficient amounts for analysis.

The stereochemistry of **9** was deduced by the relative chemical shifts of trimethylsilyl and allylic methylene groups. As indicated in Scheme 6, standard (*E*)- and (*Z*)-2-[1-(trimethylsilyl)-3-butenylidene]cyclopentenediones **17** (ratio: 79/21) were prepared from 4-hydroxy-4-[(trimethylsilyl)ethynyl]cyclobutenone **16** by the established procedure[2a] and compared with **9** obtained in entry a (Table 2). In the ^{1}H NMR spectra of these definite *E*/*Z* isomers, the relative chemical shifts due to major and minor isomers of **17** accorded well with those of the corresponding isomers of **9**.[16] Likewise, the *E*/*Z* relationships of the other products **11**−**14** were deduced and are noted in Scheme 5.

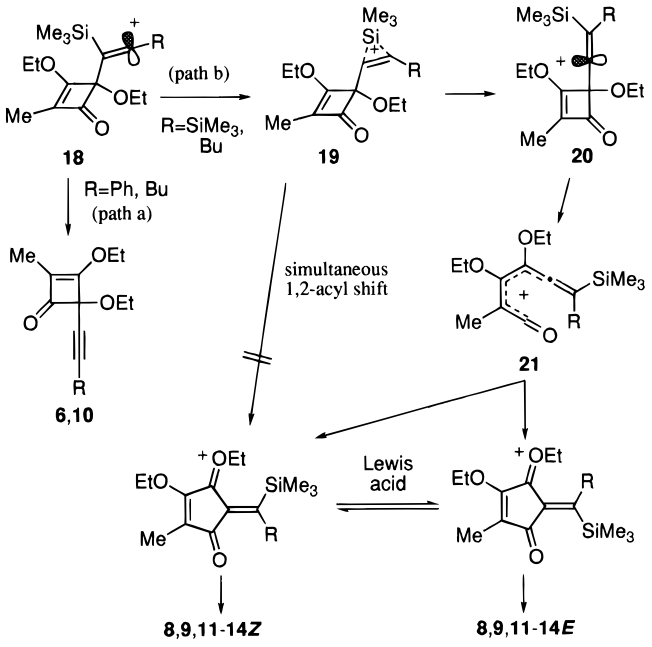
Discussion

Scheme 7 shows the plausible mechanism for the formation of alkynylation products **6** and **10** and ring-expansion products **8**, **9**, and **11**−**14**. The electrophilic addition of ethoxycarbenium ion **3** to silylacetylene **5** initially produces a vinyl cation intermediate **18**. Sub-

(15) *E*- or *Z*-isomer was formed selectively. However, because of no data for relative chemical shifts, the stereochemistry could not be confirmed.

(16) This was observed more consistently in the partially hydrogenated products of (*E*)- and (*Z*)-**17** (side-chain conversion from an allyl to a propyl group with H_2/Pd−$BaSO_4$ in hexane for 12 h): the chemical shifts obtained were 0.25 ppm (TMS) and 2.95 ppm (allylic CH_2) for *E*-isomer and 0.24 ppm (TMS) and 3.01 ppm (allylic CH_2) for *Z*-isomer.

Scheme 7



sequent 1,2-silyl migration depends on an acetylenic substituent R, which determines the course of reaction (path a *vs* path b). In the case of phenyl-substituted vinyl cation **18** (R = Ph), the benzylic stabilization allows straightforward desilylation (path a) to give 4-(phenylethynyl)cyclobutenone **6**. In contrast, trimethylsilyl-substituted vinyl cation **18** (R = $SiMe_3$) can isomerize to the other vinyl cation **20** (path b) because the rearranged cation **20** is more stabilized by the β-effect of two silyl groups than the primarily formed cation **18**. Then **20**, formed after 1,2-silyl migration, induces the subsequent ring expansion to [bis(trimethylsilyl)methylene]cyclopentenedione **8** *via* two possible routes: simple and simultaneous 1,2-acyl shift and a two-step process of ring opening and reclosure (see below). On the other hand, the behavior of the butyl-substituted vinyl cation **18** (R = Bu) is between the above two extremes. The negligible difference in stability of the intermediate cations **18** and **19** results in the formation of both the ring-expansion product **9** and the alkynylation product **10**.

The reaction of unsymmetrical acetylene (*e.g.*, **5c**) afforded stereoisomeric mixtures of (1-trimethylsilylalkylidene)cyclopentenediones. As described above, the *E*/*Z* ratio of the product **9** varied depending on the reaction conditions. When acetal **2a** was reacted with **5c**, the *E*-isomer of **9** was formed predominantly on employing 1.2 equiv of $Et_2O{\cdot}BF_3$ at 0 °C, whereas the *Z*-isomer is favored at higher temperature, in excess amounts of $Et_2O{\cdot}BF_3$, and with a stronger Lewis acid such as $SnCl_4$. These observations suggest that the *E*-isomer was initially produced and converted into the thermodynamically favored *Z*-isomer by subsequent Lewis acid-catalyzed geometrical isomerization. In fact, the control experiment in entry c (Table 2) indicated that the *E*/*Z* ratio of **9** (^{1}H NMR measurement) changed from 62/38 (1 h) to 49/51 (6 h) and nearly reached the equilibrium ratio of 33/67 (48 h). Because the *Z*-isomer should be formed primarily *via* the simultaneous stereospecific 1,2-acyl migration through a silyl-bridged cation **19**, a direct route can be ruled out.

Another ring-expansion pathway could be rationalized by considering ring opening of the vinyl cation intermediate **20** to a strain-relieved and delocalized cation intermediate **21** and subsequent ring closure to **8**, **9**, and **11**−**14**. In fact, semiempirical calculations (PM3[17]) support this option;[18] for simplicity, these two steps were calculated by using an unsubstituted system. Structures of a vinyl cation **22** and a ring-opening cation **24**, transition states **23**, **25**, and a product cation **26** were fully optimized by the EF routine with the keyword PRECISE. The resulting transition structures were subjected to a vibrational analysis, and in each case, only one imaginary frequency was found. The energy profile is outlined in Figure 1. It was revealed that the process involving two steps is exothermic by 39.1 kcal/mol, and the ring expansion evolves from the extremely low energy barrier (2.6 kcal/mol) of the ring-opening step. The ring-opened **24** has a U-shaped structure and is considered as a ketenyl- and allenyl-substituted cation. From this cation **24** to the product cation **26**, the cyclization proceeds with an energy barrier of 15.7 kcal/mol. Thus, the two-step process proposed above seems to be a reasonable route for the present ring-expansion reaction.

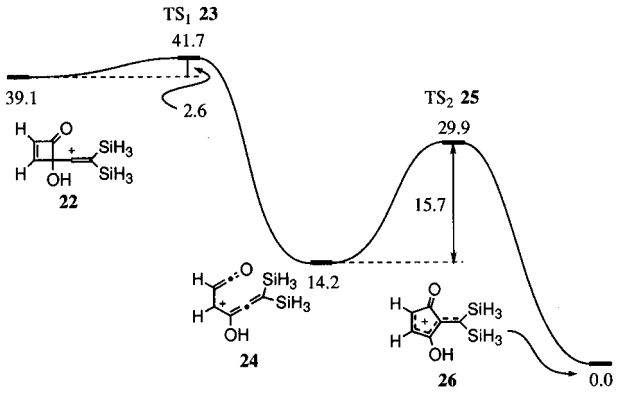


Figure 1. Schematic energy diagram for ring opening of **22** and cyclization of resulted **24**. Indicated values show relative energies, $\Delta\Delta H$ in kcal/mol.

In the above mechanism, the final ring closure of **24**, which is regarded as a pentadienyl cation, is associated with the Nazarov cyclization, and it may therefore involve the conrotatory electrocyclization to a cyclopentenyl cation **26**.[19] If such a pericyclic cyclization mechanism is operative in our case, the stereochemistry of the kinetically formed product might be controlled by a torquoselectivity at this stage.[20] In order to obtain more detailed information on the reclosure step, the intrinsic reaction coordinate (IRC) calculation[21] was further attempted. Figure 2 shows optimized structures of the starting cation **24**, the transition state **25**, the cyclized cation **26**, and representative intermediates **27** and **28**.

(17) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(18) Semiempirical calculations were carried out using MOPAC version 94.10 packaged in the CAChe Version 3.7.

(19) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; John Wiley & Sons: New York, 1976.

(20) The torquoselectivity in electrocyclic ring opening of cyclobutene derivatives has been extensively studied: (a) Kirmse, W.; Houk, K. N. *J. Am. Chem. Soc.* **1984**, *106*, 7989. (b) Rondan, N. G.; Houk, K. N. *J. Am. Chem. Soc.* **1985**, *107*, 2099. (c) Rudolf, K.; Spellmeyer, D. C.; Houk, K. N. *J. Org. Chem.* **1987**, *52*, 3708. (d) Houk, K. N.; Spellmeyer, D. C.; Jefford, C. W.; Rimbault, C. G.; Wang, Y.; Miller, R. D. *J. Org. Chem.* **1988**, *53*, 2127. (e) Buda, A. B.; Wang, Y.; Houk, K. N. *J. Org. Chem.* **1989**, *54*, 2264. (f) Niwayama, S.; Houk, K. N. *Tetrahedron Lett.* **1992**, *33*, 883. (g) Niwayama, S. *J. Org. Chem.* **1996**, *61*, 640. (h) Niwayama, S.; Kallel, E. A.; Sheu, C.; Houk, K. N. *J. Org. Chem.* **1996**, *61*, 2517. (i) Niwayama, S.; Kallel, E. A.; Spellmeyer, D. C.; Sheu, C.; Houk, K. N. *J. Org. Chem.* **1996**, *61*, 2813.

(21) (a) Fukui, K.; Kato, S.; Fujimoto, H. *J. Am. Chem. Soc.* **1975**, *97*, 1. (b) Fukui, K. *Acc. Chem. Res.* **1981**, *14*, 363.

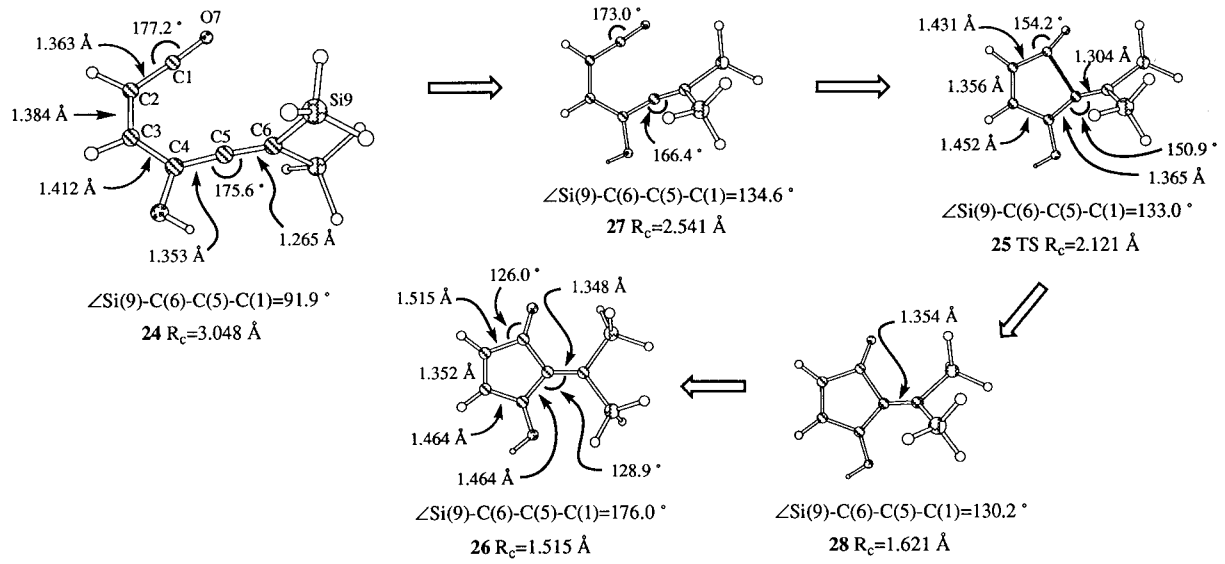


Figure 2. Calculated structures and reaction coordinates (R_c) of representative intermediates on the IRC of cyclization of **24**.

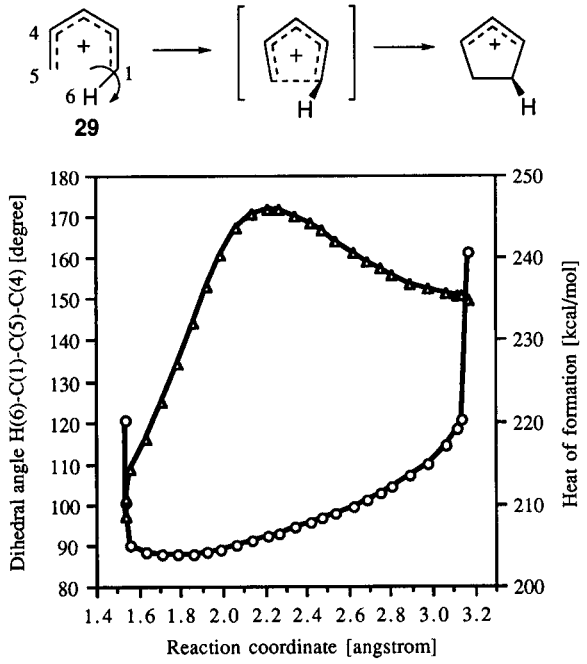


Figure 3. Plot of dihedral angle H(6)−C(1)−C(5)−C(4) [−○−] and heat of formation [−△−] vs reaction coordinate.

Initially (reaction coordinate: R_c = 3.048 Å), the cation **24** has a delocalized U-shaped structure with the C(1) and C(5) atoms almost sp-hybridized (∠C(2)−C(1)−O(7) = 177.2°, ∠C(4)−C(5)−O(6) = 175.6°) and the two silyl groups perpendicular to the molecular plane (∠Si(9)−C(6)−C(5)−C(1) = 91.9°). As the cyclization proceeds, the sp-C(5) atom is gradually rehybridized to sp^2 with the rotation at the C(5) atom. This motion seemingly agrees with the Nazarov cyclization mechanism. However, the rotation at the C(5) atom was estimated to occur differently between the cation **24** and the prototypical pentadienyl cation **29**. Figure 3 shows the gradual rotation expected for the electrocyclization of **29**. In contrast, no appreciable rotational change was observed in **24** before and after the transition state except for drastic changes at the earliest and the latest stages; as shown in Figure 4, the dihedral angle Si(9)−C(6)−C(5)−C(1) is almost constant (*ca.* 130°) at the C(1)−C(5) bond-forming stage (distance of 2.5−1.6 Å). The observed

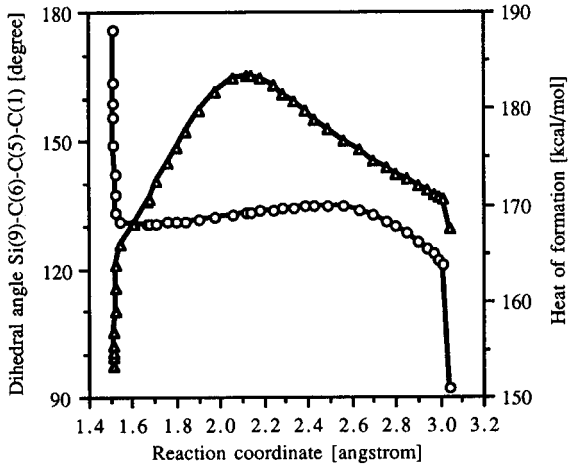
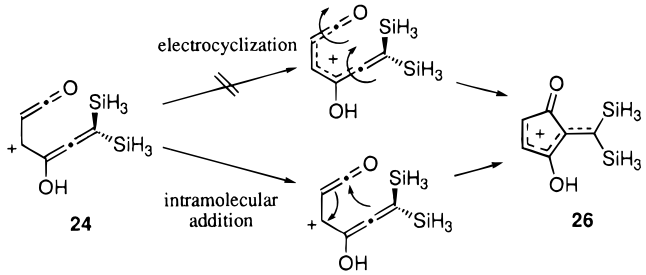


Figure 4. Plot of dihedral angle Si(9)−C(6)−C(5)−C(1) [−○−] and heat of formation [−△−] vs reaction coordinate.

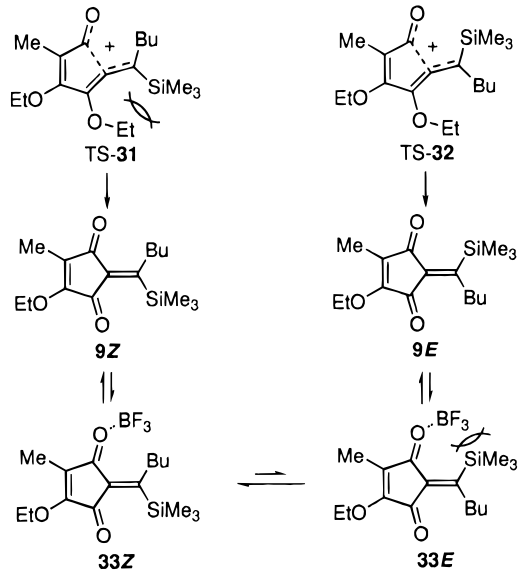
Scheme 8



contrast indicates that new bond formation results from an interaction of in-plane p-orbitals of sp-C(1) and -C(5), but not out-of-plane orbitals of these carbons, which is associated with the C(5)−C(6) bond length to be stretched from 1.265 Å of **24** to 1.354 Å of **28**. Thus, these data support our postulate that the reclosure step is performed by intramolecular addition of an acyl cation to a silylallene in a 5-*exo-trig* mode (Scheme 8).

On the basis of this mechanism, the stereochemistry of the products can be explained as in Scheme 9. The transition structure TS-**31** leading to **9*Z*** is less favorable than the transition structure TS-**32** leading to **9*E*** because of the steric repulsion between the trimethylsilyl and the ethoxy groups. Therefore, the *E* isomer was obtained

Scheme 9



predominantly as a kinetic product (Table 2). Assuming that BF_3-complexed intermediates **33*Z*** and **33*E*** are produced by coordination with the more Lewis basic carbonyl group,[22] **33*E*** inversely becomes less favorable than **33*Z*** because of the steric repulsion between the trimethylsilyl and the BF_3-coordinated carbonyl groups. Thus, the thermodynamically more favored complex **33*Z*** affords the major isomer **9*Z*** under Lewis acid-catalyzed conditions.

Conclusions

Cationic 1,2-silyl migration, which has so far been observed in cycloaddition reactions using allenyl-, allyl-, and vinyltrialkylsilanes,[6–9] emerged in the Lewis acid-catalyzed reaction of silylacetylenes with cyclobutenedione monoacetals, leading to 2-alkylidene-1,3-dione. To our knowledge, the present 1,2-silyl migration is the first example in alkynylsilane chemistry for the ring-expansion reaction. This was significant in the reaction of bis(trimethylsilyl)acetylene since one of the two silyl groups facilitated the migration of the other. On the other hand, phenyl-substituted silylacetylene gave a simple alkynylated product without the rearrangement and butyl-substituted silylacetylene gave both the alkynylated product and the rearranged product with the *E*/*Z* ratio dependent on the reaction temperature and the Lewis acid employed. Control experiments showed that the *E*-isomer was initially formed and converted into the *Z*-isomer by Lewis acid-catalyzed geometrical isomerization. This result ruled out the possibility of ring expansion *via* simultaneous silyl and acyl migrations through a silicon-bridged cation. PM3 calculations supported another two-step process of ring-opening and reclosure involving an intramolecular addition of an acyl cation to silylallene rather than a pentadienyl cation electrocyclization.

Experimental Section

General Methods. ^1H and ^{13}C NMR spectra were obtained in $CDCl_3$ solution with $SiMe_4$ as an internal standard. Flash chromatography was performed with a silica gel column (Fuji-Davison BW-300) eluted with mixed solvents [hexane (H), ethyl acetate (A)]. Dichloromethane was dried over $CaCl_2$, distilled, and stored over 4 Å molecular sieves. Squaric acid was supplied by Kyowa Hakko Kogyo Co. Ltd.

Synthesis of Cyclobutenedione Monoacetal. According to the reported procedure,[23] cyclobutenedione monoacetal **2d** was synthesized as follows: to a solution of monoacetal **2a** (2.13 g, 10.0 mmol) in dry THF (50 mL) was added methyl lithium (30.0 mL, 31 mmol; 1.04 M solution in ether) at −78 °C under a nitrogen atmosphere, and the solution was stirred for 30 min. To this solution was added trifluoroacetic anhydride (2.1 mL, 15.0 mmol). The reaction mixture was stirred for 30 min, quenched with 10% $NaHCO_3$ (20 mL), and extracted with ether (20 mL × 3). The extracts were washed with brine (30 mL), dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue (Elution H−A 40:1) gave monoacetal **2d** (850 mg, 46%) as a colorless oil. Monoacetals **2a**−**c**,**e** were reported in our previous paper.[13b]

4,4-Diethoxy-1,2-dimethyl-2-cyclobutenone (2d): IR (neat 1765, 1644 cm^{-1}; ^1H NMR δ 1.23 (6 H, t, J = 7.0 Hz), 1.75 (3 H, q, J = 1.0 Hz), 2.17 (3 H, q, J = 1.0 Hz), 3.74 (4 H, q, J = 7.0 Hz); ^{13}C NMR δ 7.2, 11.5, 15.5 (2C), 61.1 (2C), 115.6, 152.7, 179.8, 195.7; MS (EI) *m*/*z* (rel intensity) 184 (M^+, 2), 155 (25), 139 (13), 127 (100), 111 (18). Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.50; H, 8.44.

Synthesis of 4-Alkynylcyclobutenone 6 and Its Conversion to Oxaspiro[2.5]octadienone 7. To a solution of **2a** (129 mg, 0.57 mmol) and silylacetylene **5a** (316 mg, 2.50 mmol) in dry dichloromethane (2 mL) was added $Et_2O{\cdot}BF_3$ (0.091 mL, 0.72 mmol) at 0 °C under a nitrogen atmosphere. After being stirred for 13 h, the reaction mixture was quenched with 10% $NaHCO_3$ (5 mL) and extracted with dichloromethane (5 mL × 3). The extracts were dried (Na_2SO_4) and evaporated to dryness. Flash chromatography of the residue (Elution H−A 8:1) gave 4-alkynylcyclobutenone **6a** (125 mg, 81%) as a pale−yellow oil. Thermal rearrangement of **6** to **7** was carried out in the reported manner.[4]

3,4-Diethoxy-2-methyl-4-(phenylethynyl)-2-cyclobutenone (6): IR (neat) 2224, 1769, 1626 cm^{-1}; ^1H NMR δ 1.28 (3 H, t, J = 7.0 Hz), 1.50 (3 H, t, J = 7.0 Hz), 1.73 (3 H, s), 3.86 and 3.93 (each 1 H, dq, J = 9.2, 7.0 Hz), 4.54 and 4.61 (each 1 H, dq, J = 10.0, 7.0 Hz), 7.29−7.36 (3 H, m), 7.44−7.50 (2 H, m); ^{13}C NMR δ 6.6, 15.3, 15.6, 63.1, 69.4, 82.2, 88.3, 90.9, 122.3, 125.5, 128.7 (2 C), 129.3, 132.3 (2 C), 179.9, 186.8; MS (EI) *m*/*z* (rel intensity) 270 (M^+, 12), 241 (37), 224 (73), 213 (100), 185 (59). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.57; H, 6.67.

4-Ethoxy-2,5-dimethyl-7-phenyl-1-oxaspiro[2.5]octa-4,7-dien-6-one (7): 49% (*ca*. 15:1 diastereomer mixture); oil; IR (neat) 1649, 1615 cm^{-1}; ^1H NMR (signals due to a minor isomer are indicated in bracket) δ 1.35 [1.37] (3 H, t, J = 7.0 Hz), 1.54 [1.72] (3 H, d, J = 5.4 Hz), 1.97 [1.99] (3 H, s), 3.93 [3.92] (1 H, q, J = 5.4 Hz), 3.98 and 4.08 [4.05 and 4.18] (each 1 H, dq, J = 9.4, 7.0 Hz), 6.57 [6.37] (1 H, s), 7.34−7.45 (5 H, m); ^{13}C NMR δ 9.7, 14.5 [13.0], 15.8 [15.6], 58.1 [59.2], 61.6 [63.7], 70.3 [70.0], 127.7 [128.1], 128.5 [128.6] (2 C), 128.6 [128.3], 129.3 [129.1] (2 C), 136.1 [135.6], 138.6, 144.1 [143.8], 164.5, 186.8; MS (EI) *m*/*z* (rel intensity) 270 (M^+, 36), 254 (100), 241 (53), 214 (29), 197 (89). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.49; H, 6.75.

Typical Procedure for Reaction of Cyclobutenedione Monoacetal 2 and Silylacetylene 5. To a solution of monoacetal **2a** (146 mg, 0.68 mmol) and bis(trimethylsilyl)-acetylene (**5b**) (348 mg, 2.04 mmol) in dry dichloromethane (2 mL) was added $SnCl_4$ (0.096 mL, 0.82 mmol) at 0 °C under a nitrogen atmosphere. After being stirred for 1 h, the solution was quenched with 10% $NaHCO_3$ (5 mL) and extracted with dichloromethane (5 mL × 3). The extracts were dried (Na_2SO_4) and evaporated to dryness. Flash chromatography of the residue (Elution H−A 30:1) gave cyclopentenedione **8a** (179 mg, 85%) as a bright yellow oil. According to the above procedure, other cyclopentenediones **8b**−**e**, **9**, and **11**−**14** were obtained as an oil unless otherwise noted. Isolated yields are

(22) AM1 (Dewar, M. J. S.; Zeobisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.) calculations suggested that the BF_3 coordination to **9** is thermodynamically more favorable at the carbonyl group of the vinylogous ester than that of the vinylogous ketone. Also see: Rauk, A.; Hunt, I. R.; Keay, B. A. *J. Org. Chem.* **1994**, *59*, 6808.

(23) Gayo, L.; Winters, M. P.; Moore, H. W. *J. Org. Chem.* **1992**, *57*, 6896.

shown in Scheme 5 and Tables 1 and 2, in which the reactions of **2a**−**e** with **5b** and of **2a** with **5c** under various conditions are recorded. See the Supporting Information for spectral data of **8b** (mp 82−85 °C), **8c** (mp 100−104 °C), **9**, and **11**−**14**.

2-[Bis(trimethylsilyl)methylene]-4-ethoxy-5-methyl-4-cyclopentene-1,3-dione (8a): IR (neat) 1682, 1620, 1248, 844 cm^{-1}; ^1H NMR δ 0.25 (9 H, s), 0.26 (9 H, s), 1.41 (3 H, t, J = 7.0 Hz), 1.99 (3 H, s), 4.72 (2 H, q, J = 7.0 Hz); ^{13}C NMR δ 2.0 (3 C), 2.2 (3 C), 7.1, 15.9, 68.1, 134.8, 150.2, 167.0, 174.8, 188.3, 191.0; MS (EI) m/z (rel intensity) 310 (M^+, 21), 295 (70), 281 (100), 267 (53), 251 (36). Anal. Calcd for $C_{15}H_{26}O_3Si_2$: C, 58.02; H, 8.44. Found: C, 58.45; H, 8.20.

2-[Bis(trimethylsilyl)methylene]-4,5-dimethyl-4-cyclopentene-1,3-dione (8d): IR (neat) 1686, 1640, 1246, 849 cm^{-1}; ^1H NMR δ 0.26 (18 H, s), 2.05 (6 H, s); ^{13}C NMR δ 2.0 (6 C), 9.2 (2 C), 149.0, 154.5 (2 C), 177.8, 193.4 (2 C); MS (EI) m/z (rel intensity) 280 (M^+, 97), 265 (100), 250 (9), 237 (4). Anal. Calcd for $C_{14}H_{24}O_2Si_2$: C, 59.94; H, 8.62. Found: C, 60.24; H, 8.24.

2-[Bis(trimethylsilyl)methylene]-4-methyl-5-phenyl-4-cyclopentene-1,3-dione (8e): mp 67−70 °C; IR (neat) 1686, 1620, 1246, 845 cm^{-1}; ^1H NMR δ 0.30 (9 H, s), 0.31 (9 H, s), 2.24 (3 H, s), 7.45−7.57 (5 H, m); ^{13}C NMR δ 2.0 (3 C), 2.1 (3 C), 10.5, 128.9 (2 C), 129.9, 130.1 (2 C), 130.3, 149.1, 152.2, 153.6, 180.7, 192.0, 193.5; MS (EI) m/z (rel intensity) 342 (M^+, 100), 327 (88), 312 (11), 299 (4). Anal. Calcd for $C_{19}H_{26}O_2Si_2$: C, 66.61; H, 7.65. Found: C, 66.85; H, 7.41.

3,4-Diethoxy-4-(1-hexynyl)-2-methyl-2-cyclobutenone (10). This was obtained with elution H−A 10:1 as a byproduct after elution of **9**: IR (neat) 2232, 1771, 1634 cm^{-1}; ^1H NMR δ 0.91 (3 H, t, J = 7.4 Hz), 1.23 (3 H, t, J = 7.0 Hz), 1.46 (3 H, t, J = 7.0 Hz), 1.32−1.55 (4 H, m), 1.68 (3 H, s), 2.29 (2 H, q, J = 7.0 Hz), 3.74 and 3.82 (each 1 H, dq, J = 9.2, 7.0 Hz), 4.48 and 4.55 (each 1 H, dq, J = 9.8, 7.0 Hz); ^{13}C NMR δ 6.5, 13.6, 15.2, 15.5, 18.8, 22.0, 30.5, 62.6, 69.1, 73.2, 88.0, 92.4, 125.0, 180.5, 187.7; MS (EI) m/z (rel intensity) 250 (M^+, 36), 221 (100), 205 (8), 193 (57), 165 (28). Anal. Calcd for $C_{15}H_{20}O_3$: C, 71.97; H, 8.86. Found: C, 71.99; H, 8.84.

Pd-Catalyzed Ring Expansion of 4-Hydroxy-4-[(trimethylsilyl))ethynyl]cyclobutenone 16. According to the reported procedure, starting **16** was prepared as follows: to a solution of (trimethylsilyl)acetylene (0.85 mL, 6.0 mmol) in dry THF (5 mL) was added ^{n}BuLi (3.71 mL, 6.0 mmol; 1.6 M in hexane) at 0 °C under a nitrogen atmosphere, and the solution was stirred for 30 min. The resulting solution was then transferred to a solution of 3-ethoxy-4-methyl-3-cyclobutene-1,2-dione (701 mg, 5.0 mmol) in dry THF (20 mL) at −78 °C under a nitrogen atmosphere. The reaction mixture was stirred for 30 min, quenched with 10% $NaHCO_3$ (10 mL), and extracted with ether (10 mL × 3). The extracts were washed with brine (20 mL), dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue (Elution H−A 7:1) gave **16** (878 mg, 74%) as a yellow oil.

3-Ethoxy-4-hydroxy-2-methyl-4-[(trimethylsilyl)ethynyl]-2-cyclobutenone (16): IR (neat) 3337, 2166, 1763, 1624, 1252, 845 cm^{-1}; ^1H NMR δ 0.18 (9 H, s), 1.49 (3 H, t, J = 7.0 Hz), 1.67 (3 H, s), 4.10 (1 H, br s), 4.59 (2 H, q, J = 7.0 Hz); ^{13}C NMR δ −0.4 (3 C), 6.5, 15.2, 69.5, 83.4, 95.7, 99.3, 125.6, 180.7, 187.5; MS (EI) m/z (rel intensity) 238 (M^+, 26), 223 (22), 209 (100), 195 (76), 181 (12). Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.47; H, 7.61. Found: C, 60.74; H, 7.34.

According to the reported procedure,[2a] ring expansion of cyclobutenones **16** was carried out as follows: a solution of **16** (238 mg, 1.0 mmol), allyl bromide (0.87 mL, 10 mmol), propylene oxide (1.75 mL, 25 mmol), and Pd(II) trifluoroacetate (17 mg, 0.05 mmol) in dry dichloromethane (8 mL) was stirred at ambient temperature under a nitrogen atmosphere for 1 h. The reaction mixture was quenched with saturated NH_4Cl (10 mL) and extracted with dichloromethane (5 mL × 3). The extracts were washed with brine (10 mL), dried (Na_2SO_4), and evaporated to dryness. Flash chromatography of the residue (Elution H−A 30:1) gave ring-expansion product **17** (197 mg, 71%) as a yellow oil.

4-Ethoxy-5-methyl-2-[1-(trimethylsilyl)-3-butenylidene]-4-cyclopentene-1,3-dione (17): IR (neat) 1680, 1626, 1246, 847 cm^{-1}; ^1H NMR (signals due to *E*-isomer are indicated in brackets) δ 0.25 [0.24] (9 H, s), 1.41 [1.42] (3 H, t, J = 7.0 Hz), 1.98 (3 H, s), 3.79 [3.87] (2 H, dt, J = 6.0, 1.6 Hz), 4.70 (2 H, q, J = 7.0 Hz), 4.90−5.06 (2 H, m), 5.70−5.90 (1 H, m); ^{13}C NMR δ −0.1 [−0.4] (3 C), 7.0 [7.1], 15.9 [15.8], 34.8 [35.3], 67.9 [67.8], 116.5, 132.0 [134.1], 135.5, 135.8 [135.2], 165.7 [165.2], 166.6 [166.0], 189.0 [189.6], 192.4 [192.2]; MS (EI) m/z (rel intensity) 278 (M^+, 61), 263 (37), 249 (100), 233 (43). Anal. Calcd for $C_{15}H_{22}O_3Si$: C, 64.71; H, 7.96. Found: C, 65.06; H, 7.61.

Supporting Information Available: Spectral data for **8b**,**c**, **9**, and **11**−**14** (2 pages). This material is contained in 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.

JO961552W