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$W(CO)_5(L)$-catalyzed 6-*endo*-selective cyclization and formal Cope rearrangement of allenyl silyl enol ethers

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Abstract

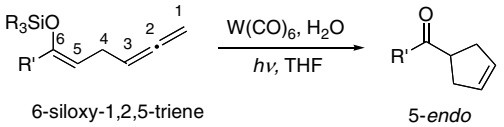
On treatment of 5-siloxy-1,2,5-trienes with a catalytic amount of $W(CO)_6$ under photoirradiation, two types of synthetically useful compounds, that is, 6-*endo*-cyclized products or formal Cope rearrangement products, are obtained selectively via the same intermediates simply by changing reaction conditions. In these reactions, electrophilic activation of the allene moiety is effectively achieved by coordination of $W(CO)_5$, allowing intramolecular attack by neutral carbon nucleophiles in a 6-*endo* manner.

Keywords: Cyclization; Cope rearrangement; Allene; Electrophilic activation; Tungsten

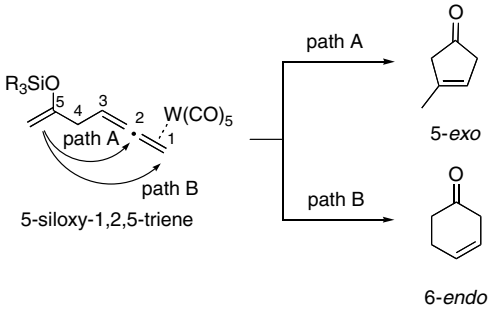
1. Introduction

Allenyl compounds play an important role in synthetic reactions due to their unique structure and high reactivity [1]. In particular, transition metal-catalyzed cyclization of allenes bearing a pro-nucleophile such as oxygen and nitrogen has attracted much attention as a useful synthetic protocol for the construction of heterocycles. A variety of transition-metal catalysts such as mercury(II), palladium(0 or II), silver(I), gold(III), and so on have been employed for this purpose [1,2] and applied for the synthesis of several natural products [3]. On the other hand, transition metal-catalyzed cyclization of allenes bearing carbon nucleophiles has remained relatively unexplored despite its high potential as a method for the formation of carbocycles [4].

In the course of our studies on $W(CO)_5(L)$-catalyzed intramolecular cyclization of silyl enol ethers, we found that $W(CO)_5$ can effectively activate the allenyl moiety as well as the alkyne moiety [5]. For example, 5-*endo*-selective cyclization of 6-siloxy-1,2,5-trienes was found to proceed smoothly to give cyclopentene derivatives by carrying out the reaction using a catalytic amount of $W(CO)_6$ under photoirradiation in the presence of H_2O (Eq. (1)) [5f]. We then decided to examine whether it would be possible to apply this reaction to 5-siloxy-1,2,5-trienes where the competitive cyclization modes (5-*exo* versus 6-*endo*) are possible (Eq. (2)). In this paper, we would like to describe a full account of our study on this type of substrate, which has led to the discovery of two distinctive reaction pathways, that is, the 6-*endo*-selective cyclization and the formal Cope rearrangement [6].



6-siloxy-1,2,5-triene — 5-*endo* (1)



5-siloxy-1,2,5-triene — 5-*exo*, 6-*endo* (2)

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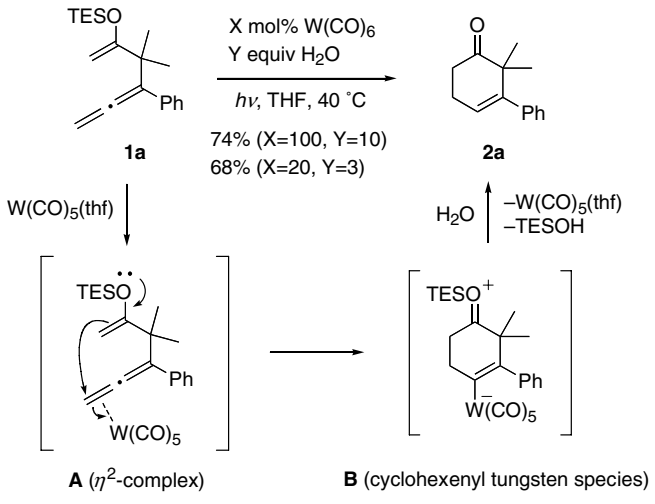
2. Results and discussion

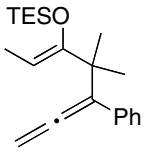
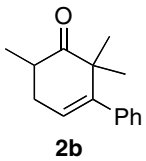
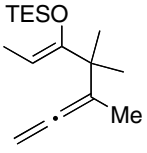
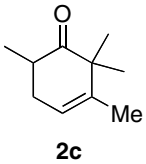
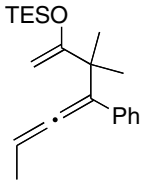
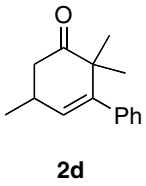
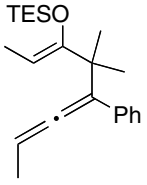
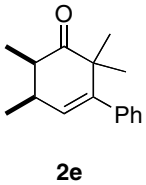
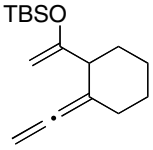
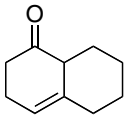
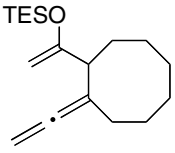
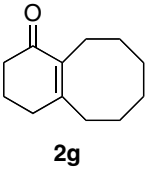
When 5-triethylsiloxy-1,2,5-triene **1a** was treated with an equimolar amount of $W(CO)_6$ in THF (0.1 M) at 40 °C under photoirradiation in the presence of H_2O (10 equiv), **1a** was completely consumed within 1 day to give the 6-*endo*-cyclized product, cyclohex-3-en-1-one **2a**, in 74% yield (Scheme 1) [7]. It should be noted here that the cyclization proceeded with high regio-selectivity, leading to the exclusive formation of the 6-*endo*-cyclized product. Although the corresponding catalytic reactions under the same concentration (0.1 M) of the substrate **1a** gave the desired cyclized product **2a** in low yield (28% yield) along with the hydrolyzed ketone as the major product, this catalytic reaction could be carried out successfully by carrying out the reaction under high concentration (1 M for **1a**) even with a catalytic amount (as little as 20 mol%) of $W(CO)_6$ in the presence of H_2O (3 equiv) to give **2a** in 68% yield. Other metal complexes such as $PtCl_2$ and $AgNO_3$ failed to give better results. The reaction pathway is assumed to proceed in a similar manner to the 5-*endo* cyclization of 6-siloxy-1,2,5-trienes [5f]. First, 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 cyclohexenyl tungsten species **B**. Finally, the carbon–tungsten bond is protonated by H_2O to give the 6-*endo*-cyclized product **2a** with regeneration of the $W(CO)_5$(thf).

The scope of this reaction was examined employing several 5-siloxy-1,2,5-trienes using a catalytic amount of $W(CO)_6$ (Table 1). The catalytic process worked well with substrates **1b** and **1c** containing a tri-substituted silyl enol ether moiety to give the corresponding products **2b** and **2c** in good yield (entries 1–2). On the other hand, the reaction of **1d** bearing a tri-substituted allene moiety gave the



Scheme 1.

Table 1
6-*endo*-Selective cyclization of 5-siloxy-1,2,5-triene **1** using a catalytic amount of $W(CO)_6$ in THF

Entry	Substrate	Product	Yield/%
1	 **1b**	 **2b**	77[a]
2	 **1c**	 **2c**	71[a]
3	 **1d**	 **2d**	26[b]
4	 **1e**	 **2e**	71[a]
5	 **1f**	 **2f**	84[c]
6	 **1g**	 **2g**	69[a]

[a] Conditions A: $W(CO)_6$ (20 mol%), H_2O (3.0 equiv), THF (1.0 M), 40 °C, *hv*.
[b] Conditions B: $W(CO)_6$ (100 mol%), H_2O (1.0 equiv), THF (0.1 M), 40 °C, *hv*.
[c] Conditions C: $W(CO)_6$ (10 mol%), H_2O (3.0 equiv), THF (0.1 M), 40 °C, *hv*.

product **2d** in only 26% yield even with a stoichiometric amount of $W(CO)_6$ due to the facile hydrolysis of the silyl enol ether moiety during the reaction (entry 3). In the case of substrate **1e** containing both of these tri-substituted silyl enol ether and allene moieties, the reaction gave the product **2e** as a single diastereoisomer in 71% yield (entry 4). The stereochemistry of **2e** was assigned as *cis* on the basis of a differential NOE study. It is thought that the intermediate *cis*-**B** may be more favorable than the *trans*-**B** due to the considerable steric repulsion in the *trans*-**B** between the pentacarbonyltungsten moiety and the methyl group on the C-5 (Fig. 1). Furthermore, this 6-*endo* cyclization reaction was also found to proceed smoothly with cyclic substrates **1f** and **1g**. Compound **2f** was obtained in 84% yield even with 10 mol% amount of $W(CO)_6$, while **2g** was produced by isomerization of the double bond after cyclization (entries 5 and 6).

During these studies, we found that the reaction of the same substrate **1a** in the absence of H_2O under similar conditions proceeded via a different pathway to give a formal Cope rearrangement product, 2-siloxy-1-en-5-yne **3a**, in good yield (Table 2) [8–10]. Thus, when 5-siloxy-1,2,5-triene **1a** was treated with a catalytic amount of $W(CO)_6$ (20 mol%) in THF at 40 °C under photoirradiation for 1 day, the product **3a** was obtained in 81% yield together with a trace amount of the cyclized product **2a** (Table 2, entry 1). It should be noted that thermal Cope rearrangement of 1,2,5-trienes normally requires high reaction temperature (>250 °C) [8–10]. In fact, when the substrate **1a** was heated at 250 °C for 4 h in the absence of the catalyst, the Cope rearrangement gradually proceeded to give a 3:1 mixture of **1a** and **3a**. Furthermore, no reaction occurred when the substrate **1a** was irradiated in the absence of $W(CO)_6$ (entry 2), and thus, activation of the substrate

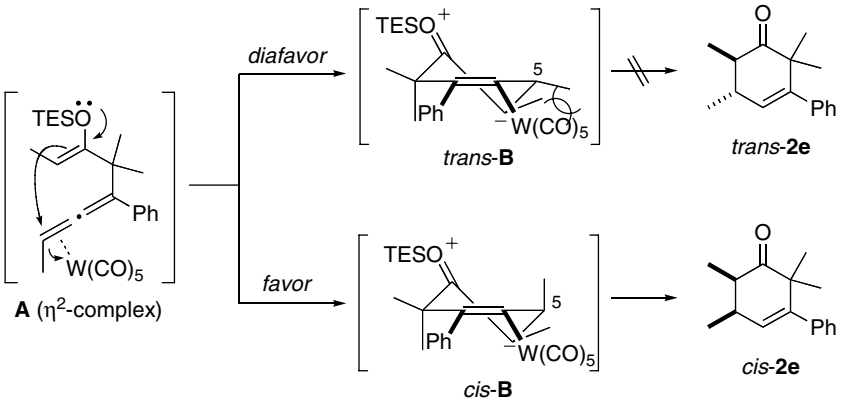
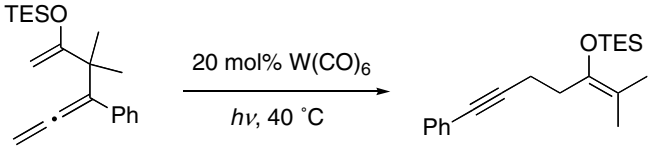


Fig. 1. Stereoselectivity of 6-*endo* cyclization of the substrate **1e**.

Table 2
Reaction of 5-siloxy-1,2,5-triene **1a** using a catalytic amount of $W(CO)_6$ in the absence of H_2O[a]



1a **3a**

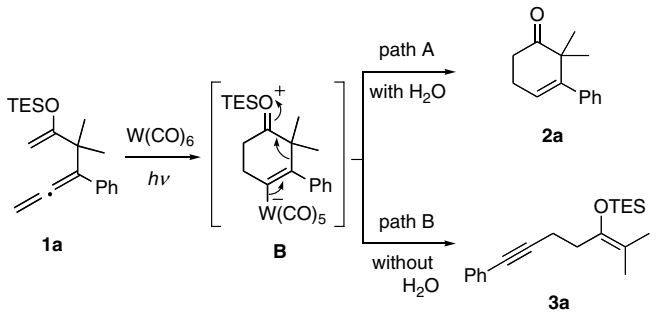
Entry	Solvent	Additive	Time/h	**3a**/%[b]
1	THF	–	24	81
2	THF	–	24	nr[c]
3	Toluene	–	2	71
4	Toluene	DABCO	2	90
5	Toluene	*n*-Bu_3N	2	72
6	Toluene	*i*-Pr_2NEt	2	62

Abbreviations: nr, no reaction; –, no additive.

[a] Unless otherwise noted, the reaction was carried out with **1a** (0.2 mmol), additive (0.02 mmol) in solvent (2.0 mL) in the presence of $W(CO)_6$ (0.04 mmol).

[b] Isolated yield.

[c] In the absence of $W(CO)_6$.



Scheme 2.

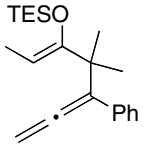
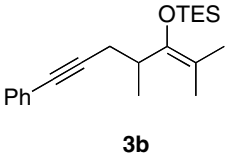
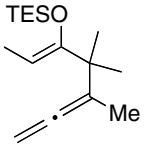
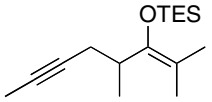
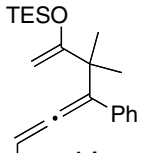
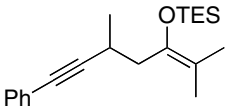
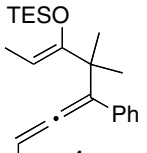
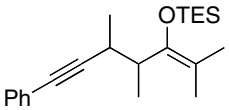
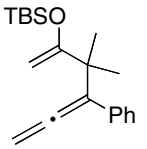
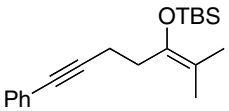
1a by $W(CO)_5$ is essential for this transformation. Use of toluene as a solvent allowed the reaction time to be greatly diminished from 1 day to 2 h (entry 3). Furthermore, the addition of an amine (0.1 equiv) suppressed the formation of minor unidentified products, and in particular, the use of DABCO as a less sterically demanding amine gave the product **3a** in 90% yield as a sole isolable product (entry 4).

This novel rearrangement reaction is thought to proceed as shown in Scheme 2. Treatment of 5-siloxy-1,2,5-triene **1a** with $W(CO)_6$ under photoirradiation would form the same cyclohexenyl tungsten species **B** as already described in the mechanism of the formation of the 6-*endo* cyclized product (Scheme 1). In the presence of H_2O, the protonation of the carbon–tungsten bond occurs to give the 6-*endo*-cyclized product **2a** (path A). On the contrary, in the absence of H_2O, electron-donation from $W(CO)_5$ anion into the silyloxonium moiety induces the carbon–carbon bond cleavage with the liberation of neutral $W(CO)_5$ species to give the formal Cope rearrangement product **3a** (path B).

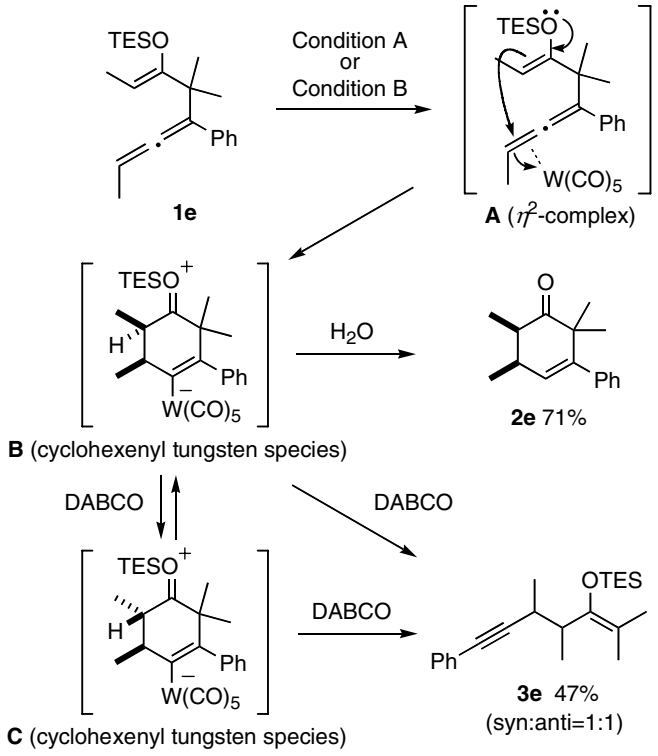
Other examples of the $W(CO)_5$(L)-catalyzed formal Cope rearrangement of 5-siloxy-1,2,5-trienes under these optimized conditions are listed in Table 3. The reaction of 5-siloxy-1,2,5-trienes **1b–d** containing either a tri-substituted silyl enol ether moiety or a trisubstituted allene moiety afforded the corresponding products **3b–d** in good yield (entries 1–3). In this formal Cope rearrangement, it is interesting to note that the reaction of **1d**, which gave the cyclized product **2d** in low yield due to the hydrolysis of the silyl enol ether moiety of the starting material, gave the rearranged product in high yield. In the case of substrate **1e** containing both of these tri-substitution moieties, the reaction gave the product **3e** in moderate yield as a 1:1 mixture of *syn* and *anti* isomers (entry 4), while the reaction in the presence of H_2O gave the cyclized product **2e** in good yield stereoselectively (Table 1, entry 4). It is likely that the epimerization occurred at the cyclohexenyl tungsten species **B** and/or **C** by DABCO (Scheme 3). The reaction of TBS enol ether **1h** gave the corresponding product **3h** in excellent yield (entry 5).

We next examined a ring-expansion reaction by formal Cope rearrangement of cyclic 5-siloxy-1,2,5-trienes for the purpose of preparing large-membered cyclic alkynes [11]. The reaction of cyclohexane derivative **1f** did not proceed well under the optimum reaction conditions, and only deprotonation product **5** was obtained (Eq. (3)). Probably the ring-expanded product **4** with an enyne moiety in 10-membered carbocycle would suffer from ring strain, and only deprotonation occurred by the added base. In contrast, when cyclooctane derivative **1g** was irradiated in the presence of $W(CO)_6$ (100 mol %) and DABCO (0.1 equiv) in toluene, the reaction proceeded as expected to give the ring-expanded 12-membered cyclic product **6**

Table 3
Formal Cope rearrangement of 5-siloxy-1,2,5-triene **1** using a catalytic amount of $W(CO)_6$ in toluene[a]

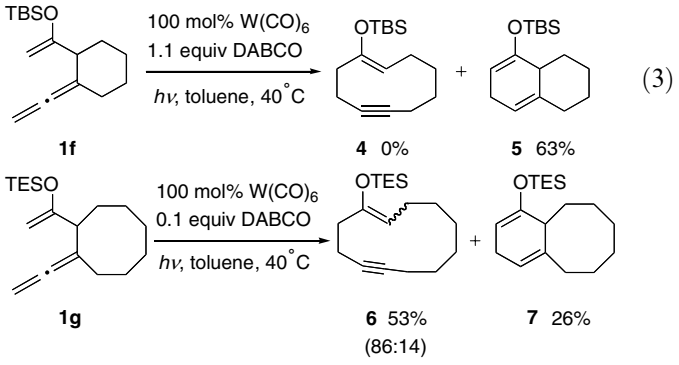
Entry	Substrate	Product	Yield/%
1	 **1b**	 **3b**	68[a]
2	 **1c**	 **3c**	61[a]
3	 **1d**	 **3d**	86[a]
4	 **1e**	 **3e**	47[c,d]
5	 **1h**	 **3h**	99[b]

[a] Conditions: $W(CO)_6$ (20 mol%), DABCO (0.1 equiv), toluene (0.1 M), 40 °C, *hv*.
[b] DABCO (1.1 equiv) was added.
[c] A 1.0 M toluene solution was used.
[d] *syn:anti* = 1:1.



Scheme 3.

in 53% yield as an 86:14 mixture of *E* and *Z* isomers [12] together with 26% yield of deprotonation product **7** (Eq. (4)) [13].



(3)

(4)

3. Conclusion

We have developed a novel 6-*endo*-selective cyclization of allenyl silyl enol ethers using a catalytic amount of $W(CO)_6$. Two types of synthetically useful compounds, that is, 6-*endo*-cyclized products or the formal Cope rearrangement products, are prepared selectively from the same starting materials via the same intermediates simply by changing the reaction conditions. It is also noted that electrophilic activation of the allene moiety is effectively achieved by coordination of $W(CO)_5$, allowing intramolecular attack by neutral carbon nucleophiles efficiently.

4. Experiment

4.1. General

All operations were performed under an argon atmosphere. ^1H and ^{13}C NMR spectra were recorded on a Bruker DRX500, a JEOL AL-400, or a JEOL Lambda-400 spectrometer using $CHCl_3$ (^1H, $\delta = 7.24$), C_6H_6 (^1H, $\delta = 7.15$) and $CDCl_3$ (^{13}C, $\delta = 77.0$) as internal standards. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. Photochemical reactions were performed with an USHIO INC. super high-pressure mercury lamp. Flash column chromatography was conducted on silica gel (Kanto 60N) and preparative thin-layer chromatography (PTLC) was carried out on silica gel (Wakogel B-5F). Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl, and all other solvents were distilled according to the standard procedures and stored over molecular sieves or KOH. $W(CO)_6$ was purchased from Soekawa Chemical Co., Ltd. and used without further purification.

Experimental procedures for the preparation of 5-siloxy-1,2,5-trienes were described in the previous communications [5f,5g].

4.2. General procedure for 6-endo-selective cyclization of 5-siloxy-1,2,5-triene *1*

To a degassed THF (0.2 mL) solution of 5-siloxy-1,2,5-triene **1** (0.2 mmol) was added $W(CO)_6$ (14.1 mg, 0.04 mmol) and H_2O (10.8 μL, 0.6 mmol) at room temperature. The mixture was irradiated using high-pressure 250 W mercury lamp at ambient temperature (rt ~ 40 °C) until the starting material disappeared, and then the resulting mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane:ethyl acetate = 10:1) to give 6-*endo*-cyclized product, cyclohex-3-en-1-one **2**, as a colorless oil.

4.2.1. 2,2-Dimethyl-3-phenylcyclohex-3-en-1-one (*2a*)

Yield 68% (20 mol% WCO_6). IR (neat): 3022, 2971, 1713, 1463 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 1.17$ (6H, s), 2.48–2.55 (2H, m), 2.62–2.67 (2H, m), 5.64 (1H, t, $J = 4.1$ Hz), 7.11–7.16 (2H, m), 7.25–7.31 (3H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 24.8$, 25.3, 35.6, 47.9, 125.1, 126.8, 127.6, 129.2, 140.9, 146.8, 214.6. Anal. Calc. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.70; H, 8.10%.

4.2.2. 2,2,6-Trimethyl-3-phenylcyclohex-3-en-1-one (*2b*)

Yield 77% (20 mol% $W(CO)_6$). IR (neat): 3021, 2971, 2929, 1712, 1462 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 1.07$ (3H, s), 1.13 (3H, d, $J = 6.3$ Hz), 1.25 (3H, s), 2.14 (1H, ddd, $J = 17.0$, 11.9, 2.0 Hz), 2.59 (1H, dt, $J = 17.0$, 6.0 Hz), 2.93–3.05 (1H, m), 5.59 (1H, dd, $J = 6.0$, 2.0 Hz), 7.10–7.17 (2H, m), 7.22–7.35 (3H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 14.4$, 22.7, 27.7, 34.2, 38.8, 48.3, 124.3, 126.7, 127.5, 129.3, 140.8, 146.8, 215.7.

Anal. Calc. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.04; H, 8.68%.

4.2.3. 2,2,3,6-Tetramethylcyclohex-3-en-1-one (**2c**)

Yield 71% (20 mol% WCO_6). IR (neat): 2971, 2931, 1712, 1450 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 1.02$ (3H, d, $J = 6.0$ Hz), 1.12 (3H, s), 1.18 (3H, s), 1.68–1.69 (3H, m), 1.90–1.99 (1H, m), 2.35–2.43 (1H, m), 2.74–2.83 (1H, m), 5.45 (1H, d, $J = 6.0$ Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 14.3$, 18.3, 21.9, 26.7, 33.8, 38.8, 48.0, 120.4, 140.6, 216.4; HRMS (EI^+) Calcd for $C_{10}H_{16}O$, M 152.1201. Found for *m*/*z* 152.1209.

4.2.4. 3-Phenyl-2,2,5,6-tetramethylcyclohex-3-en-1-one (**2e**)

The stereochemistry was assigned to be *cis* on the basis of the measurement of differential NOE spectra. Yield 71% (20 mol% $W(CO)_6$). IR (neat): 2970, 2931, 1713, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 0.86$ (3H, d, $J = 7.2$ Hz), 1.08 (3H, d, $J = 6.8$ Hz), 1.08 (3H, s), 1.20 (3H, s), 2.63 (1H, sext, $J = 6.8$ Hz), 3.20 (1H, quint, $J = 6.8$ Hz), 5.70 (1H, d, $J = 6.0$ Hz), 7.13–7.15 (2H, m), 7.26–7.31 (3H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 11.6$, 15.8, 23.0, 27.2, 37.2, 43.3, 48.4, 126.7, 127.5, 129.4, 131.8, 140.7, 145.3, 215.8; HRMS (EI^+) Calcd for $C_{16}H_{20}O$, M 228.1514. Found for *m*/*z* 228.1493.

4.2.5. Bicyclo[4.4.0]dec-1-en-5-one (**2f**)

Since **2f** has already been prepared [14], NMR spectra are only presented. Yield 84% (10 mol% $W(CO)_6$). ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 1.10$–1.42 (3H, m), 1.45–1.54 (1H, m), 1.70–2.21 (4H, m), 2.22–2.50 (4H, m), 2.57–2.67 (1H, m), 5.50 (1H, br s); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 25.3$, 25.9, 27.4, 30.1, 34.6, 37.8, 50.2, 118.1, 139.8, 212.9.

4.2.6. Bicyclo[6.4.0]dodec-1(8)-en-9-one (**2g**)

Since **2g** has already been prepared [15], NMR spectra are only presented. Yield 69% (20 mol% $W(CO)_6$). ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 1.35$–1.54 (6H, s), 1.61–1.70 (2H, m), 1.92 (2H, quint, $J = 6.4$ Hz), 2.33–2.38 (6H, m), 2.43 (2H, t, $J = 6.4$ Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 22.7$, 23.2, 26.5, 26.7, 28.7, 29.7, 31.1, 33.9, 37.9, 135.4, 159.7, 198.4.

4.3. General procedure for the formal Cope rearrangement of 5-siloxy-1,2,5-triene (**1**)

To a degassed toluene (2.0 mL) solution of 5-siloxy-1,2,5-triene **1** (0.2 mmol) was added $W(CO)_6$ (14.1 mg, 0.04 mmol) and DABCO (2.2 mg, 0.02 mmol) at room temperature. The mixture was irradiated using high-pressure 250 W mercury lamp at ambient temperature (rt ~ 40 °C) until the starting material disappeared, and then the resulting mixture was concentrated under reduced pressure. The residue was purified by preparative thin-layer chromatography (hexane) to give the formal Cope rearrangement product, 2-siloxy-1-en-5-yne **3**, as a colorless oil.

4.3.1. 1-Phenyl-6-methyl-5-triethylsiloxyhept-5-en-1-yne (**3a**)

Yield 90% (20 mol% $W(CO)_6$). IR (neat): 2955, 2914, 1680, 1258, 1198 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 0.67$ (6H, q, $J = 8.0$ Hz), 0.98 (9H, t, $J = 8.0$ Hz), 1.62 (3H, s), 1.65 (3H, s), 2.41–2.44 (2H, m), 2.52–2.56 (2H, m), 7.23–7.28 (3H, m), 7.35–7.39 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 5.6$, 6.9, 17.9, 18.0, 18.9, 32.1, 80.6, 90.0, 110.8, 124.0, 127.4, 128.1, 131.4, 142.7. Anal. Calc. for $C_{20}H_{30}OSi$: C, 76.37; H, 9.61. Found: C, 76.17, H, 9.87%.

4.3.2. 4,6-Dimethyl-1-phenyl-5-triethylsiloxy-hept-5-en-1-yne (**3b**)

Yield 68% (20 mol% $W(CO)_6$). IR (neat): 2957, 1672, 1262, 1189 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 0.72$ (6H, q, $J = 8.0$ Hz), 0.99 (9H, t, $J = 8.0$ Hz), 1.12 (3H, d, $J = 6.8$ Hz), 1.60 (3H, s), 1.66 (3H, s), 2.36 (1H, dd, $J = 8.0$, 16.8 Hz), 2.46 (1H, dd, $J = 6.8$, 16.8 Hz), 2.98 (1H, sext, $J = 6.8$ Hz), 7.22–7.27 (3H, m), 7.35–7.37 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 6.1$, 7.1, 17.8, 18.9, 19.0, 24.8, 35.0, 81.2, 89.7, 108.4, 124.1, 127.3, 128.1, 131.4, 146.6. Anal. Calc. for $C_{21}H_{32}OSi$: C, 76.77; H, 9.82. Found: C, 76.57; H, 10.09%.

4.3.3. 2,4-Dimethyl-3-triethylsiloxyoct-2-en-6-yne (**3c**)

Yield 61% (20 mol% $W(CO)_6$). IR (neat): 2957, 2917, 2877, 1671, 1261, 1190 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 0.68$ (6H, q, $J = 8.0$ Hz), 0.96 (9H, t, $J = 8.0$ Hz), 1.04 (3H, d, $J = 6.8$ Hz), 1.56 (3H, s), 1.60 (3H, s), 1.75–1.77 (3H, m), 2.02–2.11 (1H, m), 2.14–2.20 (1H, m), 2.80 (1H, sext, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 3.6$, 6.0, 7.1, 17.6, 18.87, 18.89, 24.1, 35.1, 76.1, 78.6, 108.0, 147.0. Anal. Calc. for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. Found: C, 71.84; H, 11.13%.

4.3.4. 3,6-Dimethyl-1-phenyl-5-triethylsiloxyhept-5-en-1-yne (**3d**)

Yield 86% (20 mol% $W(CO)_6$). IR (neat): 2958, 1680, 1250, 1174 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): $\delta = 0.67$ (6H, q, $J = 7.6$ Hz), 0.98 (9H, t, $J = 7.6$ Hz), 1.22 (3H, d, $J = 7.2$ Hz), 1.64 (3H, s), 1.66 (3H, s), 2.26 (1H, dd, $J = 8.0$, 14.0 Hz), 2.47 (1H, dd, $J = 6.4$, 14.0 Hz), 2.92 (1H, sext, $J = 7.2$ Hz), 7.21–7.28 (3H, m), 7.33–7.37 (2H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 5.6$, 6.9, 18.0, 19.3, 20.4, 25.0, 39.7, 80.4, 94.7, 111.7, 124.1, 127.3, 128.0, 131.5, 141.9. Anal. Calc. for $C_{21}H_{32}OSi$: C, 76.77; H, 9.82. Found: C, 76.50; H, 9.59%.

4.3.5. 1-Phenyl-5-triethylsiloxy-3,4,6-trimethylhept-5-en-1-yne (**3e**)

This compound was obtained as a 1:1 mixture of *syn* and *anti* isomers. 47% yield (20 mol% $W(CO)_6$). IR (neat): 2957, 1672, 1261, 1197 cm^{-1}; ^1H NMR ($CDCl_3$) (400 MHz): (*syn*, *anti* mixture) $\delta = 0.61$–0.70 (6.0H, m), 0.90–0.95 (9.0H, m), 0.97 (1.5H, d, $J = 6.8$ Hz), 1.10 (1.5H, d, $J = 6.0$ Hz), 1.15 (1.5H, d, $J = 6.4$ Hz), 1.19

(1.5H, d, $J = 6.8$ Hz), 1.53 (1.5H, s), 1.55 (1.5H, s), 1.56 (1.5H, s), 1.62 (1.5 H, s), 2.52–2.61 (1.5H, m), 2.66–2.73 (0.5H, m), 7.16–7.26 (4H, m), 7.33–7.35 (1H, m); ^{13}C NMR ($CDCl_3$) (100 MHz): (*syn*, *anti* mixture) $\delta = 6.1$, 6.2, 7.1, 7.2, 15.4, 17.7, 18.7, 18.8, 19.0, 19.1, 19.4, 19.5, 30.2, 30.3, 40.4, 40.9, 80.8, 81.3, 94.7, 94.8, 108.4, 109.0, 124.1, 124.4, 127.1, 127.3, 128.0, 128.1, 131.3, 131.4, 145.6, 147.0. Anal. Calc. for $C_{22}H_{34}OSi$: C, 77.13; H, 10.00. Found: C, 77.22; H, 9.82%.

4.3.6. 1-Phenyl-6-methyl-5-(t-butyldimethylsiloxy)hept-5-en-1-yne (**3h**)

Yield 99% (20 mol% $W(CO)_6$). IR (neat) 2928, 1680, 1257, 1163 cm^{-1}; ^{1}H NMR ($CDCl_3$) (500 MHz): $\delta = 0.12$ (6H, s), 0.95 (9H, s), 1.61 (3H, s), 1.66 (3H, s), 2.40–2.48 (2H, m), 2.50–2.58 (2H, m), 7.21–7.27 (3H, m), 7.35–7.40 (2H, m); ^{13}C NMR ($CDCl_3$) (125 MHz): $\delta = -3.8$, 18.2, 18.5, 18.7, 19.4, 26.3, 32.2, 81.0, 90.4, 111.4, 124.5, 127.9, 128.6, 131.9, 143.1. Anal. Calc. for $C_{20}H_{30}OSi$: C, 76.37; H, 9.61. Found: C, 76.08; H, 9.71%.

4.3.7. 2-Triethylsiloxycyclododec-1-en-5-yne (**6**)

This compound was obtained as a 86:14 mixture of geometrical isomers. The geometry was not determined. NMR data were described for the major product. Yield 53% (100 mol% $W(CO)_6$). IR (neat): 2917, 1672, 1148, 1005, 729 cm^{-1}; ^{1}H NMR (C_6D_6) (400 MHz): $\delta = 0.60$ (6H, q, $J = 8.0$ Hz), 0.98 (9H, t, $J = 8.0$ Hz), 1.37 (2H, quint, $J = 6.4$ Hz), 1.44–1.63 (6H, m), 2.03 (2H, t, $J = 6.0$ Hz), 2.11–2.14 (2H, m), 2.25 (2H, q, $J = 6.8$ Hz), 2.32–2.36 (2H, m), 4.51 (1H, t, $J = 6.8$ Hz); ^{13}C NMR ($CDCl_3$) (100 MHz): $\delta = 5.5$, 6.9, 16.8, 17.4, 23.5, 24.5, 25.2, 26.1, 26.3, 36.3, 80.1, 81.8, 110.9, 148.0. Anal. Calc. for $C_{18}H_{32}OSi$: C, 73.90; H, 11.03. Found: C, 73.80; H, 10.77%.

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