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The synthesis and reactivity of polysilylacetylenes: Diels–Alder reactions to give bis(silyl)benzenes

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Six bis(silyl)acetylenes ($XMe_2Si—C{\equiv}C—SiMe_2X$) with the following varied silicon substituents X were prepared: 1 (Me, Me); 2 (H, H); 3 (Cl, H); 4 (Cl, Cl); 5 (MeO, H); 6 (MeO, MeO). While 1 and 2 may be prepared by the reaction of dilithio- or bis(bromomagnesium)-acetylide with the appropriate chlorosilane, similar reactions designed to give 3–6 yielded oligomers, $XMe_2Si—(—C{\equiv}C—SiMe_2)_n—X$, 7, X = Cl, MeO, as the major products, indicating that the acetylenic functionality on silicon activates the chlorosilane towards nucleophilic substitution. Compounds 3 and 4 were prepared by free radical chlorination of 2. Methanolysis of 3 and 4 gave quantitative yields of 5 and 6 respectively.

Compounds 1–6 undergo a Diels–Alder reaction with α-pyrone to produce, after loss of carbon dioxide, bis(silyl)-substituted benzene derivatives. The order of reactivity has been determined to be: $4 = 6 > 3 = 5 > 1 > 2$, indicating that chloro or alkoxy substituents favor the cycloaddition with 2-pyrone. The adducts formed by compounds 3–6 undergo an unusually facile hydrolysis or elimination to give 1,1,3,3-tetramethyl-1,3-disila-2-oxaindane.

Keywords: Silylalkynes, Diels–Alder, α-pyrone, reactivity, synthesis, bis(silyl)benzenes

INTRODUCTION

Several years ago Seyferth and White reported that the reactions of a series of bis[Group 14 (Group 4)]-substituted acetylenes with α-pyrone give synthetically useful yields of bis(Group 14)benzenes.[1,2] The order of reactivity was found to correlate with the steric requirements of the Group 14 (Group 4) substituent.[2]

More recently Sakurai and coworkers found significant electronic effects in the reactions of bis(silyl)acetylenes with α-pyrone.[3] Bis(silyl)-benzenes with functionality on silicon have value as monomers or co-monomers for polymers possessing useful physical properties.[4] Because of our interest in the electronic effects of silicon substituents on the reactions of unsaturated organosilanes,[5] and the potential utility of the products, we have investigated the reactions of α-pyrone with bis(silyl)acetylenes bearing silicon functionality.

RESULTS AND DISCUSSION

Acetylene syntheses

Bis(trimethylsilyl)acetylene 1, was obtained commercially. Bis(dimethylsilyl)acetylene, 2,[1] was synthesized by the reaction of dilithioacetylide[6] or bis(bromomagnesium)acetylide[7] with dimethylchlorosilane in 64% or 65% yields, respectively. When we attempted to prepare bis(chlorodimethylsily)acetylene, 4, using similar reaction conditions the oligomeric polysilylpolyynes, 7, were the major products (Eqn [1]). Even when the acetylide was added to a four-fold excess of dimethyldichlorosilane, 4 was obtained in only 20% yield, accounting for about 50% of the isolated products. Higher oligomers which could not be conveniently analyzed by GC are produced in these reactions. These oligomers possess some intriguing physical and chemical properties which will be reported elsewhere.

Similar results were obtained in the attempted syntheses of 5 and 6 by the reaction of the

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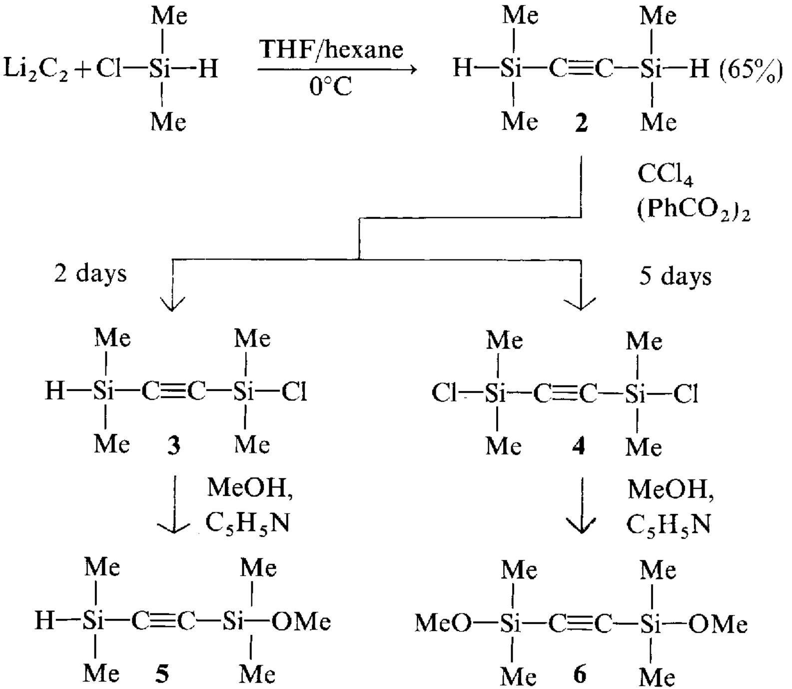
$$\text{Excess } Me_2SiCl_2 + Li_2C_2 \text{ or } (BrMg)_2C_2 \xrightarrow{THF} ClMe_2Si(\text{—}C{\equiv}C\text{—}SiMe_2\text{—})_nCl \qquad [1]$$

$$\mathbf{7},\ n=1\ (50\%),\ n=2\ (34\%),\ n=3\ (10\%),\ n=4\ (5\%)$$

acetylenic Grignard with chloromethoxydimethylsilane. Given our reaction conditions and the product distribution obtained, it appears that the alkynyl substituent activates the chlorosilane in **4** or **7** by more than an order of magnitude over dichlorodimethylsilane towards reaction with the lithium or Grignard reagent.* This effect is consistent with the electron-withdrawing effect of the alkyne (*sp*-hybridized carbon) activating the silicon towards nucleophilic substitution. The activation is also reflected in the fact that **4**–**7** show a higher susceptibility towards hydrolysis than typical trialkyl chloro- or alkoxy-silanes. Their reactivity is similar to or greater than that of polychlorosilanes. Extreme caution to exclude any trace of moisture had to be exercised when collecting these compounds from the preparative GC. This necessitated rinsing the collection tubes with hexamethyldisilazane and heating for an hour at >130°C prior to use. The collection vessel was purged with an inert gas throughout the collection process. Failure to use these precautions resulted in facile hydrolysis to give polymeric alkynylsiloxanes.

Acetylenes **3**–**6** were ultimately synthesized in reasonable yields from bis(dimethylsilyl)acetylene using the methods illustrated in Scheme 1.

Free-radical chlorination of **2** in refluxing carbon tetrachloride provided either chlorodimethylsilyl(dimethylsilyl)acetylene, **3**, or bis(chlorodimethylsilyl)acetylene, **4**, depending on reaction time. Shorter reactions times, e.g. two days, gave greater than 80% yields of mixtures of **3** and **4** with the monochlorinated isomer, **3** predominating. Refluxing for five days gave an 80% yield of a 31:69 mixture of **3** and **4**. The chlorinated silylacetylenes were essentially quantitatively converted to the corresponding methoxy derivatives, **5** and **6**, by methanolysis using methanol/pyridine at reflux for 1 h. The bis(chlorodimethylsilyl)acetylene, **4**, has been reported in a patent but no synthesis or characterization was given.[8] To our knowledge, **3**, **5** and **6** have not been reported previously.



Scheme 1

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*When added to the electrophile only 20% of the acetylenic organometallic reacts with dichlorodimethylsilane or chloromethoxydimethysilane despite the fact that these compounds are present in four-fold excess.

Diels–Alder reactions of bis(trimethylsilyl)acetylene

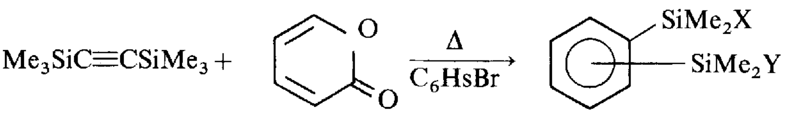
Consistent with Seyferth's results,[2] the reaction of bis(trimethysilyl)acetylene, **1**, with α-pyrone in refluxing bromobenzene (135°C) for six days gave a 55% yield of a mixture of 1,2-; 1,3-, and 1,4-bis-(trimethylsilyl)benzene (*o*, *m* and *p*-**8**, X = Y = Me) with a distribution of 30:65:5, respectively (eqn [2]). In addition, a small amount of phenyltrimethylsilane (generally < 5%) is obtained in the reaction.

When decalin is used as the solvent for the reaction both the rate of the reaction and the product distribution are affected. After 2 and 3 h at 165°C only *o*-**8** was formed in 2 and 3% yields, respectively. After four days at 165°C the yield of disubstituted benzenes was 89% with a distribution of 76% *o*-**8** and 24% *m*-**8**. The isomerization of the *ortho* adduct has been shown to be catalyzed by acid.[9] Evidently even small traces of acid remaining on the glassware are sufficient to catalyze the isomerization over a period of time.

We have tested the Diels–Alder reaction of **1** with a variety of other dienes. The rather disappointing results are given in Table 1. With the exception of a trace amount of a material which had a GCMS spectrum consistent with a possible adduct to 1,3-cyclohexadiene, no Diels–Alder adducts of **1** with any diene other than α-pyrone were observed. As can be seen in Table 1, attempted Lewis acid catalysis of the desired cycloaddition was not successful. In view of the relative reactivities of various silyl-substituted acetylenes with α-pyrone (*vide infra*), which indicate **1** to be a relatively unreactive dienophile, these results appear to be reasonable.

Diels–Alder reactivity of the silylacetylenes with α-pyrone

The relative reactivity of the silylacetylenes, **1–6**, with α-pyrone were determined under standardized reaction conditions consisting of equimolar amounts of α-pyrone in refluxing decalin (175–180°C). Samples of the reaction mixtures were analyzed at various times by GC using internal standard calibration. With all of the acetylenes bearing at least one functional group on silicon two *o*-disilyl-substituted products were obtained, the expected *o*-disilylbenzene, **8**, and the cyclic siloxane, 1,1,3,3-tetramethyl-1,3-disila-2-oxaindane, **9** (Eqn [3]).



1

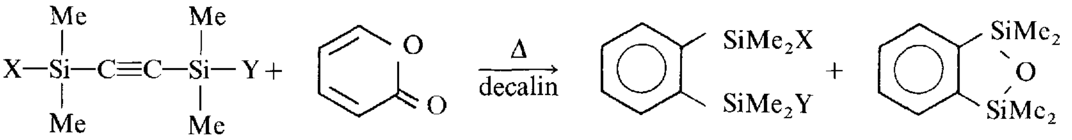
8, X = Y = Me

[2]

Table 1 Attempted reactions of **1** with dienes[a]

Diene	Solvent and temperature (°C)	Time (days)	Major product
Cyclopentadiene	None, 48	4	Dicyclopentadiene
Cyclopentadiene	Decalin, 165	4	Dicyclopentadiene
Cyclopentadiene/BF_3	Decalin, 165	2	Dicyclopentadiene
Dicyclopentadiene	Decalin, 165	4	None
2,3-Dimethyl-1,3-butadiene	Decalin, 165	4	Polymer
Thiophene	None, 70	4	None
Thiophene/BF_3	None, 70	4	None
Thiophene/BF_3	Decalin, 165	4	None
Thiophene/$AlCl_3$	None, 70	4	None
Thiophene/$AlCl_3$	Decalin, 165	4	None

[a] Reactions were conducted in refluxing solvent. For the attempted catalyzed reactions 10 mol% of the Lewis acid catalyst was used.



8 **9** [3]

Compound **9** has been described in a Dow-Corning patent.[10] Its formation in the reaction of *o*-dichlorobenzene with chlorodimethylmethoxysilane and sodium in refluxing toluene has been reported.[11] We have repeated this reaction and verified that **9** is produced (Eqn [4]).

The *o*-cyclic siloxane, **9**, is rapidly formed on exposure of **8**, X = Y = Cl, or **8**, X = Cl, Y = H, to moist air. As an example, when a sealed NMR tube containing *o*-bis(chlorodimethylsilyl)benzene was opened and immediately injected into the GC MS the cyclic siloxane **9** was the only compound detected. The other functional *o*-disilylbenzenes, **8**, X = Y = OMe, and **8**, X = OMe, Y = H, also form **9** at an unexpectedly rapid rate. These latter compounds, in addition to giving **9** as the major product in the Diels–Alder reaction, also form **9** during distillation or in preparative GC collections, presumably by the unusually facile elimination of dimethyl ether or hydrolysis to hydrolysis to give methanol.

The results of the α-pyrone experiments are given in Table 2. Because of problems with hydrolysis with **5** and its adducts, yields for its reactions could not be determined. It appeared to have a reactivity comparable with that of **3**. Clearly the chloro or methoxy substituents on silicon favor the Diels–Alder reaction between α-pyrone and the bis(silyl)acetylenes with the dhichloro, **4**, and dimethoxy, **6**, compounds having the highest reactivity. These alkynes react to give disilyl-substituted benzenes more than six times faster than the least reactive bis(dimethylsilyl)acetylene, **2**.

One might be tempted to attribute this order of reactivity to electronegativity effects. However, if this were the determining factor, it would seem that the order of reactivity for the trimethyl compound, **1**, and the dimethyl compound, **2**, should be reversed inasmuch as methyl is electron-releasing relative to hydrogen. The order of reactivity is reminiscent of that observed for Diels–Alder reactions with inverse electron demand in which electron-rich dienophiles are more reactive than electron-poor dienophiles.[12] The ultraviolet spectra of some of the acetylenes (Table 3) do not show any significant variations in the energies of transitions, although the methoxy substituents appear to decrease the intensity of the absorptions. However, if one examines the ^{13}C chemical shifts for **1**–**6** (Table 4), it can be seen that the acetylenic carbons are *more shielded* by 3–4 ppm for the more reactive

Table 2 Relative reactivity of the silylacetylenes with α-pyrone[a]

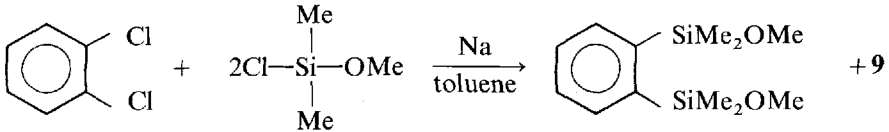
$\mathrm{X{-}\overset{Me}{\underset{Me}{Si}}{-}C{\equiv}C{-}\overset{Me}{\underset{Me}{Si}}{-}Y}$			Yield of disilylbenzenes (%)			Product distribution (%)	
			Reaction time				
Compd	X	Y	1 h	3 h	8 h	**8**	**9**
1	Me	Me	4.9	10.9	28.1	100	—
2	H	H	2.8	5.6	13.0	100	—
3	Cl	H	13.8	27.3	65.7	58	42
4	Cl	Cl	16.3	31.2	84.1	45	55
6[b]	MeO	MeO	17.0	33.1	82.5	50	50

[a]Yields for reaction with equimolar amounts of α-pyrone in refluxing decalin (175–180°C). [b]Compound **6** gave a 91.6% yield of disilyl-substituted benzenes in 12 h with a distribution of 34% **8** and 66% **9**.

Table 3 Electronic spectra of some (bis(silyl)acetylenes[a]

Compd	X	Y	λ_{max} (nm) (log ε)
1	Me	Me	199 (3.059), 206 (3.037), 214 (2.839)
2	H	H	201 (3.004), 208 (3.074), 217 (2.826)
5	MeO	H	200 (2.919), 207 (2.903), 215 (2.681)
6	MeO	MeO	199 (2.613), 206 (2.623), 214 (2.415)

[a]Cyclohexane solvent.



8, with X = Y = OMe [4]

acetylenes relative to the rather sluggish methyl- or hydrogen-substituted acetylenes. This could reflect increased π-electron density for **3**–**6**. The order of reactivity in the Diels–Alder reactions is thus consistent with silicon acting as a π-acid. Interaction of the chlorine or methoxy lone-pair electrons with silicon diminishes its acidity towards the π-electrons of the acetylene, enhancing their reactivity in the Diels–Alder reactions with α-pyrone.

EXPERIMENTAL

All reactions were carried out under an atmosphere of dry argon or nitrogen in glassware which was either oven-dried and assembled hot, or flame-dried. Solvents were dried by standard methods. Methanol was predried with 4a molecular sieves, refluxed over and distilled from calcium hydride immediately prior to use. Reagents and solvents were transferred using standard syringe or cannula techniques. GC analyses of reaction mixtures were carried out using a Perkin–Elmer Sigma-3 gas chromatograph equipped with a 25 m SE-54 capillary column, flame ionization detection, and a Hewlett–Packard 3390A reporting integrator. Yields were determined using an internal standard method based on response factors determined for each of the compounds.

Samples for characterization were ultimately purified by preparative GC using a Varian series 1800 thermal conductivity gas chromatograph with a 15% OV-17 on 45/60 mesh Supelcoport stationary phase in a 10 ft × $\frac{3}{8}$ in (3.05 m × 1 cm) glass column. NMR spectra were obtained using a JEOL FX-90Q spectrometer on purified samples in capillary tubes inserted in ordinary sample tubes containing D_2O as the lock solvent. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were obtained using a Hewlett–Packard 5970A series GC mass sensitive detector and data system. Ultraviolet spectra were obtained in cyclohexane using a Cary-14 spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN, USA.

Bis(dimethylsilyl)acetylene, 2[1]

(A) Dilithioacetylide method

To a solution of 100 mmol of dilithioacetylide[6] in THF cooled to 0°C was added 220 mmol of freshly distilled chlorodimethylsilane (Petrarch) dropwise. After the addition was complete, the ice bath was removed and the mixture was stirred for an additional hour. After filtration of the precipitated salts, GC analysis of the mixture indicated a 64% yield based on acetylide of bis(dimethylsilyl)acetylene.

(B) Grignard method[7]

Acetylene gas was bubbled through a suspension of ethylmagnesium bromide in THF prepared by the reaction of 23.1 g of ethyl bromide (212 mmol) with 6.15 g (253 mmol) of shiny magnesium

Table 4 Carbon and proton NMR data for the acetylenes[a]

			^{13}C[b]			^{1}H[c]		
Compd	X	Y	C≡C	SiMe	OMe	SiH	SiMe	OMe
1	Me	Me	113.65	0.01				
2	H	H	111.50	−3.64		3.76[d]	−1.54	
3	Cl	H	109.96	−3.71		4.86[e]	−0.08(d)	
			112.76	3.51			0.20	
4	Cl	Cl	110.43	3.38			0.40	
5	MeO	H	109.90	−3.80	49.80	3.62[f]	−0.25	2.93
			112.04	−1.11			−0.25(d)	
6	MeO	MeO	110.35	−1.17	49.81		−0.11	3.14

[a] δ in ppm downfield from tetramethylsilane. [b] The multiplicities of the off-resonance proton decoupled spectra are consistent with these assignments. [c] Except for those indicated all resonances are singlets. [d] Septet, $J = 4.0$ Hz. [e] Septet, $J = 3.5$ Hz. [f] Septet, $J = 3.6$ Hz.

turnings. The reaction was exothermic and the acetylene flow was continued until the mixture had cooled to room temperature (*ca* 1 h). After stirring for an additional 2 h, 20.9 g (221 mmol) of chlorodimethylsilane was added dropwise to the mixture which was then stirred for 1 h. After vacuum transfer of the volatiles from the precipitated salts, GC analysis of the mixture showed a 65% yield of **2** based on ethyl bromide. Distillation of the mixture using a spinning band column gave 10.5 g (55% isolated yield) of **2**, a colorless liquid, b.p. 120–122°C; lit. 120–122°C.[1]

MS: *m/z* (realtive intensity), 142 (1.4) P^+, 141 (8) $[P—H]^+$, 128 (15), 127 (100), 116 (14), 83 (37), 73 (90), 69 (14), 67 (13), 59 (18), 53 (12), 43 (37).

Attempted preparation of bis(chlorodimethylsilyl)acetylene, 4, by the Grignard method

A solution of 80 mmol of bis(bromomagnesium)-acetylide in THF prepared as described above from 80.0 cm^3 of 2.0 mol dm^{-3} methylmagnesium bromide was transferred by cannula to a dropping funnel and added dropwise over a period of 75 min to 41.1 g (318 mmol) of dimethyldichlorosilane, resulting in the formation of copious amounts of white precipitate. The mixture was stirred for an additional 2 h prior to vacuum transfer of the volatiles from the precipitate. The precipitate was washed with three portions of dry hexanes and these washings were combined with the volatiles. Analysis of the resulting red–orange mixture by GC and GC MS showed that in addition to an approximately 20% yield of **4** it contained the oligomers $ClMe_2Si(—C{\equiv}C—SiMe_2—)_nCl$, **7**, with distribution based on percentage GC area corrected using response factors estimated from the CH ratios for the oligomers of $n=1(\equiv$**4**), 50%; $n=2$, 34%; $n=3$, 10%; $n=4$, 5%. Similar results were obtained in a reaction employing dilithioacetylide.[6] GC MS methods permitted obtaining the mass spectra of the oligomers with isotopic ratios consistent with their formulas. These are presented in the following:

7, $n=1$ ($\equiv$**4**): *m/z* (relative intensity) =210 (2.8) and 212 (2.3) P^+; 195 (100), 196 (18), 197 (71), 198 (11) and 199 (15) $[P-Me]^+$; 185 (34) and 187 (14) $[P-Cl]^+$; 117 (10), 97 (32), 93 (17), 90 (12), 67 (23), 66 (13), 65 (27), 63 (41), 55 (10), 53 (17), 43 (19).

7, $n=2$: 292 (31) and 294 (25) P^+; 277 (100), 278 (25), 279 (76), 280 (19), and 281 (18) $[P-Me]^+$, 199 (24), 184 (16), 179 (38), 132 (17), 131 (23), 121 (11), 97 (18), 95 (10), 93 (26), 83 (12), 73 (40), 67 (18), 65 (14), 63 (20), 53 (10), 43 (21).

7, $n=3$: 374 (10) and 376 (10) P^+; 359 (57), 360 (20), 361 (47), 362 (16), and 363 (14) $[P-Me]^+$, 253 (25), 252 (15), 251 (54), 232 (17), 231 (62), 173 (11), 140 (17), 97 (10), 95 (10), 93 (25), 73 (100), 43 (12).

7, $n=4$: 441 (59), 442 (25), 443 (57), 444 (24), 445 (17) and 446 (8) $[P-Me]^+$, 378 (15), 365 (12), 364 (12), 363 (27), 336 (18), 335 (50), 334 (37), 333 (100), 315 (10), 314 (14), 313 (38), 255 (17), 232 (10), 231 (26), 177 (10), 175 (19), 97 (18), 95 (10), 93 (24), 83 (10), 73 (82), 45 (10).

Free radical chlorination of 2

A 100 cm^3 three-neck flask fitted with a reflux condenser, gas inlet and septum was charged with 1.40 g (5.8 mmol) of benzoyl peroxide, 20.0 g (130 mmol) of carbon tetrachloride which was freshly distilled from phosphorus pentoxide, and 8.2 g (58 mmol) of bis(dimethylsilyl)acetylene, **2**. The mixture was refluxed for five days at which time GC analysis indicated a mixture of chlorodimethylsilyl(dimethylsilyl)acetylene, **3**, and bis(chlorodimethylsilyl)acetylene, **4**, in 26% and 60% yields, respectively. The relative amount of **3** could be enhanced by shorter reaction time. After three days reflux the relative yields of **3** and **4** were 57% and 40% respectively. Distillation of the reaction mixtures afforded 83% pure **3** as a colorless highly moist air- and moisture-sensitive liquid, b.pt 80–86°C. Vacuum transfer from the pot residue afforded 83% pure **4**, a colorless highly moist air- and moisture-sensitive liquid, lit.b.p$_{65}$ 113°C.[8]

Final purification of both **3** and **4** was accomplished by preparative GC. The ease of hydrolysis of these compounds required scrupulous exclusion of moisture. The collection tubes had to be rinsed with hexamethyldisilazane and dried at 130°C for at least an hour to avoid hydrolysis. MS [*m/z* (relative intensity)]: **3**, 176 (14) P^+, 161 (29) $[P-Me]^+$, 93 (12) Me_2SiCl^+, 83 (90) $Me_2SiC_2H^+$, 73 (100) Me_3Si^+, **4**, 195 (100) $[P-Me]^+$, 197 (76), 199 (21), 97 (28) $Me_3SiC_2{}^+$, 63 (20). Because of their ease of hydrolysis the compounds were converted to their methoxy derivatives for elemental analysis.

Methoxydimethylsilyl(dimethylsilyl)-acetylene 5, and bis(dimethylmethoxysilyl)acetylene, 6

A chlorination of 10.6 g (74 mmol) of **2** was carried out as described above with refluxing for four days. The mixture was cooled to room temperature and 4.8 g (61 mmol) of pyridine followed by 12 g (0.38 mol) of dry methanol were added. After refluxing for 1 h, the mixture was distilled to give a mixture of **5** and **6**, b.pt 130–150°C, in 32% and 40% overall yields, respectively. Samples for characterization and further reactions were purified by preparative GC.

5: Colorless moderately moisture-sensitive liquid. MS: *m/z* (relative intensity) = 157 (100) $[P-Me]^+$, 127 (47) $[P-CH_2O]^+$, 89 (15), 73 (22), 59 (46) Me_2SiH^+, 43 (21) $SiMe^+$. Analysis: Calcd for $C_7H_{16}OSi_2$: C, 48.77; H, 9.36. Found: C, 48.40; H, 9.32%.

6: Colorless liquid, b.pt 141–143°C. MS: *m/z* (relative intensity) = 187 (100) $[P-Me]^+$, 157 (94) $[187-CH_2O]^+$, 127 (27) $[157-CH_2O]^+$, 86 (16), 73 (15), 71 (17), 59 (47) Me_2SiH^+, 43 (12) $MeSi^+$. Analysis: Calcd for $C_8H_{18}O_2Si_2$: C, 47.47, H, 8.96. Found: C, 47.37, H, 8.70%.

General procedure for the reactions of the bis(silyl)acetylenes with α-pyrone

Reactions were carried out in 25 or 50 cm³ flasks equipped with a magnetic stirring bar, reflux condenser, and septum which were rigorously oven-dried, rinsed with hexamethyldisilazane, and redried in the oven. All joints were sealed with Teflon tape and the reactions were carried out under an atmosphere of argon which had been bubbled through concentrated sulfuric acid. The reaction vessels were charged with equimolar amounts (1–5 mmol scale) of the acetylene and α-pyrone (Fluka) in an equal volume of decalin, with tert-butylbenzene as the internal standard. The mixtures were stirred and heated to 170–180°C using an oil bath. Samples were withdrawn at various times during the course of the reaction for analysis by GC. The results are given in Table 2. Similar methods were used for the unsuccessful reactions of bis(trimethylsilyl)acetylene with other dienes listed in Table 1.

Characterization of the disilylbenzenes

1,2-Bis(trimethylsilyl)benzene, **8**, X = Y = Me;[2] and 1,2-bis(dimethylsilyl)benzene, **8**, X = Y = H, have previously been reported.[9,10]

1,2-bis(methoxydimethylsilyl)benzene, 8, X = Y = OMe[13]

Colorless liquid, lit. b.pt$_{20}$ 142–145°C.[13] ^{1}H NMR (neat, ext. D_2O lock) $\delta = -0.12$ (12H) s, SiMe; 2.89 (6H) s, SiOMe; 6.19–7.24 (4H) m, aryl protons. ^{13}C NMR (neat): δ (multiplicity of off-resonance proton decoupled spectra) = −1.11 (q) SiMe; 49.16 (q) OMe; 127.78 (d), 134.09 (d), and 143.58 (s) aryl carbons. MS: *m/z* (relative intensity) = 241 (10), 240 (22), 239 (100) $[P-Me]^+$, 209 (12), 194 (12), 193 (63), 179 (30), 163 (16), 135 (18), 119 (10), 105 (13), 89 (24), 59 (46), 43 (10). Analysis: Calcd for $C_{12}H_{22}O_2Si_2$: C, 56.64; H, 8.71. Found: C, 56.39; H, 8.44%.

1,2-bis(chlorodimethylsilyl)benzene, 8, X = Y = Cl

Colorless liquid which fumes in moist air to give **9**. ^{1}H NMR: $\delta = 0.40$ (12H) s, SiMe; 6.88–7.53 (4H) m, aryl protons. ^{13}C NMR: $\delta = 5.14$ (q) SiMe; 129.15 (d), 135.39 (d) and 141.31 (s), aryl carbons. MS: *m/z* (relative intensity) = 264 (1) $[P+2]^+$; 251 (16), 250 (15), 249 (80), 248 (22), and 247 (100) $[P-Me]^+$; 213 (17), 211 (34), 175 (14), 134 (13), 119 (44), 105 (15), 95 (14), 93 (53), 91 (28), 67 (13), 65 (40), 63 (46), 53 (14), 43 (20). Careful methanolysis with dry methanol as described for **6** above gave **8**, X = Y = OMe, quantitatively.

1-chlorodimethylsilyl-2-dimethylsilylbenzene, 8, X = Cl, Y = H

Colorless liquid which slowly converts in moist air to **9**. ^{1}H NMR (neat, D_2O external lock): $\delta = -0.16$ (6H) d, $J = 3.5$ Hz, $SiH\underline{Me}$; 0.25 (6H) s, $SiCl\underline{Me}$; 4.42 (1H) sept, SiH; 6.86–7.31 (4H) m, aryl protons. ^{13}C NMR: $\delta = -2.80$ (q) SiHMe; 4.29 (q) SiClMe; 128.04 (d), 129.02 (d), 134.02 (d), 134.41 (d), 141.57 (s), and 143.45 (s) aryl carbons. MS: *m/z* (relative intensity) = 228 (5) P^+; 227 (14) $[P-H]^+$; 215 (37) and 213 (100) $[P-Me]^+$, 211 (16), 177 (23), 175 (10), 136 (12), 135 (59), 119 (19), 105 (14), 93 (20), 91 (10), 65 (11), 63 (14), 59 (10), 53 (15), 43 (16). Methanolysis with dry methanol gave **8**, X = OMe, Y = H.

1,1,3,3-Tetramethyl-1,3-disila-2-oxaindane, 9[11,13]

This compound was obtained in the α-pyrone reactions with acetylenes **3**, **4**, **5** and **6** and by hydrolysis of the corresponding bis(silyl)benzenes, **8**. An authentic sample was prepared by the method of Andrianov.[11] ^{1}H NMR (neat, D_2O external lock): $\delta = -0.03$ (12H) s, SiMe; 6.63–6.99 (4H) m, aryl protons. ^{13}C NMR: $\delta = 0.58$ (q) SiMe; 128.43 (d), 130.45 (d), and 147.55 (s) aryl carbons. MS: *m/z* (relative intensity) = 208 (5) P^+, 193 (100) $[P-Me]^+$.

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