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Cyclopropanation and Carbonyl Olefination Utilizing 2-(Alk-1-yn-1-yl)-2-(trialkylsilyl)-1,3-dithianes via Regioselective Generation of Titanium Alkynylcarbene Complexes

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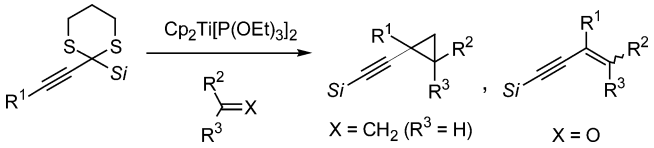

$Cp_2Ti[P(OEt)_3]_2$-promoted reactions of 2-(alk-1-yn-1-yl)-2-(trialkylsilyl)-1,3-dithianes $(RS)_2C(Si)C{\equiv}CR$ with terminal olefins and carbonyl compounds produced (trialkylsilylethynyl)cyclopropanes and 1-(trialkylsilyl)alk-3-en-1-ynes, respectively. These compounds were suggest to be produced via the formation of intermediary titanium α-(trialkylsilylethynyl)carbene complexes $Cp_2Ti{=}C(R)C{\equiv}CSi$ in preference to their regioisomers, α-(trialkylsilyl)alkynylcarbene complexes $Cp_2Ti{=}C(Si)C{\equiv}CR$.

Introduction

The unique reactivities of transition metal carbene complexes and their application to organic synthesis including olefin metathesis, cyclopropanation, and carbonyl olefination have attracted considerable attention.[1] We have developed a variety of transformations of organic compounds utilizing a thioacetal−titanocene(II) system, in which titanium carbene complexes are assumed to be formed as active intermediates. Thus alkyl-, alkenyl-, and alkynylcarbene complexes were readily generated by desulfurizative titanation of thioacetals and related organosulfur compounds with the titanocene(II) species $Cp_2Ti[P(OEt)_3]_2$ (**1**).[2] This methodology, however, suffers a serious drawback in that the formation of α-substituted alkylidenetitanocenes is seriously affected by steric hindrance;[3] only thioacetals derived from less hindered ketones such as cyclobutanone can be employed for the generation of the alkylidene complexes.[4]

Previously, we have found that cyclopropanes were produced by reaction of terminal olefins with the titanium alkynylcarbene complexes generated from β,γ-acetylenic thioacetals.[5] Although various types of heteroatom-substituted alkynylcarbene complexes have been prepared and applied to organic synthesis,[1] only limited work has been done on the chemistry of nonheteroatom-substituted alkynylcarbene complexes.[6] Therefore we were intrigued with the generation of highly substituted alkynylcarbene complexes from the acetylenic thioacetals bearing an α-substituent. We expected that the less bulky alkynyl group would alleviate the steric crowding of the thioacetals, and hence these organotitanium species could be obtained. Our major interest in the chemistry of highly substituted alkynylcarbene complexes is their regioselective formation, which is of crucial importance for their synthetic application.

Here we report highly regioselective cyclopropanation and carbonyl olefination utilizing α-silylalkynyl thioacetals **2** which involve unprecedented allylic rearrangement directed by the trialkylsilyl group.[7]

Results and Discussion

Preparation of 2-(Alk-1-yn-1-yl)-2-(trialkylsilyl)-1,3-dithianes 2. The alkynyl thioacetals employed in this

(1) Dörwald, F. Z. *Metal Carbenes in Organic Synthesis*; Wiley-VCH: Weinheim, Germany, 1999.

(2) (a) Takeda, T. In *Titanium and Zirconium in Organic Synthesis*; Marek, I., Ed.; Wiley-VCH: Weinheim, Germany, 2002; p 480. (b) Takeda, T.; Tsubouchi, A. In *Modern Carbonyl Olefination*; Takeda, T., Ed.; Wiley-VCH: Weinheim, Germany, 2004; p 178. (c) Takeda, T. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 195.

(3) Takeda, T.; Sasaki, R.; Fujiwara, T. *J. Org. Chem.* **1998**, *63*, 7286.

(4) Fujiwara, T.; Iwasaki, N.; Takeda, T. *Chem. Lett.* **1998**, 741.

(5) Takeda, T.; Kuroi, S.; Yanai, K.; Tsubouchi, A. *Tetrahedron Lett.* **2002**, *43*, 5641.

(6) For Re-complexes, see: (a) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2000**, *122*, 3771. (b) Casey, C. P.; Kraft, S.; Kavana, M. *Organometallics* **2001**, *20*, 3795. (c) Casey, C. P.; Kraft, S.; Powell, D. R. *Organometallics* **2001**, *20*, 2651. (d) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 2584. For Mn-complexes, see: (e) Ortin, Y.; Coppel, Y.; Lugan, N.; Mathieu, R.; McGlinchey, M. J. *Chem. Commun.* **2001**, 1690. (f) Casey, C. P.; Dzwiniel, T. L.; Kraft, S.; Kozee, M. A.; Powell, D. R. *Inorg. Chem. Acta* **2003**, *345*, 320. (g) Ortin, Y.; Sournia-Saquet, A.; Lugan, N.; Mathieu, R. *Chem. Commun.* **2003**, 1060. For Rh-complexes, see: (h) Padwa, A.; Austin, D. J.; Gareau, Y.; Kassir, J.; Xu, S. L. *J. Am. Chem. Soc.* **1993**, *115*, 2637. For W-complexes, see: (i) Iwasawa, N.; Maeyama, K.; Saitou, M. *J. Am. Soc. Chem.* **1997**, *119*, 1486.

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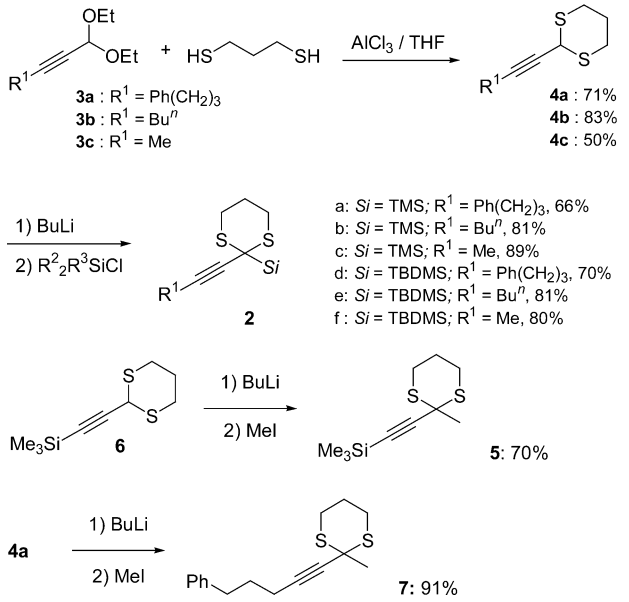
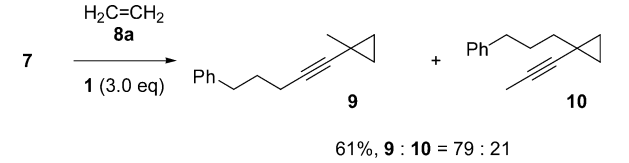
SCHEME 1. Preparation of Alkynyl Thioacetals



SCHEME 2. Cyclopropanation with 2-Methyl-2-(5-phenylpent-1-yn-1-yl)-1,3-dithiane (7)

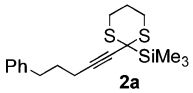
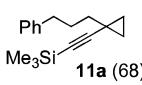
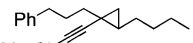
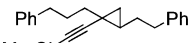
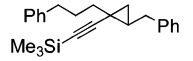
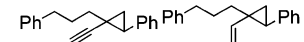
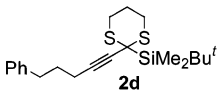
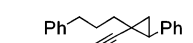
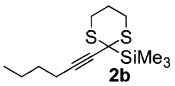
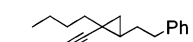
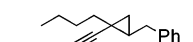
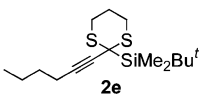
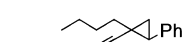
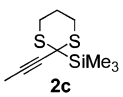
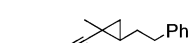
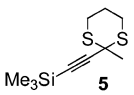
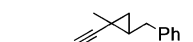


study were prepared as summarized in Scheme 1. Transthioacetalization of β,γ-acetylenic acetals **3** with 1,3-propanedithiol in the presence of $AlCl_3$ gave the 2-alkynyl-1,3-dithianes **4**. The α-(trialkylsilyl)-β,γ-acetylenic thioacetals **2** were obtained by successive treatment of **4** with buthyllithium and trialkylchlorosilanes. 2-Methyl-2-(trimethylsilylethynyl)-1,3-dithiane (**5**) was prepared by the treatment of 2-(trimethylsilylethynyl)-1,3-dithiane (**6**)[8] with butyllithium followed by the alkylation with methyl iodide. The alkylation of the dithiane **4a** with methyl iodide also gave 2-methyl-2-(5-phenylpent-1-yn-1-yl)-1,3-dithiane (**7**).

Reaction of Alkynyl Thioacetals with Terminal Olefins in the Presence of the Titanocene(II) Reagent. Initially we examined the titanocene(II)-promoted cyclopropanation of the α-methyl-β,γ-acetylenic thioacetal **7** under ethylene (**8a**). Treatment of **7** with the titanocene(II) reagent **1** (3 equiv) under ethylene atmosphere afforded a mixture of the alkynylcyclopropane **9** and its regioisomer **10** in 61% yield with a ratio of 79:21 in favor of the less steric crowding cyclopropane (Scheme 2).

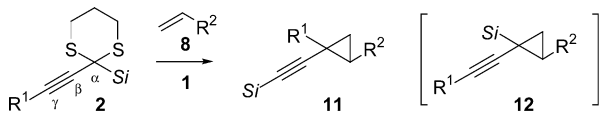
When more sterically hindered 2-(5-phenylpent-1-yn-1-yl)-2-(trimethylsilyl)-1,3-dithiane (**2a**) was treated with **1** (2 equiv) under **8a** at 25 °C for 1 h, the trimethylsilylethynyl-substituted cyclopropane **11a** was exclusively produced in 68% yield (Table 1, entry 1). Similar titanocene(II)-promoted reactions of the α-trialkylsilyl-β,γ-acetylenic thioacetals **2** with various terminal olefins **8** also gave the (trialkylsilylethynyl)cyclopropanes **11** without formation of their possible regioisomers **12** (Scheme 3). When styrene (**8e**) was used as an olefin component, partial reduction of the triple bond of the alkynylcyclopropane proceeded to form the alkenylsilane **13** (entry 5). The coupling constant of its vinyl protons (14.5 Hz) suggests that its configuration is *Z*.[9] This reduction was

TABLE 1. Regioselective Formation of the (Trialkylsilylethynyl)cyclopropanes 11

entry	acetylenic thioacetal **2**	olefin **8**	product **11** (yield / %; ratio of isomers)
1[a]	 **2a**	 **8a**	 **11a** (68)
2	**2a**	 **8b**	 **11b** (67; 57 : 43)
3	**2a**	 **8c**	 **11c** (67; 61 : 39)
4	**2a**	 **8d**	 **11d** (69; 62 : 38)
5	**2a**	 **8e**	 **11e** (54; >99 : 1) **13** (15; >99 : 1)
6[b]	 **2d**	**8e**	 **11f** (75; >99 : 1)
7	 **2b**	**8c**	 **11g** (52; 81 : 19)
8	**2b**	**8d**	 **11h** (52; 69 : 31)
9[b]	 **2e**	**8e**	 **11i** (70; >99 : 1)
10	 **2c**	**8c**	 **11j** (63; 81 : 19)
11	 **5**	**8c**	**11j** (70; 80 : 20)
12	**2c**	**8d**	 **11k** (52; 79 : 21)

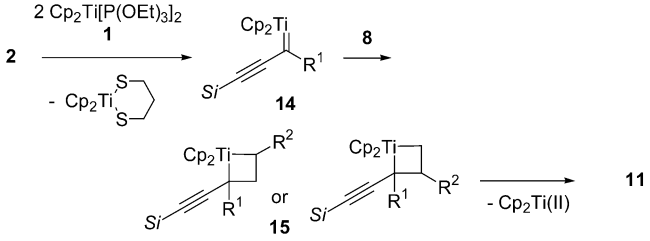
[a] Carried out under ethylene. [b] 3 equiv of **1** and 4 equiv of **8e** were used.

SCHEME 3. Silyl Group Directed Regioselective Cyclopropanation with the α-(Trialkylsilyl)-β,γ-acetylenic Thioacetals 2

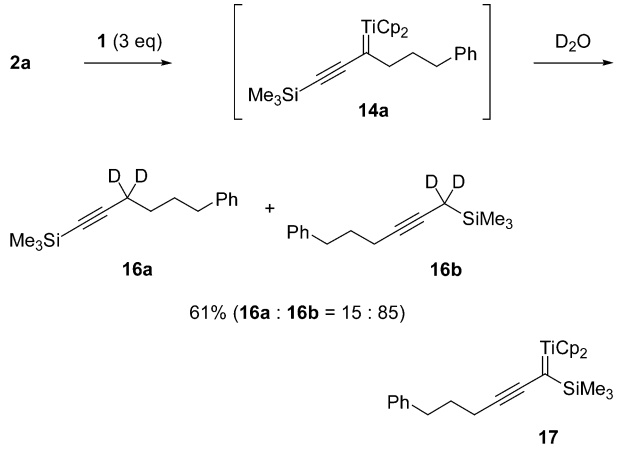


(7) Preceding paper: Takeda, T.; Kuroi, S.; Ozaki, M.; Tsubouchi, A. *Org. Lett.* **2004**, *6*, 3207.
(8) Andersen, N. H.; Dennistone, A. D.; McCrae, D. A. *J. Org. Chem.* **1982**, *47*, 1145.

SCHEME 4. Reaction Pathway for the Regioselective Formation of (Trialkylsilylethynyl)cyclopropanes 11



SCHEME 5. Formation of the Dideuterio Alkynylsilanes 16

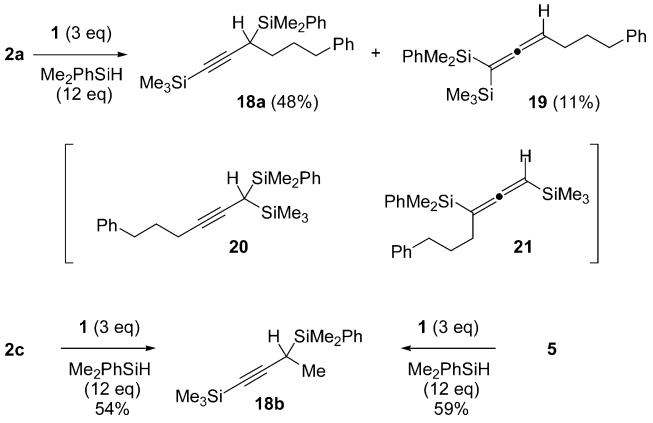


suppressed by use of more bulky *tert*-butyldimethylsilyl-substituted acetylenic thioacetals (entries 6 and 9). Interestingly, the position γ to the thioacetal group of **2** was predominantly cyclopropanated in all the reactions examined. This regioselectivity is in sharp contrast to that observed in the reaction of α-unsubstituted thioacetals, in which cyclopropanation took place at the α-position.[5] Furthermore, it is noteworthy that both the cyclopropanation of 4-phenylbut-1-ene (**8c**) with the α-(trimethylsilyl)-β,γ-acetylenic thioacetal **2c** and its regioisomer, γ-(trimethylsilyl)-β,γ-acetylenic thioacetal **5**, regioselectively produced the (trimethysilylethynyl)cyclopropane **11j** with the same ratio of stereoisomers (entries 10 and 11). These results indicate that the regioselectivity of the cyclopropanation depends on the relative steric bulkiness of α (R^1)- and γ (R^2)-substituents of acetylenic thioacetals $R^2C{\equiv}CC(SR)_2R^1$.

The regioselectivity of the formation of (trialkylsilylethynyl)cyclopropanes **11** strongly suggests exclusive formation of intermediary α-(trialkylsilylethynyl)carbene complexes **14** ($Cp_2Ti{=}C(R)C{\equiv}CSi$). Accordingly, we assume that the cyclopropanation proceeds through the formation of the titanacyclobutane intermediate **15** formed from **14** and a terminal olefin **8**. Subsequent reductive elimination affords the cyclopropane **11** (Scheme 4).

Indeed, the formation of alkynylcarbene complex **14** was supported by the fact that the dideuterated 1- and 2-alkynylsilanes **16a** and **16b** (>95% D) were produced by successive treatment of the thioacetal **2a** with the titanocene(II) reagent **1** and deuterium oxide (Scheme

SCHEME 6. Reaction of the Alkynylcarbene Complexes with Dimethylphenylsilanes



5). It is rational to assume that **16b** is produced by deuteration of the alkynylcarbene complex **14a** with allylic rearrangement. However, the result does not exclude the formation of the α-(trimethylsilyl)alkynylcarbene complex **17**.

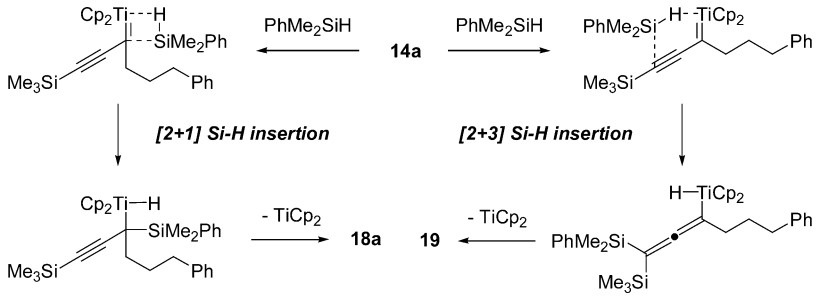
Reaction of the Alkynylcarbene Complexes with Dimethylphenylsilane. A more persuasive evidence for the intermediary trialkylsilylethynly-substituted carbene complex **14** was obtained by using a carbenoid insertion-type reaction of titanium carbene complexes with group 14 metal hydrides[10] as a probe. Desulfurizative titanation of **2a** with **1** in the presence of dimethylphenylsilane produced propargylsilane **18a** as a major product along with the allenylsilane **19** (Scheme 6). It is apparent that these compounds are formed by the [2+1] and [2+3] carbenoid insertion-type reactions of the (trialkylsilylethynyl)carbene complex **14a** (Scheme 7). No formation of the propargylsilane **20** or allenylsilane **21**, which would be formed via the α-trialkylsilyl carbene complex **17**, was observed, thus indicating exclusive formation of **14a** by the desulfurization of **2a** with **1**. The selective generation of the silylethynyl carbene complex is further supported by the fact that a similar reaction of **2c** with dimethylphenylsilane gave only the propargylsilane **18b**, which was also produced by the reaction of the isomeric silylethynyl thioacetal **5**. The mechanism for the regioselective formation of **14a** is obscure at present. Although it is reasonable to assume that the desulfurizative titanation of **2** with **1** proceeds with allylic rearrangement to give **14**, the isomerization of the initially formed carbene complexes such as **17** to **14** cannot be excluded because the equilibrium between regioisomers of rhenium,[6b,d] manganese,[6e] and rhodium[6h] alkynylcarbene complexes, LnM=C(R)C≡CR′ and LnM=C(R′)C≡CR, was observed.

Titanocene(II)-Promoted Reaction of the α-Substituted Alkynyl Thioacetals 2 with Carbonyl Compounds. On the basis of the regioselective formation of **14** suggested by the above investigation, we next examined the regioselective preparation of enynes **22** by the olefination of carbonyl compounds **23** with the alkynylcarbene complexes **14** (Scheme 8). Contrary to our expectations, the successive treatment of acetylenic thioacetal **2a** with the titanocene(II) reagent **1** (3 equiv) and

(9) (a) Miura, K.; Oshima, K.; Utimoto, K. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2356. (b) Dash, A. K.; Wang, J. Q.; Eisen, M. S. *Organometallics* **1999**, *18*, 4724.

(10) Takeda, T.; Nozaki, N.; Fujiwara, T. *Tetrahedron Lett.* **1998**, *39*, 3533.

SCHEME 7. Reaction Pathway for the Formation of Propargyl- and Allenylsilanes



SCHEME 8. Carbonyl Olefination Utilizing the Acetylenic Thioacetals 2

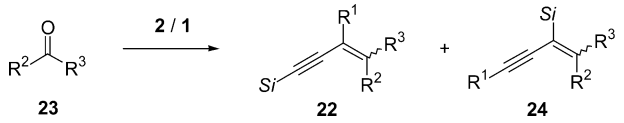
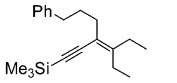
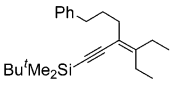
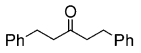
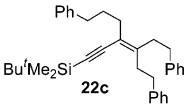
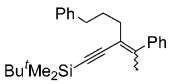
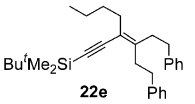
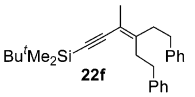
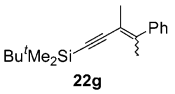


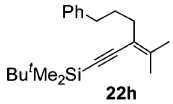
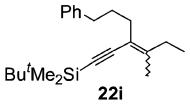
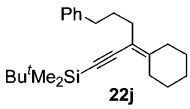
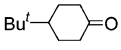
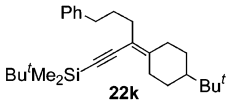
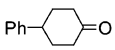
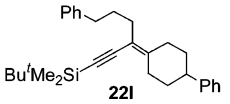
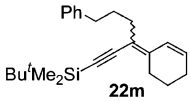
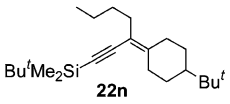
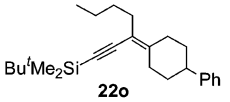
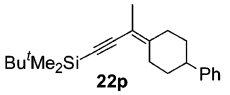
TABLE 2. Reaction of the Acetylenic Thioacetals 2 with Dialkyl Ketones 23

entry	thioacetal **2**	ketone **23**	product **22**	yield / % (**22** : **24**)
1	**2a**	 **23a**	 , **24a**	75 (80 : 20)
2	**2d**	**23a**	 , **24b**	72 (94 : 6)
3	**2d**	 **23b**	 , **24c**	60 (88 : 12)
4	**2d**	 **23c**	 , **24d**	67 (88 : 12)
5	**2e**	**23b**	 , **24e**	69 (87 : 13)
6	**2f**	**23b**	 **22f**	71
7	**2f**	**23c**	 **22g**	68 (54 : 46)[a]

[a] Ratio of stereoisomers.

3-pentanone (**23a**) (1.2 equiv) produced a mixture of the two regioisomers of the carbonyl olefination products, the conjugated dienes **22a** and **24a** (80:20) in 75% yield (Table 2, entry 1). The regioselectivity increased when the more sterically hindered *tert*-butyldimethylsilyl-substituted counterpart **2d** was employed (entry 2). Although the reactions of dialkyl ketones and acetophenone with acetylenic thioacetals generally gave mixtures of regioisomers, complete regioselectivity was observed when the less bulky methyl-substituted thioacetal **2f** was employed (entries 6 and 7).

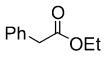
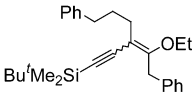
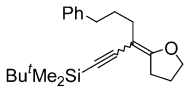
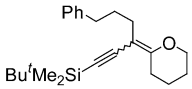
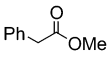
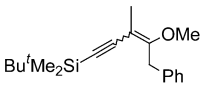
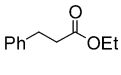
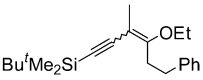
TABLE 3. Reaction of the Acetylenic Thioacetals 2 with Sterically Less Hindered Ketones 23

entry	thioacetal **2**	ketone **23**	product **22**	yield / %
1	**2d**	 **23d**	 **22h**	68
2	**2d**	 **23e**	 **22i**	71 (83 : 17)[a]
3	**2d**	 **23f**	 **22j**	72
4	**2d**	 **23g**	 **22k**	60
5	**2d**	 **23h**	 **22l**	72
6	**2d**	 **23i**	 **22m**	70 (85 : 15)[a]
7	**2e**	**23g**	 **22n**	69
8	**2e**	**23h**	 **22o**	58
9	**2f**	**23h**	 **22p**	66

[a] Ratio of stereoisomers.

Unlike the reactions of dialkyl ketones, less bulky ketones such as acetone, butan-2-one, and 4-substituted cyclohexanones were exclusively transformed into the corresponding silylacetylenes **22**, regardless of the γ-sub-

TABLE 4. Reaction of the Acetylenic Thioacetals 2 with Esters and Lactones 23

entry	thioacetal **2**	ester or lactone **23**	product **22**[a]	yield / %
1	**2d**	 **23j**	 **22q**	63
2	**2d**	 **23k**	 **22r**	70
3	**2d**	 **23l**	 **22s**	71
4	**2f**	 **23m**	 **22t**	63
5	**2f**	 **23n**	 **22u**	68

[a] Single stereoisomers were obtained.

stituents of the β,γ-acetylenic thioacetals **2** (Table 3). The dienyne **22m** was also obtained in good yield by the reaction of **2d** with cyclohex-2-en-1-one (**23i**) (entry 6).

Similarly to the conventional carbonyl olefinations with titanium carbene complexes,[11] the present reaction is applicable to the transformation of esters and lactones into enynes **22** (Table 4). In contrast to the reactions of dialkyl ketones, the reaction proceeded regioselectively to produce silylethynyl group-substituted enol ethers as sole products. It is also of special interest that every reaction examined gave a single stereoisomer. Olefination of carboxylic acid derivatives utilizing a thioacetal–titanocene(II) system generally produces *Z* stereoisomers, in which there is less steric interaction between the alkyl group originating from the acyl group and the alkyl substituent at the β carbon.[12] Therefore, it is reasonable to assume that the configuration of these enol ethers is *E*. A similar stereoselectivity was also observed in other olefination reactions of esters with use of titanium carbene complexes.[13]

Protodesilylation of the (Trialkylsilylethynyl)-cyclopropanes 11 and 1-(Trialkylsilyl)alk-3-en-1-ynes 22. The major products of the reactions can be transformed into synthetically useful terminal alkynes (Scheme 9). Treatment of the (trialkylsilyethynyl)cyclopropanes **11** with tetrabutylammonium fluoride (TBAF) gave the ethynylcyclopropanes **25**. Similarly the trialkylsilyl group-substituted enynes **22** were transformed to the terminal alkynes **26** (Table 5).

SCHEME 9. Protodesilylation of the (Trialkylsilylethynyl)cyclopropanes 11 and 1-(Trialkylsilyl)alk-3-en-1-ynes 22

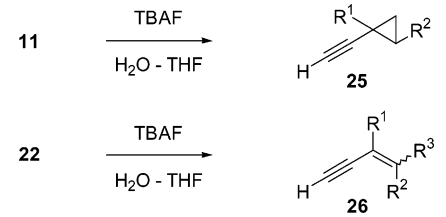
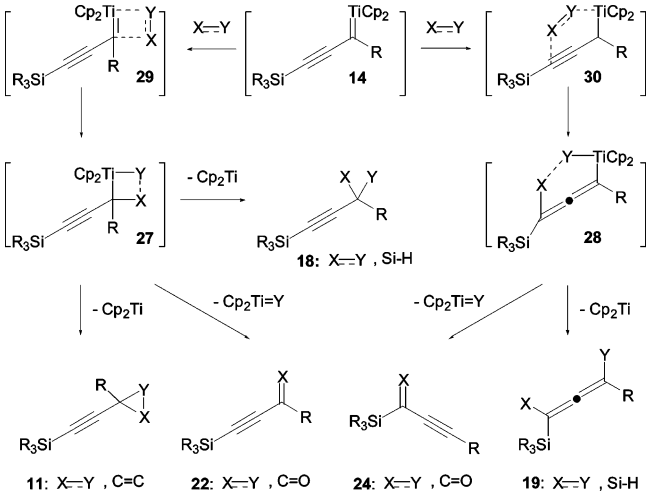


TABLE 5. Protodesilylaton of the (Trimethylsilylethynyl)cyclopropanes 11 and 1-(*tert*-Butyldimethylsilyl)alk-3-en-1-ynes 22

entry	silylacetylene **11** or **22**	terminal alkyne **25** or **26**	yield/% (ratio of stereoisomers)
1	**11b**	**25a**	92 (56:44)
2	**11c**	**25b**	78 (62:38)
3	**11g**	**25c**	93 (83:17)
4	**22b**	**26a**	74
5	**22d**	**26b**	75 (70:30)
6	**22f**	**26c**	76
7	**22h**	**26d**	76
8	**22i**	**26e**	77 (82:18)
9	**22j**	**26f**	80
10	**22k**	**26g**	82
11	**22o**	**26h**	93

SCHEME 10. Pathways for the Reactions of the Alkynylcarbene Complexes 14



Reaction Pathways. The results of the carbenoid insertion-type reactions indicate that only the α-(trialkylsilylethynyl)carbene complex **14** is generated by the desulfurization of the alkynyl thioacetal **2** with the low-valent titanocene **1**. Therefore all the reactions of **2** are explained by the formation of two types of organotitanium intermediates **27** and **28** (Scheme 10). The reaction sequence involving the formation of the propargyltitanium intermediate **27** via the more stable 4-membered transition state **29** and its metathesis-type degradation or reductive elimination affords the major products of cyclopropanation **11**, carbenoid insertion-type reaction **18**, or carbonyl olefination **22**. The minor products of the latter two reactions **19** and **24** are produced by similar degradations of the allenyltitanium intermediate **28**,

(11) Pine, S. H. *Org. React*. **1993**, *43*, 1.
(12) (a) Horikawa, Y.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Am. Chem. Soc.* **1997**, *119*, 1127. (b) Takeda, T.; Watanabe, M.; Nozaki, N.; Fujiwara, T. *Chem. Lett.* **1998**, 115.
(13) (a) Petasis, N. A.; Bzowej, E. I. *J. Org. Chem*. **1992**, *57*, 1327. (b) Petasis, N. A.; Akritopoulou, I. *Synlett* **1992**, 665. (c) Hart, S. L.; McCamley, A.; Taylor, P. C. *Synlett* **1999**, 90.

which is formed via the less stable 6-membered transition state **30**. In the case of the reactions of sterically hindered dialkyl ketones or dimethylphenylsilane, the four-membered transition state **29** is destabilized by steric repulsion between the α-substituent of the carbene complex and the substrate, hence the reaction partially follows the pathway involving the six-membered transition state **30** to produce the minor products. On the contrary, a bulky *tert*-butyldimethylsilyl group destabilizes **30**, which would be the reason the carbonyl olefination with *tert*-butyldimethylsilyl group-substituted acetylenic thioacetals is more regioselective than the reaction of the trimethylsilyl group-substituted counterparts.

Conclusion

We have demonstrated that the highly regioselective reactions of alkynyl thioacetals with terminal olefins and carbonyl compounds are achieved by the introduction of the bulky trialkylsilyl group. The products of these reactions together with the results of the reaction of the thioacetals with dimethylphenylsilane suggested that the reaction preceeded via the regioselective formation of silylethynyl group-substituted titanium carbene complexes. It should be noted that the reactions described here are convenient synthetic methods for the preparation of functionalized terminal alkynes.

Experimental Section

Preparation of 2-(5-Phenylpent-1-yn-1-yl)-1,3-dithiane (4a). A THF (50 mL) solution of $AlCl_3$ (5.87 g, 44 mmol) was cooled to 0 °C. To the solution was added 1,3-propanedithiol (2.0 mL, 20 mmol) under argon and then a THF (10 mL) solution of 1,1-diethoxy-6-phenylhex-2-yne (**3a**) (4.93 g, 20 mmol). After being stirred for 2 days, the reaction was quenched with H_2O and organic materials were extracted with ether. The organic layer was washed with 1 M NaOH, H_2O, and brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (hexane/AcOEt = 98/2) to give **4a** (3.74 g, 71%). **4a**: IR (neat) 3060, 3024, 2901, 2231, 1602, 1496, 1454, 1275, 1243, 1223, 1030, 910, 744, 700 cm^{-1} ;^{1}H NMR δ 1.87 (tt, J = 7.2, 7.2 Hz, 2H), 2.01−2.08 (m, 2H), 2.30 (dt, J = 2.2, 7.1 Hz, 2H), 2.71−2.85 (m, 4H), 3.17 (ddd, J = 5.9, 5.9, 13.8 Hz, 2H), 4.65 (s, 1H), 7.17−7.32 (m, 5H); ^{13}C NMR δ 18.3, 25.7, 28.4, 30.2, 33.6, 34.8, 76.7, 86.3, 125.9, 128.3, 128.5, 141.4. Anal. Calcd for $C_{15}H_{18}S_2$: C, 68.65; H, 6.91. Found: C, 69.01; H, 7.03.

In a similar manner, the 2-(alk-1-yn-1-yl)-1,3-dithianes **4b** and **4c** were prepared.

Preparation of 2-(*tert*-Butyldimethylsilyl)-2-(5-phenylpent-1-yn-1-yl)-1,3-dithiane (2d). To a THF (3.0 mL) solution of the dithiane **4a** (262 mg, 1.0 mmol) was added butyllithium (1.37 M in hexane, 0.73 mL, 1.0 mmol) at −78 °C under argon. After the solution was stirred for 2 h, a THF (2 mL) solution of *tert*-butylchlorodimethylsilane (151 mg, 1.0 mmol) was added and the mixture was gradually warmed to room temperature and stirred overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4-Cl, and organic materials were extracted with ether. The extract was washed with H_2O and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel (hexane/AcOEt = 99/1) to give **2d** (263 mg, 70%). **2d**: IR (neat) 3026, 2930, 2210, 1496, 1249, 917, 824, 698 cm^{-1}; ^{1}H NMR δ 0.29 (s, 6H), 1.79 (s, 9H), 1.79−2.18 (m, 4H), 2.39 (t, J = 7.1 Hz, 2H), 2.60 (ddd, J = 3.5, 3.5, 14.1 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 3.52 (ddd, J = 2.6, 13.3, 13.3 Hz, 2H), 7.15−7.33 (m, 5H); ^{13}C NMR δ −7.3, 18.8, 19.6, 25.9, 26.4, 28.0, 30.8, 34.3, 35.1, 80.2, 86.3, 125.9, 128.4, 128.5, 141.7. Anal. Calcd for $C_{21}H_{32}S_2Si$: C, 66.96; H, 8.56. Found: C, 66.75; H, 8.52.

The α-(trialkylsilyl)-β,γ-acetylenic thioacetals **2a**−**c**,**e**,**f** were also obtained by a similar procedure described above.

Preparation of 2-Methyl-2-(trimethylsilylethynyl)-1,3-dithiane (5). Similarly to the preparation of α-(trialkylsilyl)-β,γ-acetylenic thioacetals **2**, the thioacetal **5** (193 mg, 70%) was prepared by the alkylation of 2-(trimethylsilylethynyl)-1,3-dithiane (**6**) (260 mg, 1.2 mmol) with MeI (0.09 mL, 1.4 mmol). **5**: IR (neat) 2957, 2903, 2157, 1419, 1252, 1159, 1067, 926, 859, 833, 764, 652 cm^{-1}; ^{1}H NMR δ 0.22 (s, 9H), 1.72−1.85 (m, 1H), 1.77 (s, 3H), 2.15 (dtt, J = 14.5, 2.8, 4.2 Hz, 1H), 2.79 (ddd, J = 3.6, 3.6, 13.8 Hz, 2H), 3.32 (ddd, J = 2.3, 12.7, 14.8 Hz, 2H); ^{13}C NMR δ 0.13, 25.0, 28.8, 29.1, 41.3, 89.7, 105.1. Anal. Calcd for $C_{10}H_{18}S_2Si$: C, 52.11; H, 7.87. Found: C, 51.73; H, 7.94.

Similarly, 2-methyl-2-(5-phenylpent-1-yn-1-yl)-1,3-dithiane (**7**) (251 mg, 91%) was obtained by the alkylation of **4a** (262 mg, 1 mmol) with MeI (0.08 mL, 1.2 mmol). **7**: IR (neat) 2903, 2240, 1496, 1453, 1421, 1071, 740, 700 cm^{-1}; ^{1}H NMR δ 1.80 (s, 3H), 1.77−1.93 (m, 3H), 2.11−2.14 (m, 1H), 2.34 (t, J = 7.2 Hz, 2H), 2.75 (t, J = 7.9 Hz, 2H), 2.80 (ddd, J = 3.7, 3.7, 13.8 Hz, 2H), 3.35 (ddd, J = 2.5, 13.6, 13.6 Hz, 2H), 7.17−7.32 (m, 5H); ^{13}C NMR δ 18.4, 25.1, 29.1, 29.6, 30.6, 35.0, 41.4, 81.6, 85.1, 125.9, 128.4, 128.5, 141.5. Anal. Calcd for $C_{16}H_{20}S_2$: C, 69.51; H, 7.29. Found: C, 69.43; H, 7.44.

Titanocene(II)-Promoted Reaction of 7 with Ethylene. Cp_2TiCl_2 (224 mg, 0.9 mmol), magnesium turnings (26 mg, 1.1 mmol; purchased from Nacalai Tesque Inc. Kyoto, Japan), and finely powdered molecular sieves 4 A (90 mg) were placed in a flask and dried with heating in vacuo. After cooling, THF (1.8 mL) and $P(OEt)_3$ (0.31 mL, 1.8 mmol) were added successively with stirring at 25 °C under ethylene. After 3 h, a THF (0.9 mL) solution of **7** (83 mg, 0.3 mmol) was added to the mixture. The mixture was stirred for 1 h at 25 °C and then refluxed for 1 h. The reaction was quenched by addition of 1 M NaOH, and the resulting insoluble materials were filtered off through Celite and washed with ether. The organic materials were extracted with ether and dried. After removal of the solvent, the residue was purified by PTLC (hexane) to give a mixture of 1-methyl-1-(5-phenylpent-1-yn-1-yl)cyclopropane (**9**) and 1-(3-phenylpropyl)-1-(prop-1-yn-1-yl)cyclopropane (**10**) (34 mg, 57%, **9**:**10** = 79:21). A mixture of **9** and **10**: IR (neat) 3084, 3025, 2933, 2859, 1603, 1496, 1454, 1379, 1337, 1080, 1020, 745, 699 cm^{-1}; ^{1}H NMR δ 0.48 (dd, J = 4.0, 6.4 Hz, 0.42H), 0.53 (dd, J = 4.0, 6.4 Hz, 1.58H), 0.79 (dd, J = 4.0, 6.4 Hz, 0.42H), 0.82 (dd, J = 4.0, 6.4 Hz, 1.58H), 1.25 (s, 2.37H), 1.72−1.83 (m, 2.42H), 1.76 (s, 0.63H), 2.14 (t, J = 7.1 Hz, 1.58H), 2.64 (t, J = 7.2 Hz, 0.42H), 2.69 (t, J = 7.5 Hz, 1.58H), 7.14−7.32 (m, 5H); ^{13}C NMR δ 3.6, 6.7, 11.8, 14.9, 16.1, 18.2, 24.6, 29.5, 30.7, 34.8, 35.6, 38.1, 71.9, 75.0, 83.9, 86.8, 125.6, 125.8, 128.2, 128.3, 128.4, 128.5, 141.8, 142.6. Anal. Calcd for $C_{15}H_{18}$: C, 90.85; H, 9.15. Found: C, 90.38; H, 9.23.

Titanocene(II)-Promoted Cyclopropanation of Terminal Olefins 8 with the α-(Trialkylsilyl)-β,γ-acetylenic Thioacetals 2. To a THF (1.2 mL) solution of **1**, prepared from Cp_2TiCl_2 (149 mg, 0.6 mmol), magnesium turnings (17 mg, 0.7 mmol), molecular sieves 4 A (60 mg), and $P(OEt)_3$ (0.21 mL, 1.2 mmol) in the presence of **8c** (0.36 mL, 2.4 mmol), was added a THF (0.9 mL) solution of **2a** (100 mg, 0.3 mmol) at 25 °C under argon. The mixture was stirred for 1 h at 25 °C. The workup and purification described above gave **11c** (73 mg, 67%). **11c**: IR (neat) 3063, 3025, 2938, 2858, 2156, 1603, 1495, 1454, 1248, 1031, 840, 758, 698, 635 cm^{-1}; ^{1}H NMR δ 0.13 (s, 5.49H), 0.16 (s, 3.51H), 0.24 (dd, J = 4.3, 6.5 Hz, 0.61H), 0.58 (dd, J = 3.8, 5.4 Hz, 0.39H), 0.67−0.76 (m, 0.78H), 1.04 (dd, J = 4.2, 8.8 Hz, 0.61H), 1.14−1.53 (m, 3.61H), 1.66−1.95 (m, 3H), 2.56−2.86 (m, 4H), 7.15−7.30 (m, 10H); ^{13}C NMR δ −0.03, 0.00, 16.4, 18.2, 21.4, 21.6, 25.5, 26.7, 29.0, 29.2, 30.4, 31.2, 32.6, 35.1, 35.2, 35.3, 35.5, 37.7, 79.6, 82.7, 109.3, 112.9, 125.3, 125.4, 127.86, 127.88, 127.90, 127.94, 128.01, 128.07, 128.12,

141.7, 142.1, 142.18, 142.23. Anal. Calcd for $C_{25}H_{32}Si$: C, 83.27; H, 8.94. Found: C, 83.57; H, 9.21.

The cyclopropanes **11a**,**b**,**d**−**k** were also obtained by similar reactions of **2** with terminal olefins **8**.

Deuteration of the Organotitanium Intermediate. To a THF (1.8 mL) solution of **1**, prepared from Cp_2TiCl_2 (224 mg, 0.9 mmol), magnesium turnings (26 mg, 1.1 mmol), molecular sieves 4 A (90 mg), and $P(OEt)_3$ (0.31 mL, 1.8 mmol), was added a THF (0.9 mL) solution of **2a** (100 mg, 0.3 mmol) at 25 °C under argon. After the solution was stirred for 10 min, D_2O (0.3 mL) was added and the mixture was further stirred for 30 min. The usual workup and purification afforded a mixture of the dideuterated 1- and 2-alkynylsilanes **16a** (>95% D) and **16b** (>95% D) (43 mg, 61%, **16a**:**16b** = 15:85). A mixture of **16a** and **16b**: ^{1}H NMR δ 0.11 (s, 7.56H), 0.15 (s, 1.35H), 1.50−1.57 (m, 0.3H), 1.67−1.72 (m, 0.3H), 1.78 (tt, J = 7.3, 7.3 Hz, 1.7H), 2.17 (t, J = 6.9 Hz, 1.7H), 2.62 (t, J = 7.6 Hz, 0.3H), 2.72 (t, J = 7.7 Hz, 1.7H), 7.13−7.32 (m, 5H); ^{13}C NMR (major isomer) δ −2.24, 0.00, 18.3, 31.0, 34.7, 77.8, 78.2, 125.6, 128,1, 128.4, 142.1.

Reaction of 2 with Dimethylphenylsilane. To a THF (1.2 mL) solution of **1**, prepared from Cp_2TiCl_2 (224 mg, 0.9 mmol), magnesium turnings (26 mg, 1.1 mmol), molecular sieves 4 A (90 mg), and $P(OEt)_3$ (0.31 mL, 1.8 mmol), was added a THF (0.9 mL) solution of **2a** (100 mg, 0.3 mmol) at 25 °C under argon. After the solution was stirred for 10 min, dimethylphenylsilane (0.54 mL, 3.6 mmol) was added and the mixture was stirred for 3 h. The usual workup and purification afforded 3-(dimethylphenylsilyl)-6-phenyl-1-(trimethylsilyl)-hex-1-yne (**18a**) (53 mg, 48%) and 1-(dimethylphenylsilyl)-2-(3-phenylpropyl)-1-(trimethylsilyl)hex-1,2-diene (**19**) (12 mg, 11%). **18a**: IR (neat) 2957, 2157, 1427, 1249, 1115, 840, 646 cm^{-1}; ^{1}H NMR δ 0.13 (s, 9H), 0.37 (s, 6H), 1.41 (dt, J = 7.5, 7.5 Hz, 2H), 1.59−1.98 (m, 2H), 1.93 (t, J = 7.3 Hz, 1H), 2.46−2.66 (m, 2H), 7.11−7.57 (m, 10H); ^{13}C NMR δ −5.2, −4.5, 0.3, 20.8, 28.5, 31.0, 35.2, 85.5, 109.2, 125.6, 127.6, 128.2, 128.4, 129.3, 134.1, 136.8, 142.5. Anal. Calcd for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.72; H, 9.03. **19**: IR (neat) 2955, 1919, 1248, 1111, 896, 839, 805, 698 cm^{-1}; ^{1}H NMR δ 0.04 (s, 9H), 0.44 (s, 6H), 1.72 (tt, J = 7.8, 7.5 Hz, 2H), 2.04 (dt, J = 6.9, 7.5 Hz, 2H), 2.68 (t, J = 7.8 Hz, 2H), 4.52 (t, J = 6.9 Hz, 1H), 7.21−7.25 (m, 3H), 7.30−7.41 (m, 5H), 7.33−7.57 (m, 2H); ^{13}C NMR δ −1.39, −1.35, 0.04, 27.1, 32.0, 35.5, 76.0, 125.6, 127.6, 128.2, 128.4, 128.9, 133.9, 139.2, 142.6, 211.9. Anal. Calcd for $C_{23}H_{32}Si_2$: C, 75.75; H, 8.84. Found: C, 75.74; H, 8.71.

3-(Dimethylphenylsilyl)-1-(trimethylsilyl)but-1-yne (**18b**) was also obtained by the reactions of both **2c** and **5** with dimethylphenylsilane.

Titanocene(II)-Promoted Olefination of Ketones 23a−i with 2. To a THF (1.8 mL) solution of **1**, prepared from Cp_2TiCl_2 (224 mg, 0.9 mmol), magnesium turnings (26 mg, 1.1 mmol), molecular sieves 4 A (90 mg), and $P(OEt)_3$ (0.31 mL, 1.8 mmol), was added a THF (0.9 mL) solution of **2f** (82 mg, 0.3 mmol) at 25 °C. After 10 min, 1,5-diphenylpentan-3-one (**23b**) (86 mg, 0.36 mmol) in THF (0.9 mL) was added dropwise over 5 min and the mixture was stirred for 1 h. The usual workup and purification gave 1-(*tert*-butyldimethylsilyl)-3-methyl-4-phenethyl-6-phenylhex-3-en-1-yne (**22f**) (83 mg, 71%). **22f**: IR (neat) 2928, 2137, 1604, 1496, 1454, 1249, 697 cm^{-1}; ^{1}H NMR δ 0.14 (s, 6H), 0.96 (s, 9H), 1.79 (s, 3H), 2.40 (dd, J = 6.1, 10.4 Hz, 2H), 2.63−2.81 (m, 6H), 7.16−7.32 (m, 10H); ^{13}C NMR δ −4.4, 16.7, 18.4, 26.2, 34.1, 34.2, 34.7, 37.5, 94.0, 107.4, 114.1, 125.8, 126.0, 128.3, 128.36, 128.41, 141.7, 142.1, 147.9. Anal. Calcd for $C_{27}H_{36}Si$: C, 83.44; H, 9.34. Found: C, 83.74; H, 9.24.

The enynes **22a**−**e**,**g**−**p** and their isomers **24a**−**e** were also obtained by similar reactions of **2** with ketones **23**.

Titanocene(II)-Promoted Olefination of Esters and Lactones 23j−n with 2. To a THF (1.8 mL) solution of **1**, prepared from Cp_2TiCl_2 (224 mg, 0.9 mmol), magnesium turnings (26 mg, 1.1 mmol), molecular sieves 4 A (90 mg), and $P(OEt)_3$ (0.31 mL, 1.8 mmol), was added a THF (0.9 mL) solution of **2d** (113 mg, 0.3 mmol) at 25 °C. After 10 min, γ-butyrolactone (**23k**) (31 mg, 0.36 mmol) in THF (0.9 mL) was added and the mixture was stirred for 3 h. The usual workup and purification by chromatography on Al_2O_3 (eluted with 1% triethylamine in hexane) gave 2-[1-(*tert*-butyldimethylsilyl)-6-phenylhex-1-yn-3-ylidene]oxorane (**22r**) (72 mg, 70%). **22r**: IR (neat) 2929, 2129, 1655, 1459, 1251, 1177, 827, 776, 699 cm^{-1}; ^{1}H NMR δ 0.11 (s, 6H), 0.95 (s, 9H), 1.82 (tt, J = 7.7, 7.7 Hz, 2H), 2.02 (tt, J = 7.2, 7.2 Hz, 2H), 2.18 (t, J = 7.3 Hz, 2H), 2.63 (t, J = 7.8 Hz, 2H), 2.76 (t, J = 7.6 Hz, 2H), 4.18 (t, J = 6.8 Hz, 2H), 7.12−7.30 (m. 5H); ^{13}C NMR δ −4.2, 16.7, 24.5, 26.2, 28.0, 29.6, 30.0, 35.4, 72.1, 91.7, 92.4, 107.1, 125.4, 128.1, 128.5, 142.9, 164.8. Anal. Calcd for $C_{22}H_{32}OSi$: C, 77.59; H, 9.47. Found: C, 77.40; H, 9.76.

The enynes **22q**,**s**−**u** were also obtained by similar reactions of **2** with the esters **23j**,**m**,**n** and lactone **23*l***.

Protodesilylation. To the enyne **22j** (35 mg, 0.1 mmol) was added TBAF (1 M in THF, 1 mL, 1 mmol) at 0 °C. After being stirred for 2 h, the reaction was quenched by addition of H_2O. The organic materials were extracted with ether, successively washed with 1 M HCl and H_2O, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by PTLC (hexane) to give (6-phenylhex-1-yne-3-ylidene)cyclohexane (**26f**) (19 mg, 80%). **26f**: IR (neat) 3305, 3026, 2927, 2854, 2087, 1604, 1496, 1452, 1030, 745, 699 cm^{-1}; ^{1}H NMR δ 1.45−1.66 (m, 6H), 1.83 (tt, J = 7.7,7.7 Hz, 2H), 2.16−2.24 (m, 4H), 2.43−2.54 (m, 2H), 2.62 (t, J = 7.9 Hz, 2H), 3.01 (s, 1H), 7.14−7.30 (m, 5H); ^{13}C NMR δ 26.5, 27.9, 30.0, 30.5, 30.9, 34.0, 35.3, 79.0, 84.5, 112.8, 125.6, 128.2, 128.4, 142.5, 149.7. Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.49; H, 9.34.

The alkenylcyclopropanes **25a**−**c** and enynes **26a**−**e**,**g**,**h** were also obtained by a similar procedure.

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Supporting Information Available: Characterization data for the compounds **4b**,**c**, **2a**−**c**,**e**,**f**, **11a**,**b**,**d**−**k**, **13**, **18b**, **22a**−**e**,**g**−**q**,**s**−**u**, **24a**−**e**, **25a**−**c**, and **26a**−**e**,**g**,**h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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