needles, mp 121–123 °C dec: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.64 (d, 1 H, J = 9.0 Hz), 1.68 (s, 3 H), 2.06 (d, 1 H, J = 9.0 Hz), 2.10 (d, 1 H, J = 9.3 Hz), 2.42 (d, 1 H, J = 9.3 Hz), 2.87 (s, 3 H), 3.64 (d, 1 H, J = 9.1 Hz), 3.89 (d, 1 H, J = 9.1 Hz), 5.10 (s, 1 H), 5.19 (s, 1 H), 7.36–7.45 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 14.9 (q), 25.5 (q), 53.6 (t), 54.2 (d), 54.3 (s), 55.7 (d), 61.3 (s), 63.0 (d), 64.3 (d), 68.4 (t), 126.9 (d), 128.2 (d), 128.7 (d), 135.4 (s), 151.9 (s), 152.0 (s), 159.0 (s), 159.9 (s), 170.9 (s), 171.2 (s). Anal. Calcd for $C_{22}H_{19}N_3O_5$: C, 65.18; H, 4.72; N, 10.36. Found: C, 64.86; H, 5.00; N, 10.41.

***anti,endo,endo*-1-Methyl-11-phenyl-6,14-dioxahexacyclo[9.5.1.1^{3,9}.0^{2,10}.0^{4,8}.0^{12,16}]octadec-2(10)-ene-5,7,13,15-tetrone (8).** To 52.0 mg (0.267 mmol) of 1 in 10 mL of CH_2Cl_2 was added 26.0 mg (0.265 mmol) of MA in 5 mL of CH_2Cl_2 and stirred at ca. 20 °C for 24 h. After the solution was cooled to −20 °C, 26.2 mg (0.267 mmol) of MA in 5 mL of CH_2Cl_2 was added and the solution stirred at ca. 20 °C for 2 h. Crystallization from ethanol yielded 83 mg (79%) bis-adduct 8 as yellow needles, mp 176–177 °C dec: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.52 (s, 3 H), 1.58–2.05 (complex m, consisting of 3 AB-systems, 6 H), 3.43–3.72 (m, 4 H), 7.33–7.45 (m, 5 H, Ph); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.1 (q), 45.7 (d), 46.9 (d), 48.0 (d), 48.5 (d), 54.5 (s), 54.8 (d), 55.8 (d), 59.0 (t), 62.3 (s), 67.2 (t), 127.8 (d), 128.6 (d), 128.8 (d), 136.4 (s), 155.2 (s), 155.8 (s), 170.0 (s), 170.4 (s), 170.6 (s), 171.5 (s). Anal. Calcd for $C_{23}H_{18}O_6$: C, 70.76; H, 4.65. Found: C, 71.02; H, 4.59.

***anti,endo,endo*-1-Methyl-12-phenylhexacyclo[10.6.1.1^{2,9}.0^{2,11}.0^{3,8}.0^{13,18}]eicos-10-ene-4,7,14,17-tetrone (9).** From 200 mg (1.03 mmol) of 1 and 230 mg (2.12 mmol) of BQ in 35 mL of EtOH and stirring at ca. 20 °C for 3 d was obtained, after recrystallization from MeOH/EtOH (5:1), 310 mg (75%) 9 as yellow plates, mp 184–186 °C: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.29 (dd, 1 H, J = 1.3, 8.9 Hz), 1.48 (dd, 1 H, J = 1.1, 8.9 Hz), 1.84 (d, 1 H, J = 11.1 Hz), 1.85 (s, 3 H), 2.08 (d, 1 H, J = 11.1 Hz), 3.31 (m, 2 H), 3.53 (m, 2 H), 4.21 (d, 1 H, J = 11.4 Hz), 5.77 (d, 1 H, J = 2.5 Hz), 6.68 (2 AB-systems, 4 H), 7.19–7.52 (m, 5 H); ^{13}C NMR acetone-d_6, 50 MHz) δ 16.5 (q), 49.5 (d), 50.8 (d), 52.6 (d), 52.9 (s), 54.2 (t), 55.8 (d), 56.6 (d), 57.2 (s), 58.9 (t), 73.7 (s), 125.5 (d), 127.0 (d), 127.6 (d), 128.8 (d), 140.6 (s), 142.6 (d), 142.8 (d), 143.0 (d), 143.5 (d), 158.6 (s), 197.4 (s), 199.2 (s), 199.8 (s), 202.1 (s). Anal. Calcd for $C_{27}H_{22}O_4$: C, 79.01; H, 5.40. Found: C, 79.12; H, 5.37.

1-Methyl-8-phenylhexacyclo[6.5.1.0^{2,7}.0^{4,12}.0^{5,10}.0^{9,13}]tetradec-9(13)-ene-3,6-dione (11). From 200 mg (1.03 mmol) of 1 and 113 mg (1.05 mmol) of BQ in 35 mL of EtOH after stirring at ca. 20 °C for 1 d was obtained after radial chromatography, besides 45.0 mg (21%) of 9, 87.0 mg (28%) of 11 (silica gel, 5:1 CH_2Cl_2/EtOAc, R_f = 0.45) as colorless needles: mp 106–108 °C; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.42 (s, 3 H), 1.48 (dd, 1 H, J = 1.0, 10.2 Hz), 1.78 (d, 1 H, J = 10.2 Hz), 1.96 (ddd, 1 H, J = 1.3, 1.4, 10.2 Hz), 2.12 (d, 1 H, J = 10.2 Hz), 2.70 (dd, 1 H, J = 2.9, 8.1 Hz), 2.77 (m, 2 H), 3.21 (dd, 1 H, J = 2.6, 8.1 Hz), 3.51 (m, 2 H), 7.19–7.40 (m, 5 H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 15.1 (q), 42.5 (t), 51.7 (d), 52.5 (d), 56.0 (t), 56.8 (d), 57.2 (d), 60.2 (s), 62.9 (d), 65.3 (d), 68.4 (s), 127.3 (d), 128.7 (d), 138.8 (s), 148.3 (s), 155.4 (s), 158.1 (s), 210.3 (s), 210.5 (s). Anal. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 5.99. Found: C, 83.68; H, 6.04.

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$(Me_3Si)_3SiH$: An Efficient Hydrosilylating Agent of Alkenes and Alkynes

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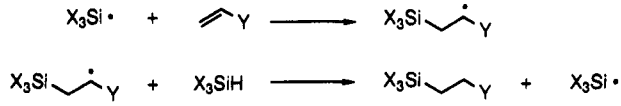
Tris(trimethylsilyl)silane adds across the double bond of a variety of mono-, di-, and trisubstituted olefins under free-radical conditions in good yields. The reaction, which proceeds via a free-radical chain mechanism, is highly regioselective (anti-Markovnikov). Addition to prochiral olefins bearing an ester group is highly stereoselective. The factors that control the stereochemistry have been discussed in terms of preferred conformations of the intermediate carbon-centered radicals and are thought to be of steric origin.

Introduction

Hydrosilylation of carbon–carbon multiple bonds has been studied extensively for the last half century.[2] The reaction is used for the production of organosilicon compounds on both industrial and laboratory scales and is an important method of forming silicon–carbon bonds. In the early years, the reactions were performed under free-radical conditions;[3-5] i.e., ultraviolet light or organic peroxides were widely used. The choice of substrates, however, was limited to silanes such as Cl_3SiH and $MeCl_2SiH$ and to C,C multiple bonds mostly with alkyl substituents. For example, oligomerization was a serious problem when olefins such as methyl acrylate were used.[4] With the discovery that transition metals and their complexes catalyze hydrosilylation, the photo- and peroxide-initiated reactions have been largely superseded.[2,6] Platinum catalysts, especially chloroplatinic acid, have become the most commonly used while other transition-metal catalysts of nickel, palladium, cobalt, rhodium, iridium, iron, ruthenium, and osmium have also been developed.[2] Some of these processes are very efficient irrespective of the nature of the silane and can be used for the simple preparation of a desired product or for asymmetric hydrosilylation. Recently, hydrosilylation catalyzed by metal colloids has also been reported.[7]

Scheme I



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(2) Ojima, I. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds; Wiley: Chichester, 1989; Vol. 2, Chapter 25.

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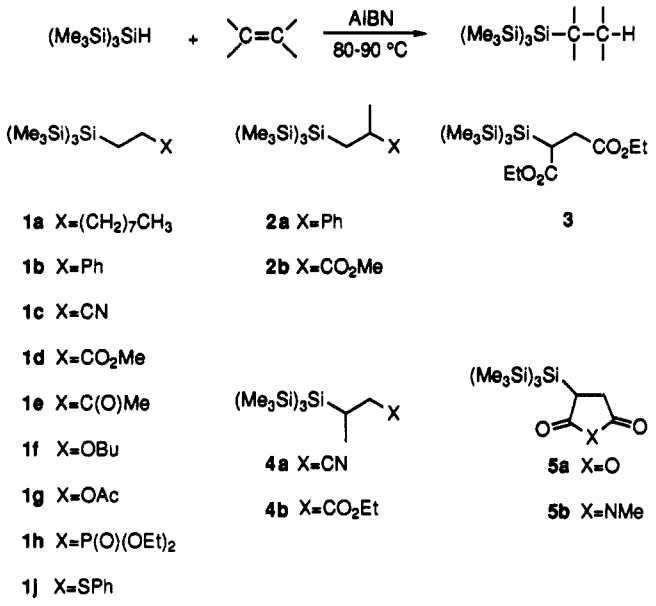
Scheme II



The difficulty of the free-radical hydrosilylation reaction under normal conditions for silanes other than Cl_3SiH, $MeCl_2SiH$, and Ph_2SiH_2[8] is presumably due to the inefficiency of the silanes to donate hydrogen to alkyl radicals. Although trialkylsilyl radicals are amongst the most reactive species known for addition to C,C multiple bonds,[9] free-radical hydrosilylation using $(alkyl)_3SiH$ is generally limited to nonpolymerizable alkenes using *tert*-butyl peroxide as initiator.[10]

We have recently demonstrated that silicon hydrogen bonds can be dramatically weakened by successive substitution of silyl groups at the Si–H function. In fact, the bond dissociation energy of the silicon–hydrogen bond in $(Me_3Si)_3SiH$ is 11 kcal mol^{-1} lower than that in $(alkyl)_3SiH$.[11] Furthermore, we have shown that tris(trimethylsilyl)silane is a good hydrogen donor, the rate constants for the reaction with simple alkyl radicals being $(2–4) \times 10^5$ M^{-1} s^{-1} at ambient temperature[12] and that the $(Me_3Si)_3Si^\bullet$ radical adds to some olefins in a fast and reversible manner at ordinary temperatures.[13] These results, together with the fact that $(Me_3Si)_3SiH$ is an excellent radical-based reducing agent of a variety of functional groups,[14] persuaded us to undertake a detailed study of the free-radical hydrosilylation of alkenes and alkynes by tris(trimethylsilyl)silane.[15]

Results and Discussion

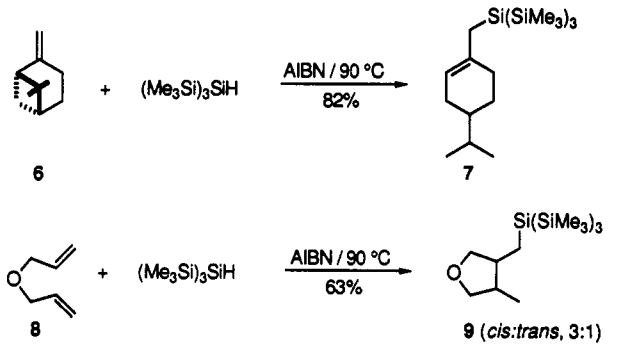
Reactions with Alkenes. Hydrosilylation of a variety of alkenes was carried out by using tris(trimethylsilyl)silane (TTMSS). Reaction of each olefin with TTMSS at 80–90 °C in toluene and in the presence of a radical initiator, i.e., AIBN (azoisobutyronitrile), gave the corresponding hydrosilylation products **1–5**. A slight excess of TTMSS (1.2 equiv) was sufficient in most cases to avoid polymerization of the alkenes.

Table I. Hydrosilylation of Some Mono- and Disubstituted Alkenes by Tris(trimethylsilyl)silane

alkene	product	yield,[a] %
1-decene	**1a**	81
styrene	**1b**	74
acrylonitrile	**1c**	85
methyl acrylate	**1d**	79
methyl vinyl ketone	**1e**	85
butyl vinyl ether	**1f**	92
vinyl acetate	**1g**	80
diethyl vinylphosphonate	**1h**	86
phenyl vinyl sulfide	**1j**	78
α-methylstyrene	**2a**	79
methyl methacrylate	**2b**	77
diethyl fumarate	**3**	85
crotononitrile	**4a**	74
ethyl crotonate	**4b**	71
maleic anhydride	**5a**	89
maleimide	**5b**	83

[a] Yield of isolated compounds.

Scheme III



The data of Table I show that the additions occur with high regioselectivity and yields. The formation of anti-Markovnikov products is in accord with a radical chain mechanism. For monosubstituted and *gem*-disubstituted olefins the tris(trimethylsilyl)silyl radical adds exclusively to the less crowded end of the double bond yielding hydrosilylated compounds **1** and **2**, respectively. The fact that the reaction proceeds with both electron-rich and electron-poor olefins indicates that the addition of $(Me_3Si)_3Si^\bullet$ radicals to the olefins is a facile process which is in agreement with kinetic data available for the addition of $Et_3Si^\bullet$ to alkenes.[9] It is also worth mentioning that the carbon-centered adduct radical is able to abstract a H-atom from the TTMSS independently of the nature of the α-substituent indicating once again the good hydrogen-donating ability of TTMSS.[13] When the double bond is substituted at both ends in either a cis or trans manner, hydrosilylation is still an efficient process, although it requires slightly longer reaction times. The hydrosilylation of crotonitrile and ethyl crotonate gave exclusively **4a** and **4b**, respectively, indicating that the regioselectivity is that expected for alkyl radicals on the basis of steric and polar effects.[16]

In order to gain further insight into the reaction mechanism and to test the compatibility of this method with the formation or the breaking of a C,C bond, the hydrosilylation of β-pinene (**6**) and diallyl ether (**8**) were per-

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(15) For a preliminary communication, see: Kulicke, K. J.; Giese, B. *Synlett.* **1990**, 91.
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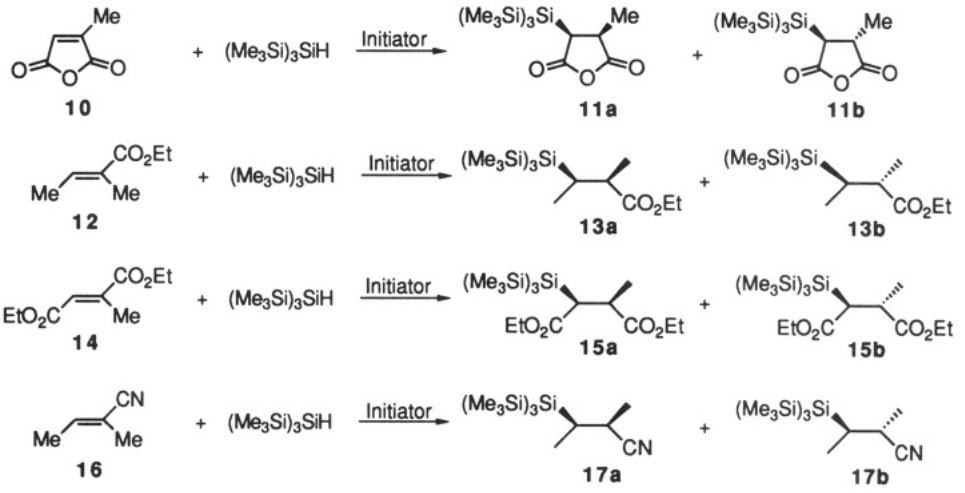
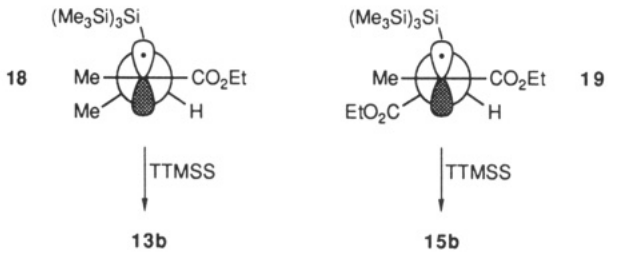
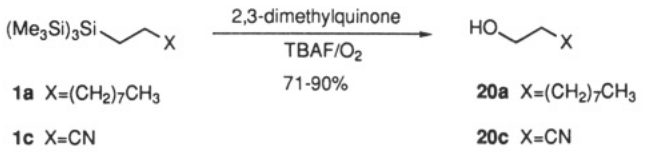
Scheme IV



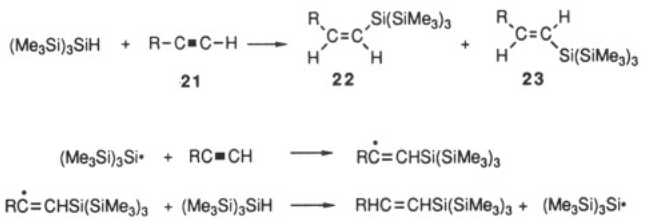
Scheme V



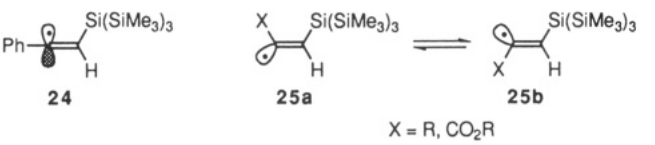
Scheme VI



Scheme VII



Scheme VIII



formed. The addition of TTMSS to β-pinene in toluene solution afforded an 82% yield of **7**. Thus, the addition of a tris(trimethylsilyl)silyl radical to β-pinene gives a carbon-centered radical which rearranges by opening of the four-membered ring[17] prior to H-atom transfer.

On the other hand, diallyl ether is a suitable candidate for free-radical cyclization studies since the alkyl radical, formed after the addition of the silyl radical to one double bond, cyclizes very fast and yields tetrahydrofuran derivatives.[18] A mixture of TTMSS, diallyl ether, and catalytic amounts of AIBN in toluene, heated at 85 °C for 2 h, produced the expected tetrahydrofuran derivative **9** in 63% yield (GC analysis of the crude reaction mixture indicates a cis:trans ratio of 3:1).[19]

The factors controlling the stereoselectivity in radical reactions are of current interest,[20] and therefore we undertook some stereochemical experiments in order to evaluate the potentials of free-radical hydrosilylation in this area. The hydrosilylation of methylmaleic anhydride (**10**) was carried out in the temperature range of −15 to 90 °C using either AIBN or Et_3B/O_2 as radical initiator.[21]

The results are reported in Table II. Thus, the tris(trimethylsilyl)silyl radical, initially generated by small amounts of AIBN or Et_3B/O_2, adds regiospecifically to cyclic alkene **10** from the less crowded end of the double bond and forms a carbon-centered radical as intermediate which abstracts a hydrogen atom either from the anti or syn end of the silyl group. The thermodynamically less stable cis product **11a** was formed preferentially in accordance with previous studies on the addition of alkyl radicals to the same substrate.[22] However, the presence of the large tris(trimethylsilyl)silyl group favors even more the anti attack. The stereoselectivity decreased with increasing reaction temperature, indicating the difference in enthalpy of activation for syn versus anti attack.

In contrast to additions to cyclic systems, the acyclic alkenes **12** and **14** gave adducts **13b** and **15b**, respectively. This is in accord with our observation that the stereoselectivity of ester-substituted radicals with an adjacent, tertiary chiral center is determined by allylic strain effects.[23] Thus, **18** and **19** are the preferred conformations that lead to products **13b** and **15b**, respectively.[24]

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(24) The structures of **15a** and **15b** were proven via comparison with the esters generated by hydrolysis of **11a** and **11b** and subsequent esterification. Compounds **13a** and **13b** were assigned by comparison of their ^{1}H-NMR spectra with those of **15a** and **15b**. The coupling constants between the tertiary protons are as follows: **15a**, J = 4.9 Hz; **15b**, J = 10.8 Hz; **13a**, J = 2.6 Hz; **13b**, J = 6.5 Hz.

Table II. Hydrosilylation of Some Trisubstituted Alkenes by Tris(trimethylsilyl)silane

alkene	condns	product ratio (a:b)	yield,[a] %
methylmaleic anhydride (10)	AIBN/90 °C	**11a,b** (16:1)	89
	Et_3B, O_2/60 °C	**11a,b** (19:1)	82
	Et_3B, O_2/20 °C	**11a,b** (32:1)	72
	Et_3B, O_2/−15 °C	**11a,b** (99:1)	60
ethyl tiglate (12)	AIBN/80 °C	**13a,b** (1:5)	58
	Et_3B, O_2/60 °C	**13a,b** (1:6)	40
	Et_3B, O_2/40 °C	**13a,b** (1:10)	38
	Et_3B, O_2/20 °C	**13a,b** (1:16)	20[b]
diethyl methylfumarate (14)	AIBN/90 °C	**15a,b** (1:12)	70
	Et_3B, O_2/60 °C	**15a,b** (1:15)	65
	Et_3B, O_2/20 °C	**15a,b** (1:25)	62
	Et_3B, O_2/−15 °C	**15a,b** (1:45)	50
tiglonitrile (16)	AIBN/85 °C	**17a,b** (1:1)	57
	Et_3B, O_2/ 60 °C	**17a,b** (1:1)	48
	Et_3B, O_2/40 °C	**17a,b** (1:1)	37

[a] Yield of isolated compounds. [b] This reaction needed longer reaction times which caused partial decomposition of the starting material and products.

Table III. Hydrosilylation of Some Monosubstituted Alkynes by Tris(trimethylsilyl)silane

entry	alkynes 21	condns	(Z)-alkene 22: (E)-alkene 23	yield,[a] %
1	$CH_3(CH_2)_3$—≡—H	AIBN/90 °C	51:49	91
		Et_3B, O_2/60 °C	76:24	87
		Et_3B, O_2/25 °C	95:5	85
2	C_6H_{11}—≡—H	AIBN/80 °C	45:55	87
		Et_3B, O_2/60 °C	77:23	87
		Et_3B, O_2/25 °C	96:4	83
3	$(CH_3)_3C$—≡—H	AIBN/80 °C	<1:>99	89
		Et_3B, O_2/60 °C	<1:>99	79
4	Ph—≡—H	AIBN/90 °C	84:16	88
		Et_3B, O_2/60 °C	97:3	88
		Et_3B, O_2/25 °C	99:1	85
5	EtO_2C—≡—H	AIBN/90 °C	92:8	87
		Et_3B, O_2/60 °C	97:3	89
		Et_3B, O_2/25 °C	99:1	88

[a] Yield of isolated compounds.

In contrast to the ester-substituted alkenes, nitrile **16** reacted completely unselectively (Table II). As we have shown recently,[23] in nitrile-substituted radicals there are no allylic strain effects, and therefore no preferred conformations analogous to **18** and **19** exist.

Before this hydrosilylation method can become of general synthetic utility, it is important to develop methods for the removal of $(Me_3Si)_3Si$ group. Therefore, we carried out a Tamao[25] oxidation on silanes **1a** and **1c**. Reaction with 2,3-dimethylquinone/TBAF/O_2 yielded alcohols **20a** and **20c** in 90% and 71% yield, respectively.

Reactions with Alkynes. Alkynes also react with TTMSS in a radical chain reaction. Monosubstituted alkynes yielded alkenes in high yield and stereoselectivity (Table III).

Normally, *Z*-alkenes **22** were formed. This is because in the phenyl-substituted π-radical **24** and in the pair of σ-radicals **25a** and **25b** the bulky tris(trimethylsilyl)silyl group hinders syn attack. But with *tert*-butylacetylene the *E*-product was formed exclusively. Presumably, radical **25a** (R = *t*-C_4H_9) is so strained that only **25b** plays a role.

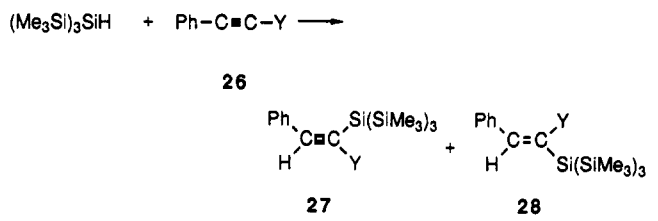
(25) Tamao, K.; Ischida, N.; Tanaka, T.; Kumada, M. *Organometallics* **1983**, *2*, 1694. Tamao, K.; Ischida, N. *J. Organomet. Chem.* **1984**, *269*, C37. Tamao, K.; Hayaslu, T.; Ito, Y. *Tetrahedron Lett.* **1989**, *47*, 6533.

Table IV. Hydrosilylation of Some Disubstituted Alkynes by Tris(trimethylsilyl)silane

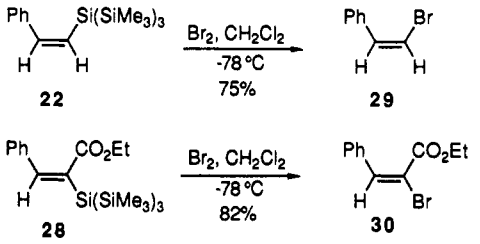
entry	alkynes 26	condns	(Z)-alkene 27: (E)-alkene 28	yield,[a] %
1	Ph—≡—CHO	AIBN/90 °C	50:50	82
		Et_3B, O_2/70 °C	75:25	72
		Et_3B, O_2/20 °C	87:13	55
2	Ph—≡—CN	AIBN/80 °C	65:35	84
		Et_3B, O_2/45 °C	80:20	68
		Et_3B, O_2/20 °C	89:11	62
		Et_3B, O_2/0 °C	92:8	54
3	Ph—≡—$(CH_2)_4CH_3$	AIBN/80 °C	45:55	60
		Et_3B, O_2/60 °C	61:39	23[b]
		Et_3B, O_2/40 °C	67:33	10[b]
4	Ph—≡—CO_2Et	AIBN/90 °C	<1:<99	85
		Et_3B, O_2/60 °C	<1:<99	58
		Et_3B, O_2/40 °C	<1:<99	30

[a] Yield of isolated compounds. [b] These reactions needed longer reaction times which caused partial decomposition of the starting material and products.

Scheme IX



Scheme X



Hydrogen abstraction by **25b** only gives *E*-alkene **23**.

1,2-Disubstituted phenylacetylenes **26** were attacked exclusively β to the phenylated alkyne carbon atom (Table IV). With formyl and nitrile groups at the attacked carbon atom *Z*-isomers **27** were formed predominantly at low temperatures. The alkylated phenylacetylene reacted with low stereoselectivity, and ester-substituted acetylenes gave *E*-isomer **28** exclusively. A possible explanation is that the shielding effect of the substituents Y increases in this order, so that the attack anti to the substituent Y increases.

The structures were determined by X-ray analysis of the ester and nitrile substituted products and by comparison of the NMR spectra.[26]

Although it is not the purpose of this paper to explore the removal of the silyl auxiliary in detail, we carried out the replacement of the silyl moiety by bromine atom. It is well documented[27] that the addition of bromine to β-(trimethylsilyl)styrene leads to formation of bromostyrene with overall retention of configuration. The reaction takes place in two discrete steps; both of them are stereoselec-

(26) The vinylic hydrogen of the *Z*-isomer **27** absorbs at lower field than that of the *E*-isomer **28**.

(27) Brook, M. A.; Neuy, A. *J. Org. Chem.* **1990**, *55*, 3609 and references cited therein.

tive.[28] We found that also silylated alkenes **22** and **28** react with bromine in CH_2Cl_2 at −78 °C and give the bromides **29** and **30** stereoselectively.

Experimental Section

Materials. Tris(trimethylsilyl)silane (TTMSS)[29] and phenylpropiolnitrile[30] were prepared according to literature methods. All other materials were commercially available and were used as received.

General Procedure for Hydrosilylation of Alkenes (Table I). A 100-mL round-bottomed flask equipped with a magnetic stirring bar, dry argon inlet, reflux condenser, and septum was charged with 4 mmol of alkene and 157 mg (0.96 mmol) of AIBN in 40 mL of toluene. The solution was flushed with argon, and 1.19 g (4.8 mmol) of TTMSS was added. The solution was heated at 90 °C for 2–4 h until the alkene was consumed (followed by GC). The reaction mixture was concentrated in vacuo. Distillation gave 71–92% of product. J valves are given in Hz for NMR data.

1-[Tris(trimethylsilyl)silyl]decane (1a): bp 100 °C (10^{-1} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27–1.41 (m, 16 H), 0.89 (t, 3 H, J = 6.9), 0.74–0.79 (m, 2 H), 0.16 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 29.05–34.14 (7 C), 22.51, 13.90, 7.34, 0.92. GC/MS m/z 388 (M^+), 315 (M^+ − 73), 175 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{19}H_{48}Si_4$: C, 58.67; H, 12.44. Found: C, 58.48; H, 12.28.

1-[Tris(trimethylsilyl)silyl]-2-phenylethane (1b): bp 170 °C (2×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07–7.37 (m, 5 H), 2.67–2.73 (m, 1 H), 1.10–1.27 (m, 1 H), 0.22 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.20, 128.60, 128.22, 125.85, 35.33, 10.34, 0.91; GC/MS m/z 352 (M^+), 279 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{17}H_{36}Si_4$: C, 57.84; H, 10.28. Found: C, 57.49; H, 9.98.

3-[Tris(trimethylsilyl)silyl]propionitrile (1c): bp 100 °C (10^{-1} mbar); IR (neat) 2240 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.31–2.37 (m, 2 H), 1.20–1.25 (m, 2 H), 0.19 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 121.65, 15.78, 4.71, 0.72; MS (FD) m/z 301 (M^+), 73 $(TMS)^+$. Anal. Calcd for $C_{12}H_{31}NSi_4$: C, 47.76; H, 10.35; N, 4.64. Found: C, 47.78; H, 10.40; N, 4.64.

Methyl 3-[tris(trimethylsilyl)silyl]propionate (1d): bp 190 °C (14 mbar); IR (neat) 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.65 (s, 3 H), 2.30–2.36 (m, 2 H), 1.06–1.12 (m, 2 H), 0.16 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.48, 51.53, 32.92, 2.61, 0.78. GC/MS m/z 319 (M^+ − 15), 261 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{13}H_{34}O_2Si_4$: C, 46.64; H, 10.23. Found: C, 46.58; H, 10.18.

3-Oxo-1-[tris(trimethylsilyl)silyl]butane (1e): bp 150 °C (0.5 mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.46–2.41 (m, 2 H), 2.14 (s, 3 H), 0.98–1.04 (m, 2 H), 0.16 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.87, 42.62, 37.25, 28.97, 0.81; GC/MS m/z 319 (M^+), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{13}H_{34}OSi_4$: C, 48.98; H, 10.75. Found: C, 48.58; H, 10.56.

2-(Butyloxy)-1-[tris(trimethylsilyl)silyl]ethane (1f): bp 135 °C (8×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.39–3.5 (m, 4 H), 1.18–1.59 (m, 6 H), 0.93 (t, 3 H, J = 7.3), 0.17 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 70.73, 70.18, 31.76, 19.19, 13,72, 9.07, 0.80; GC/MS m/z 277 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{15}H_{40}OSi_4$: C, 51.50; H, 11.81. Found: C, 51.48; H, 11.69.

1-[Tris(trimethylsilyl)silyl]ethyl acetate (1g): bp 120 °C (4×10^{-2} mbar); IR (neat) 1740 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.07–4.13 (m, 2 H), 2.02 (s, 3 H), 1.16–1.21 (m, 2 H), 0.16 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 64.5, 20.9, 8.4, 0.91; GC/MS m/z 319 (M^+ − 15), 261 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{13}H_{34}O_2Si_4$: C, 46.64; H, 10.23. Found: C, 46.58; H, 10.08.

Diethyl 2-[tris(trimethylsilyl)silyl]ethylphosphonate (1h): bp 150 °C (10^{-2} mbar); IR (neat) 1240 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.01–4.11 (m, 4 H), 1.66–1.77 (m, 2 H), 1.30 (t, 6 H, J = 7.1), 0.95–1.04 (m, 2 H), 0.15 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 61.46, 61.37, 25.33, 23.53, 16.28, 16.21, 0.75. MS (EI) m/z 412 (M^+), 397 (M^+ − 15), 339 (M^+ − 73), 73 $(TMS)^+$. Anal. Calcd for $C_{15}H_{41}PO_3Si_4$: C, 43.64; H, 10.01. Found: C, 43.58; H, 9.86.

2-(Phenylthio)-1-[tris(trimethylsilyl)silyl]ethane (1j): bp 175 °C (4×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.33 (m, 5 H), 2.97–3.04 (m, 2 H), 1.16–1.22 (m, 2 H), 0.17 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 129.33, 129.05, 129.01, 126.00, 33.58, 8.21, 0.86; GC/MS m/z 312 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{17}H_{36}SSi_4$: C, 53.05; H, 9.42. Found: C, 52.79; H, 9.18.

1-[Tris(trimethylsilyl)silyl]-2-phenylpropane (2a): bp 180 °C (2×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.07–7.28 (m, 5 H), 1.88 (d, 1 H, J = 14.2), 1.32 (s, 3 H), 1.29–1.30 (m, 2 H), 0.05 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 130.17, 129.13, 127.17, 126.06, 48.44, 24.23, 16.71, 0.91; GC/MS m/z 366 (M^+), 293 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{18}H_{38}Si_4$: C, 58.93; H, 10.44. Found: C, 58.63; H, 10.28.

Methyl 3-[tris(trimethylsilyl)silyl]-2-methylpropionate (2b): bp 160 °C (6×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.68 (s, 3 H), 2.47–2.54 (m, 1 H), 1.35–1.41 (m, 1 H), 1.22 (d, 3 H, J = 7.1), 0.84–0.91 (m, 1 H), 0.18 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.39, 51.51, 38.41, 20.52, 12.33, 0.90; GC/MS m/z 339 (M^+), 334 (M^+ − 15), 290 (M^+ − 59), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{14}H_{36}O_2Si_4$: C, 48.07; H, 10.66. Found: C, 47.98; H, 10.59.

Diethyl 2-[tris(trimethylsilyl)silyl]butanedioate (3): bp 100 °C (6×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.62–4.27 (m, 4 H), 2.94 (dd, 1 H, J = 12.7), 2.67 (dd, 1 H, J = 2.6, 12.7), 2.39 (dd, 1 H, J = 2.6, 12.7), 1.14–2.99 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.12, 172.96, 60.56, 60.27, 35.74, 26.09, 13.92, 13.81, 1.49; GC/MS m/z 349 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{17}H_{40}O_4Si_4$: C, 48.41; H, 9.79. Found: C, 48.38; H, 9.72.

3-[Tris(trimethylsilyl)silyl]butanenitrile (4a): bp 100 °C (8×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.32–2.41 (m, 1 H), 1.95–2.06 (m, 1 H), 1.39–1.45 (m, 1 H), 1.27–1.30 (m, 3 H), 0.20 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 119.14, 24.38, 19.71, 14.25; GC/MS m/z 301 (M^+ − 15), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{13}H_{33}NSi_4$: C, 49.29; H, 10.82. Found: C, 49.18; H, 10.80.

Ethyl 3-[tris(trimethylsilyl)silyl]butanoate (4b): bp 150 °C (8×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.13 (q, 2 H, J = 7.1), 2.53 (dd, 1 H, J = 2.47, 14.8), 2.18 (dd, 1 H, J = 12.5, 14.8), 1.83–1.95 (m, 2 H), 1.27 (t, 3 H, J = 7.1), 1.14 (d, 3 H, J = 7.2), 0.21 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 60.20, 41.52, 19.96, 14.31, 13.56; GC/MS m/z 347 (M^+ − 15), 289 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{15}H_{38}O_2Si_4$: C, 49.79; H, 10.31. Found: C, 49.69; H, 10.28.

2-[Tris(trimethylsilyl)silyl]butanedioic anhydride (5a): mp (pentane) 200 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.23 (dd, 1 H, J = 10.3, 18.2), 2.97 (dd, 1 H, J = 3.0, 10.3), 2.77 (dd, 1 H, J = 3.0, 18.2), 0.24 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.25, 171.92, 35.04, 24.72, 0.81; MS (CI) m/z 364 $(M + NH_4)^+$, 347 $(M + H)^+$, 90 $(TMS + NH_3)^+$. Anal. Calcd for $C_{13}H_{30}O_3Si_4$: C, 45.03; H, 8.73. Found: C, 45.28; H, 8.63.

2-[Tris(trimethylsilyl)silyl]-*N*-methylethanedicarboximide (5b): bp 110 °C (4×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.90–3.01 (m, 1 H), 2.95 (s, 3 H), 2.52–2.63 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.95, 177.62, 35.10, 24.83, 0.95; MS (EI) m/z 359 (M^+), 344 (M^+ − 15), 73 $(TMS)^+$. Anal. Calcd for $C_{14}H_{33}NO_2Si_4$: C, 46.74; H, 9.24. Found: C, 46.45; H, 9.18.

7-[Tris(trimethylsilyl)silyl]-Δ^1-*p*-menthene (7): bp 140 °C (4×10^{-2} mbar); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.29 (d, 1 H, J = 3.2), 1.15–2.03 (m, 8 H), 1.68 (s, 2 H), 0.88 (dd, 6 H, J = 6.7, 4.3), 0.17 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.39, 119.44, 39.81, 32.25, 31.06, 29.62, 26.46, 19.83, 19.53, 17.35, 0.93; GC/MS m/z 311 (M^+ − 73), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{19}H_{44}Si_4$: C, 59.40; H, 11.29. Found: C, 59.35; H, 11.13.

2-[[Tris(trimethylsilyl)silyl]methyl]-3-methyltetrahydrofuran (9): MS (CI) m/z 364 $(M + NH_4^+)^+$, 273 (M^+ − 73), 90 $(TMS + NH_3)^+$. Anal. Calcd for $C_{15}H_{38}OSi_4$: C, 51.95; H, 11.04. Found: C, 51.79; H, 10.98. **Cis isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.91 (m, 2 H), 3.43 (dd, 2 H, J = 5.3, 8.3), 2.60–2.68 (m, 2 H), 1.00 (d, 3 H, J = 6.3), 0.75 (dd, 2 H, J = 6.1, 14.8), 0.16 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 74.77, 74.64, 43.65, 37.49, 15.62, 9.55, 0.93. **Trans isomer:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.86–3.94 (m, 2 H), 3.46 (dd, 2 H, J = 8.3, 14.3), 2.25–2.30 (m,

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2 H), 0.93 (d, 3 H, J = 6.3), 0.63 (dd, 2 H, J = 10.6, 14.8), 0.14 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 75.90, 74.87, 46.66, 41.78, 15.66, 12.55, 0.93.

Hydrosilylation of Methylmaleic Anhydride (10) and Diethyl Methylfumarate (14) (Table II). Method A (Induced by AIBN). To the alkene (4 mmol) and TTMSS (5.2 mmol) in dry toluene (40 mL) under argon was added a toluene solution of AIBN (1 mmol) at 90 °C within 5 h. The solution was stirred for another 1 h, cooled, concentrated in vacuo, and flash chromatographed on silica gel using pentane/ether (9/1). **Method B (Induced by BEt_3/O_2).** A hexane solution of BEt_3 (1.0 M, 0.8 mmol) and dry air (10 mL) were injected into a solution of alkene (4 mmol) and TTMSS (5.2 mmol) in dry toluene (40 mL) at −15, 20, or 60 °C during 6–24 h by a syringe pump. The mixture was poured into water and extracted with ether three times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was flash chromatographed on silica gel.

2-[Tris(trimethylsilyl)silyl]-3-methylbutanedioic anhydride (11): bp 200 °C (4×10^{-2} mbar); GC/MS m/z 317 ($M^+ - 44$), 73 $(TMS)^+$, 69 $(C_4H_5O)^+$, 45 $(CHO_2)^+$. Anal. Calcd for $C_{14}H_{32}O_3Si_4$: C, 46.61; H, 8.94. Found: C, 46.48; H, 8.73. **Cis isomer (11a):** ^1H NMR (300 MHz, $CDCl_3$) δ 3.29 (qd, 1 H, J = 7.3, 9.2), 3.08 (d, 1 H, J = 9.2), 1.42 (d, 3 H, J = 7.3), 0.26 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.20, 173.81, 39.98, 33.22, 17.36, 1.65. **Trans isomer (11b):** ^1H NMR (300 MHz, $CDCl_3$) δ 2.96 (qd, 1 H, J = 2.8, 7.2), 2.50 (d, 1 H, J = 2.8), 1.43 (d, 3 H, J = 7.2), 0.26 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.20, 173.81, 42.39, 33.77, 19.41, 1.16.

Diethyl 2-[tris(trimethylsilyl)silyl]-3-methylbutanedioate (15): bp 200 °C (4×10^{-2} mbar); GC/MS m/z 362 ($M^+ - 73$), 73 $(TMS)^+$. Anal. Calcd for $C_{18}H_{42}O_4Si_4$: C, 49.60; H, 9.94. Found: C, 49.56; H, 9.68. **15a:** ^1H NMR (300 MHz, $CDCl_3$) δ 4.12 (qd, 4 H, J = 2.1, 7.2), 3.03 (d, 1 H, J = 4.9), 2.60 (qd, 1 H, J = 4.9, 7.2), 1.43 (m, 6 H,); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.16, 176.28, 60.50, 60.17, 42.00, 35.05, 18.80, 14.18, 13.98, 1.96. **15b:** ^1H NMR (300 MHz, $CDCl_3$) δ 4.09–4.17 (m, 4 H), 2.93 (qd, 1 H, J = 7.2, 10.8), 2.52 (d, 1 H, J = 10.8), 1.20–1.29 (m, 6 H), 0.24 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.16, 176.28, 61.59, 60.78, 36.35, 26.38, 18.51, 14.28, 14.14, 1.86.

Hydrosilylation of Ethyl Tiglate (12) and Tiglonitrile (16) (Table II). Method A (Induced by AIBN). To the alkene (4 mmol) and TTMSS (20 mmol) in dry toluene (25 mL) under argon was added a toluene solution of AIBN (5.5 mmol) at 80 °C during 12 h. Then the solution was stirred for 1 h. The reaction mixture was cooled, concentrated in vacuo, and flash chromatographed on silica gel using pentane/ether (50/1).

Method B (Induced by BEt_3/O_2). A hexane solution of BEt_3 (1.0 M, 4 mmol) and dry air (30 mL) was injected into a solution of alkene (4 mmol) and TTMSS (20 mmol) in dry toluene (40 mL) at 20, 40, or 60 °C during 24–48 h by a syringe pump. The mixture was poured into water and extracted with ether three times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was flash chromatographed on silica gel.

Ethyl 2-methyl-3-[tris(trimethylsilyl)silyl]butanoate (13): bp 165 °C (2×10^{-2} mbar); GC/MS m/z 361 ($M^+ - 15$), 301 ($M^+ - 73$), 73 $(TMS)^+$. Anal. Calcd for $C_{16}H_{40}O_2Si_4$: C, 51.06; H, 10.63. Found: C, 50.96; H, 10.59. **13a:** ^1H NMR (300 MHz, $CDCl_3$) δ 3.69 (q, 2 H, J = 7.1), 2.71 (qd, 1 H, J = 2.6, 7.1), 1.97 (qd, 1 H, J = 2.6, 7.6), 1.27 (t, 3 H, J = 7.1 Hz), 1.12 (d, 3 H, J = 7.1), 0.99 (d, 3 H, J = 7.6), 0.18 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.60, 51.56, 44.46, 22.48, 18.68, 17.76, 13.92, 1.12. **13b:** ^1H NMR (300 MHz, $CDCl_3$) δ 3.70 (q, 2 H, J = 7.0), 2.60 (qd, 1 H, J = 6.5, 7.0), 1.45 (qd, 1 H, J = 6.5, 7.5), 1.25 (t, 3 H, J = 7.0), 1.23 (d, 3 H, J = 7.0), 1.14 (d, 3 H, J = 7.5), 0.21 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.61, 51.21, 44.48, 22.18, 19.11, 17.78, 12.86, 2.21.

3-Methyl-2-[tris(trimethylsilyl)silyl]butanenitrile (17): bp 120 °C (2×10^{-2} mbar); GC/MS m/z 314 ($M^+ - 15$), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{14}H_{35}NSi_4$: C, 50.98; H, 10.69. Found: C, 50.84; H, 10.98. **17a:** ^1H NMR (300 MHz, $CDCl_3$) δ 2.91 (qd, 1 H, J = 3.0, 7.3), 1.84 (qd, 1 H, J = 3.0, 7.5), 1.30 (d, 3 H, J = 7.3), 1.26 (d, 3 H, J = 7.5), 0.23 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 123.23, 29.89, 21.32, 15.28, 14.96, 1.87. **17b:** ^1H NMR (300 MHz, $CDCl_3$) δ 2.91 (qd, 1 H, J = 0.7, 7.1), 1.79 (d, 1 H, J = 0.7), 1.39 (d, 3 H, J = 7.1), 1.30 (s, 3 H), 0.26 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 122.58, 31.21, 21.84, 19.36, 15.66, 1.92.

Oxidation Procedure for Silanes 1a and 1c. A mixture of silane (1 mmol), 2,3-dimethylquinone (2 mmol), and dry THF (10 mL) was stirred at room temperature. Tetra-*n*-butylammonium fluoride (TBAF) (1 mmol; 1 M THF) was added over 20 min while oxygen was bubbled through the solution. After being stirred for an additional 30 min, the reaction mixture was concentrated and the brown tarry residue was subjected to column chromatography (silica gel, hexane/ethyl acetate (5:1)) to give pure alcohol. Yields of 1-decanol (**20a**) and 3-hydroxypropionitrile (**20c**) were 90% and 71%, respectively.

General Procedure for Hydrosilylation of Alkynes (Table III and IV). Method A (Initiated by AIBN). A 100-mL round-bottomed flask equipped with a magnetic stirring bar, dry argon inlet, reflux condenser, and septum was charged with 4 mmol of alkyne and 157 mg (0.96 mmol) of AIBN in 40 mL of toluene. The solution was flushed with argon, and 1.19 g (4.8 mmol) of TTMSS was added. The solution was heated above 70 °C for 2–4 h until the alkyne was consumed (followed by GC). The reaction mixture was concentrated in vacuo. Distillation gave the desired product.

General Procedure for Hydrosilylation of Alkynes. Method B (Initiated by BEt_3/O_2). A hexane solution of BEt_3 (1.0 M, 0.8 mmol) and dry air (10 mL) was injected into a solution of alkyne (4 mmol) and TTMSS (5.2 mmol) in dry toluene (40 mL) at temperatures between 0 and 60 °C during 6–24 h by a syringe pump. The mixture was poured into water and extracted with ether three times. Combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residual oil was flash chromatographed on silica gel using pentane.

1-[Tris(trimethylsilyl)silyl]hexene (Table III, entry 1): bp 90 °C (10^{-2} mbar); GC/MS m/z 315 ($M^+ - 15$), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{15}H_{38}Si_4$: C, 54.46; H, 11.57. Found: C, 54.45; H, 11.12. **(*E*)-Isomer:** ^1H NMR (300 MHz, $CDCl_3$) δ 6.04 (td, 1 H, J = 5.9, 17.7), 5.45 (m, 1 H, J = 17.6), 0.89–2.16 (m, 9 H), 0.19 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.84, 120.55, 35.23, 31.85, 22.53, 13.95, 0.84. **(*Z*)-Isomer:** ^1H NMR (300 MHz, $CDCl_3$) δ 6.42 (td, 1 H, J = 2.8, 6.7), 5.45 (m, 1 H, J = 6.7), 0.89–2.16 (m, 9 H), 0.18 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.71, 119.81, 37.22, 31.24, 21.89, 13.70, 0.52.

1-[Tris(trimethylsilyl)silyl]-2-cyclohexylethene (Table III, entry 2): bp 150 °C (5×10^{-2} mbar); GC/MS m/z 356 (M^+), 283 ($M^+ - 73$), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{17}H_{40}Si_4$: C, 57.22; H, 11.29. Found: C, 57.58; H, 11.38. **(*Z*)-Isomer:** ^1H NMR (300 MHz, $CDCl_3$) δ 6.18 (dd, 1 H, J = 9.9, 13.0), 5.34 (d, 1 H, J = 13.0), 1.60–2.18 (m, 11 H), 0.2 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.93, 117.11, 43.30, 33.07, 25.96, 25.56, 1.13. **(*E*)-Isomer:** ^1H NMR (300 MHz, $CDCl_3$) δ 5.95 (dd, 1 H, J = 6.5, 18.4), 5.44 (dd, 1 H, J = 1.1, 18.4), 1.10–1.32 (m, 11 H), 0.16 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.34, 117.00, 45.06, 32.80, 26.26, 25.56, 0.77.

(*E*)-3,3-Dimethyl-1-[tris(trimethylsilyl)silyl]butene (Table III, entry 3): bp 130 °C (6×10^{-2} mbar); ^1H NMR (300 MHz, $CDCl_3$) δ 6.04 (d, 1 H, J = 18.7), 5.40 (d, 1 H, J = 18.7), 0.99 (s, 9 H), 0.17 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.04, 113.13, 35.81, 29.21, 0.81; GC/MS m/z 330 (M^+), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{15}H_{38}Si_4$: C, 54.56; H, 11.57. Found: C, 54.58; H, 11.38.

1-[Tris(trimethylsilyl)silyl]styrene (Table III, entry 4): bp 170 °C (2×10^{-2} mbar); GC/MS m/z 350 (M^+), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{17}H_{34}Si_4$: C, 58.20; H, 9.76. Found: C, 58.18; H, 9.45. **(*Z*)-Isomer:** ^1H NMR (300 MHz, $CDCl_3$) δ 7.4 (d, 1 H, J = 14.5), 7.20–7.37 (m, 5 H), 5.90 (d, 1 H, J = 14.5), 0.14 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.76, 139.24, 128.68, 127.63, 126.14, 122.83, 0.65. **(*E*)-Isomer:** bp 170 °C (2×10^{-2} mbar); ^1H NMR (300 MHz, $CDCl_3$) δ 7.20–7.37 (m, 5 H), 6.81 (d, 1 H, J = 18.7), 6.48 (d, 1 H, J = 18.7), 0.15 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.79, 140.45, 128.47, 127.99, 127.39, 124.51, 0.97.

Ethyl 3-[tris(trimethylsilyl)silyl]propenoate (Table III, entry 5): bp 100 °C (10^{-2} mbar); GC/MS m/z 347 (M^+), 274 ($M^+ - 73$), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{14}H_{34}Si_4O_2$: C, 48.49; H, 9.88. Found: C, 48.38; H, 9.89. **(*Z*)-Isomer:** ^1H NMR (300 MHz, $CDCl_3$) δ 6.75 (d, 1 H, J = 13.7), 6.58 (d, 1 H, J = 13.7), 4.16 (q, 2 H, J = 7.14), 1.27 (t, 3 H, J = 7.14), 0.18 (s,

27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.82, 148.63, 134.86, 59.74, 14.18, 1.03. **(*E*)-Isomer**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, 1 H, J = 18.4), 6.28 (d, 1 H, J = 18.4), 4.16 (q, 2 H, J = 7.14), 1.27 (t, 3 H, J = 7.14), 0.18 (s, 27 H).

3-Phenyl-2-[tris(trimethylsilyl)silyl]propenal (Table IV, entry 1): bp 170 °C (5×10^{-2} mbar); GC/MS m/z 378 (M^+), 364 ($M^+ - 15$), 305 ($M^+ - 73$), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{18}H_{34}Si_4O$: C, 57.07; H, 9.04. Found: C, 57.18; H, 9.12. **(*Z*)-Isomer**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.71 (s, 1 H), 8.08 (s, 1 H), 7.24–7.27 (m, 5 H), 0.13 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.47 155.01, 142.8, 136.01, 129.71, 129.09, 128.73, 1.48. **(*E*)-Isomer**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.97 (s, 1 H), 7.93 (s, 1 H), 7.34–7.42 (m, 5 H), 0.25 (s, 27 H).

3-Phenyl-2-[tris(trimethylsilyl)silyl]propenenitrile (Table IV, entry 2): bp 150 °C (4×10^{-2} mbar); GC/MS m/z 375 (M^+), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{18}H_{33}Si_4N$: C, 57.52; H, 8.85; N, 3.72. Found: C, 57.28; H, 9.02; N, 3.63. **(*Z*)-Isomer**: mp 92 °C (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1 H), 7.38 (s, 5 H), 0.21 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.79, 137.14, 129.72, 128.86, 128.80, 123.92 ($J_{(CN-H)}$ = 11.8 Hz), 110.39, 1.78. **(*E*)-Isomer**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25–7.81 (m, 6 H), 0.21 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.64, 135.94, 130.17, 128.79, 128.67, 120.69, 106.28, 0.95; $^3J_{(CN-H)}$ = 17.3 Hz.

1-Phenyl-2-[tris(trimethylsilyl)silyl]-1-heptene (Table IV, entry 3): bp 150 °C (6×10^{-2} mbar); GC/MS m/z 347 ($M^+ - 15$), 289 ($M^+ - 73$), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{22}H_{44}Si_4$: C, 62.77; H, 10.53. Found: C, 62.81; H, 10.38. ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.99, 140.10, 132.23, 127.44, 124.98, 123.78, 34.79, 33.53, 32.64, 22.74, 14.22, 0.54. **(*Z*)-Isomer**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08–7.63 (m, 6 H), 2.63–2.69 (m, 2 H), 1.40–1.57 (m, 6 H), 0.95–0.99 (m, 3 H), 0.16 (s, 27 H). **(*E*)-Isomer**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21–7.37 (m, 5 H), 6.79 (s, 1 H), 2.33–2.38 (m, 2 H), 1.27–1.48 (m, 6 H), 0.89 (t, 3 H, J = 6.9), 0.28 (s, 27 H).

Ethyl (*E*)-2-[tris(trimethylsilyl)silyl]-3-phenylpropenoate (Table IV, entry 4): bp 160 °C (0.8 mbar); mp 47 °C (pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.29 (m, 5 H), 6.86 (s, 1 H), 4.12 (q, 2 H, J = 7.17), 1.16 (t, 3 H, J = 7.18), 0.27 (s, 27 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.54 ($J_{(CO_2Et-H)}$ = 15.5 Hz), 142.25, 137.38, 133.75, 128.27, 127.85, 127.71, 60.51, 13.86, 1.06; MS (EI) m/z 407 ($M^+ - 15$), 349 ($M^+ - 59$), 174 $(TMS_2Si)^+$, 73 $(TMS)^+$. Anal. Calcd for $C_{20}H_{38}Si_4O_2$: C, 56.81; H, 9.05. Found: C, 56.52; H, 9.12.

Bromination Procedure for 1-[Tris(trimethylsilyl)silyl]styrene and Ethyl (*E*)-2-[Tris(trimethylsilyl)silyl]-3-phenylpropenoate. To each vinyl compound (55 mL, 0.05 M in CH_2Cl_2) at −78 °C (acetone, CO_2) was added bromine (1.0 equiv of 0.14 M in CH_2Cl_2) over 1 h. The reaction mixture was stirred for 30 min at −78 °C before being allowed to warm to room temperature. After removal of the solvent under reduced pressure, the product was flash chromatographed (pentane/ether = 9/1).

(*Z*)-Bromostyrene: GC MS m/z 183 $(M)^+$, 103 $(M^+ - Br)$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24–7.34 (m, 5 H), 7.10 (d, 1 H, J = 8.1), 6.46 (d, 1 H, J = 8.1).

Ethyl (*E*)-2-bromo-3-phenylpropenoate: GC MS m/z 256 $(M)^+$, 183 $(M^+ - Br)$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (s, 1 H), 7.26–7.35 (m, 5 H), 4.20 (q, 2 H, J = 7.1), 1.81 (t, 3 H, J = 7.1).

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Registry No. **1a**, 141527-42-6; **1b**, 141527-43-7; **1c**, 131379-56-1; **1d**, 131195-57-8; **1e**, 132162-26-6; **1f**, 141527-44-8; **1g**, 128648-08-8; **1h**, 132182-32-2; **1j**, 141527-45-9; **2a**, 141527-46-0; **2b**, 141527-47-1; **3**, 141527-48-2; **4a**, 141527-49-3; **4b**, 141527-50-6; **5a**, 141527-51-7; **5b**, 132162-25-5; **6**, 127-91-3; **7**, 141527-52-8; **8**, 557-40-4; *cis*-**9**, 141527-53-9; *trans*-**9**, 141527-54-0; **10**, 616-02-4; **11a**, 141527-55-1; **11b**, 141527-56-2; **12**, 5837-78-5; **13a**, 141527-57-3; **13b**, 141527-58-4; **14**, 2418-31-7; **15a**, 141527-59-5; **15b**, 141527-60-8; **16**, 30574-97-1; **17a**, 141527-61-9; **17b**, 141527-62-0; **20a**, 112-30-1; **20c**, 109-78-4; **21** (R = Bu), 693-02-7; **21** (R = cyclohexyl), 931-48-6; **21** (R = *t*-Bu), 917-92-0; **21** (R = Ph), 536-74-3; **21** (R = CO_2Et), 623-47-2; **22** (R = Bu), 141527-63-1; **22** (R = cyclohexyl), 141527-64-2; **22** (R = *t*-Bu), 141527-66-4; **22** (R = Ph), 139526-41-3; **22** (R = CO_2Et), 141527-67-5; **23** (R = Bu), 110577-08-7; **23** (R = cyclohexyl), 141527-65-3; **23** (R = *t*-Bu), 110577-09-8; **23** (R = Ph), 110577-10-1; **23** (R = CO_2Et), 141527-68-6; **26** (Y = CHO), 2579-22-8; **26** (Y = CN), 935-02-4; **26** (Y = pentyl), 14374-45-9; **26** (Y = CO_2Et), 2216-94-6; **27** (Y = CHO), 141527-69-7; **27** (Y = CN), 141527-71-1; **27** (Y = pentyl), 141527-73-3; **27** (Y = CO_2Et), 141527-75-5; **28** (Y = CHO), 141527-70-0; **28** (Y = CN), 141527-72-2; **28** (Y = pentyl), 141527-74-4; **28** (Y = CO_2Et), 141527-76-6; **29**, 588-73-8; **30**, 59106-34-2; tris(trimethylsilyl)silane, 1873-77-4; 1-decene, 872-05-9; styrene, 100-42-5; acrylonitrile, 107-13-1; methyl acrylate, 96-33-3; methyl vinyl ketone, 78-94-4; butyl vinyl ether, 111-34-2; vinyl acetate, 108-05-4; diethyl vinylphosphonate, 682-30-4; phenyl vinyl sulfide, 1822-73-7; α-methylstyrene, 98-83-9; methyl methacrylate, 80-62-6; diethyl fumarate, 623-91-6; crotononitrile, 4786-20-3; ethyl crotonate, 10544-63-5; maleic anhydride, 108-31-6; maleimide, 541-59-3.

Supplementary Material Available: ORTEP plots and full details of crystal data of compounds **27** (Y = CN) and **28** (Y = CO_2Et) (12 pages). This material is contained in many 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.

Photoreactions of Isoindoline-1-thiones with Alkenes: Unusual Formation of Tricyclic Isoindolines

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Photochemical cycloaddition reactions of cyclic thioamides and alkenes have been examined. Irradiation of 2-arylisoindoline-1-thiones **1** in the presence of alkenes **2** gave the unexpected tricyclic isoindolines **3–18**. The formation of tricyclic isoindolines can best be explained in terms of the intermediacy of aminospirothietane **27**, formed by [2 + 2] photocycloaddition of the C=S double bond of **1** to the C=C double bond of **2**. Ring cleavage of the resultant amino thietane, assisted by the participation of the nitrogen lone-pair electrons, produced zwitterions **28** and **29** or 1-mercaptoethylisoindole (**30**). Subsequent nucleophilic attack of the thiol anion on the iminium carbon of **29** or attack of the thiol group on C-3 of **30** gave the final products. Irradiation of isobenzofuran-1-thione (**22**) and isobenzothiophene-1-thione (**23**) in the presence of tetramethylethylene (**2a**) gave the corresponding spirothietanes **24** and **25**.

Interest in the photochemistry of thiocarbonyl compounds has been growing in recent years. The majority of the reported reactions involve thioketones, which undergo cycloaddition with alkenes, allenes, ketenes, imines, or alkynes, intramolecular or intermolecular hydrogen abstraction, and photooxidation.[1] Relatively few reports

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