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REACTION OF DISILANES WITH ACETYLENES

II *. DOUBLE SILYLATION OF 1-HEXYNE, TRIMETHYLSILYLACETYLENE AND ACETYLENE WITH METHOXYMETHYLDISILANES CATALYZED BY TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM **

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Summary

In the presence of a palladium(0) complex catalyst, methoxymethyldisilanes, $(MeO)_nMe_{3-n}SiSiMe_{3-m}(OMe)_m$ (m, n = 1, 2), added to 1-hexyne, trimethylsilylacetylene and acetylene to give double silylation products, 1,2-bis(methoxymethylsilyl)olefins, in varying yields.

Introduction

Recently, Kumada et al. and Sakurai et al. reported that in the presence of catalytic quantities of palladium complexes, disilanes of type $Me_nSi_2X_{6-n}$ (n = 2—6; X = H and F) or 1,2-disilacycloalkanes add to various acetylenic compounds to give double silylation products [1—3]. In a previous paper, we pointed out that the addition of a disilane to an acetylene to give the corresponding disilylolefin, is quite exothermic (ca. 40 kcal/mol) on the basis of thermochemical considerations [4,5]. Thus, we concluded that the double silylation of acetylenic compounds should occur not only with disilanes of special substituents or structures, such as hydro-, fluoro- and strained-disilanes, but also with other common disilanes, under appropriate reaction conditions. This was shown to be the case as evidenced by the double silylation reaction of phenylacetylene with methoxymethyldisilanes, as well as with hexamethyldisilane [5] (eq. 1) and

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* For part I see ref. 5.

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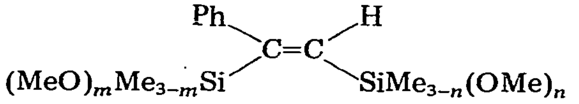
by the reaction of acetylene with chloromethyldisilanes [6].

$(MeO)_mMe_{3-m}SiSiMe_{3-n}(OMe)_n + PhC{\equiv}CH \xrightarrow{Cat.}$

$(m, n = 0{-}2)$



(1)

In order to extend the scope of the double silylation, we investigated the addition reaction of methoxymethyldisilanes with other types of acetylenes such as 1-hexyne, trimethylsilylacetylene and acetylene in the presence of a palladium(0) complex catalyst.

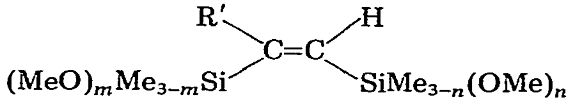
Results and discussion

Double silylation of 1-hexyne with four methoxymethyldisilanes (Ib—Ie) proceeded smoothly at 75—130°C in the presence of $Pd(PPh_3)_4$ (1.0 mol% relative to the acetylene used), giving the corresponding 1 : 1 adducts, 1,2-bis-(methoxymethylsilyl)olefins (IIb—IIe) in 37—76% yields (eq. 2). However, the reaction with hexamethyldisilane (Ia) was rather sluggish even at 140°C (7% yield) (Table 1).

$(MeO)_mMe_{3-m}SiSiMe_{3-n}(OMe)_n + RC'{\equiv}CH \xrightarrow{Pd(PPH_3)_4}$

(Ia, $m = n = 0$;
Ib, $m = 1, n = 0$;
Ic, $m = n = 1$;
Id, $m = 2, n = 1$;
Ie, $m = n = 2$)

R' = Bu, Me_3Si, H



(2)

(IIa, R' = Bu, $m = n = 0$;
IIb, R' = Bu, $m = 1, n = 0$;
IIc, R' = Bu, $m = n = 1$
IId, R' = Bu, $m = 2, n = 1$;
IIe, R' = Bu, $m = n = 2$;
IIf R' = Me_3Si; $m = n = 1$;
IIg R' = Me_3Si; $m = n = 2$;
IIh R' = H, $m = n = 1$;
IIi R' = H; $m = n = 2$)

Similarly, trimethylsilylacetylene ($Me_3SiC{\equiv}CH$) also was found to react with methoxymethyldisilanes (Ic and Ie), affording the corresponding 1,2,2-tris-(organosilyl)olefins (IIf and IIg) in 12—33% yields. In this case, the unreacted silylacetylene remained unchanged.

Double silylation of acetylene ($HC{\equiv}CH$) also was effected by bubbling it through a toluene or xylene solution containing the *sym*-methoxymethyldisilane

TABLE 1

DOUBLE SILYLATION OF 1-HEXYNE, TRIMETHYLSILYLACETYLENE AND ACETYLENE WITH METHOXYDISILANES IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM [a]

Run	Acetylene	Disilane	Temp. (°C)	Time (h)	Adduct and distributions		
					Yield (%) [b]		(Z)/(E)
1	$BuC\equiv CH$	$Me_3SiSiMe_3$ (Ia)	140	24	IIa	7	100/0
2	$BuC\equiv CH$	$(MeO)Me_2SiSiMe_3$ (Ib)	130	24	IIb	59	98 [c]/2
3 [d]	$BuC\equiv CH$	$(MeO)Me_2SiSiMe_3$ (Ib)	90	8	IIb	37	100 [e]/0
4	$BuC\equiv CH$	$(MeO)Me_2SiSiMe_2(OMe)$ (Ic)	130	24	IIc	76	84/16
5 [d]	$BuC\equiv CH$	$(MeO)Me_2SiSiMe_2(OMe)$ (Ic)	75	1.5	IIc	64	89/11
6	$BuC\equiv CH$	$(MeO)Me_2SiSiMe(OMe)_2$ (Id)	130	24	IId	50	95 [f]/5
7 [d]	$BuC\equiv CH$	$(MeO)Me_2SiSiMe(OMe)_2$ (Id)	75	1.5	IId	63	100 [g]/0
8	$BuC\equiv CH$	$(MeO)_2MeSiSiMe(OMe)_2$ (Ie)	130	24	IIe	46	100/0
9 [d]	$BuC\equiv CH$	$(MeO)_2MeSiSiMe(OMe)_2$ (Ie)	75	1.5	IIe	54	100/0
10	$Me_3SiC\equiv CH$	Ia	100	20	N.R. [h]		—
11	$Me_3SiC\equiv CH$	Ic	100	24	IIf	33	98/2
12 [d]	$Me_3SiC\equiv CH$	Ic	100	18	IIf	21	98/2
13	$Me_3SiC\equiv CH$	Ic	130	24	IIg	14	100/0
14 [d]	$Me_3SiC\equiv CH$	Ic	100	18	IIg	12	100/0
15 [i, j]	$HC\equiv CH$	Ic	110	25	IIh	32 [k]	95/5
16 [i, l]	$HC\equiv CH$	Ie	110	7	IIi	22 [k]	100/0

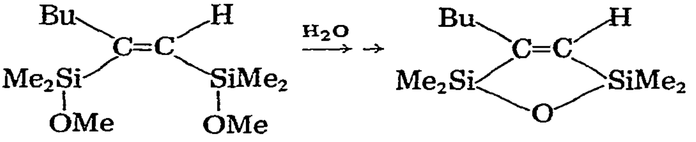
[a] Disilane/acetylene/catalyst = $10/5/5 \times 10^{-2}$ (mmol); unless otherwise specified, the reaction was carried out in an evacuated sealed tube. [b] By GLC yield based on the acetylene used. [c] α/β: 71/29. [d] The reaction was carried out by heating under argon in an open system. [e] α/β: 70/30. [f] α/β: 84/16. [g] α/β: 88/12. [h] No reaction occurred. [i] Acetylene gas was bubbled into a solution containing disilane and catalyst (1.0 mol% relative to the disilane used). [j] In toluene (10 ml). [k] Isolated yield based on the disilane used. [l] In xylene (10 ml).

(Ic and Ie) at 110°C in the presence of the palladium(0) catalyst, and gave 1,2-bis(methoxymethylsilyl)ethenes (IIh and IIi) in 22—32% yields.

Thus, it is further exemplified that the double silylation is quite a general reaction for a variety of acetylenes, giving the corresponding 1 : 1 adducts in varying yields.

Assignment of the structures of the double silylation products was made based on ^{1}H NMR, IR and mass spectroscopic studies and comparison with those of the related previous studies [5]. The results of the elemental analyses and the spectral data are summarized in Tables 2 and 3.

The previous metal-catalyzed double silylation of substituted acetylenes has been shown to give predominantly (*Z*)-stereochemistry. It was found that the present addition reactions also are highly stereoselective and regioselective to form products possessing the (*Z*)-configuration. The (*Z*)-configuration of the present product IIc was confirmed by its facile cyclization to form siloxane (III) (hydrolysis followed by the intramolecular condensation; eq. 3).



(*Z*)-IIc (III)

(3)

Such cyclization of 1,2-bis-silylolefins has been documented previously [1,5].

TABLE 2

ANALYTICAL DATA AND BOILING POINTS OF THE PRODUCTS, DISILYLOLEFINS

Compound	Formula	Analysis Found (Calcd.) (%)		b.p. (°C/mmHg)
		C	H	
IIa	$C_{12}H_{28}Si_2$	63.41 (63.17)	12.01 (12.35)	71—79/9
IIb	$C_{12}H_{28}Si_2O$	59.01 (58.94)	11.39 (11.54)	56.5/10
IIc	$C_{12}H_{28}Si_2O_2$	55.06 (55.32)	10.69 (10.83)	106/20
IId	$C_{12}H_{28}Si_2O_3$	51.82 (52.11)	10.11 (10.21)	126/12
IIe	$C_{12}H_{28}Si_2O_4$	49.59 (49.26)	9.59 ((9.65)	117/10
IIf	$C_{11}H_{28}Si_3O_2$	m.w. 214 (M^+) [a]		—
IIg	$C_{11}H_{28}Si_3O_4$	42.58 (42.82)	9.09 (9.14)	—
IIh	$C_8H_{20}Si_2O_2$	47.01 (46.97)	9.86 (9.78)	82—95/20
IIi	$C_8H_{20}Si_2O_4$	40.65 (41.00)	8.53 (8.55)	78—87/20
III	$C_{10}H_{22}Si_2O$	56.14 (56.01)	10.23 (10.34)	—

[a] By mass spectroscopy; *m/e* (intensity): 117(9), 119(8), 133(13), 143(6), 157(20), 172(25), 173(6), 199(100), 200(22), 201(10), 214(5) (M^+), 215(1) ($M^+ + 1$).

TABLE 3

NMR AND IR SPECTRA FOR THE DISILYLATED OLEFINS, $R_a(R_b)C{=}CH(R_c)$ [a]

Compound	Substituent			NMR (CCl_4) (δ, ppm)			IR (neat) (cm^{-1})		
	R_a	R_b	R_c	$=CH$	$SiOCH_3$	$SiCH_3$	$SiCH_3$	$SiOCH_3$	C=C
IIa	Bu	Me_3Si	$SiMe_3$	6.23	—	0.13, 0.16	1250	—	1542
α-IIb	Bu	Me_2Si OMe	$SiMe_3$	6.25	3.38	0.08 0.17	1250	1100	1547
β-IIb	Bu	Me_3Si	$SiMe_2$ OMe	6.03	3.36	0.13 0.17			1557
IIc	Bu	Me_2Si OMe	$SiMe_2$ OMe	6.19	3.41	0.14 0.18	1255	1100	1527 1557
IIc [b]	Bu	Me_2Si OMe	$SiMe_2$ OMe	5.92	3.35	0.14 0.18	1250	1090 1040	1560
α-IId	Bu	MeSi $(OMe)_2$	$SiMe_2$ OMe	6.27	3.48	0.17	1257	1080	1560
β-IId	Bu	Me_2Si OMe	SiMe $(OMe)_2$	6.04	3.39	0.17			
IIe	Bu	MeSi (OMe)	SiMe $(OMe)_2$	6.13	3.45 3.48	0.15 0.20	1260	1090	1530 1560 1598
IIf	Me_3Si	Me_2Si OMe	$SiMe_2$ OMe	7.09	3.46	0.08(a) 0.11 0.16	1260	1100	1505
IIg	Me_3Si	MeSi $(OMe)_2$	SiMe $(OMe)_2$	7.18	3.37 3.40	0.09(a) 0.17 0.18	1260	1080	1525
IIh	H	Me_2Si OMe	$SiMe_2$ OMe	6.63	3.38	0.18	1255	1095	[c]
IIh [b]	H	Me_2Si OMe	$SiMe_2$ OMe	6.55	3.35	0.15	1255	1090	[c]
IIi	H	MeSi $(OMe)_2$	SiMe $(OMe)_2$	6.59	3.47	0.16	1250	1080	1550
III	Bu	$Me_2Si{-}O{-}SiMe_2$		6.45	—	0.13 0.17	1251	925	1530

[a] (Z)-configuration. [b] (E)-isomer. [c] No sharp absorption band appeared.

In contrast to previous observations of bis-silylstyrene derivatives, an attempted isomerization of (*Z*)-IIc failed to give the corresponding (*E*)-isomer (see Experimental).

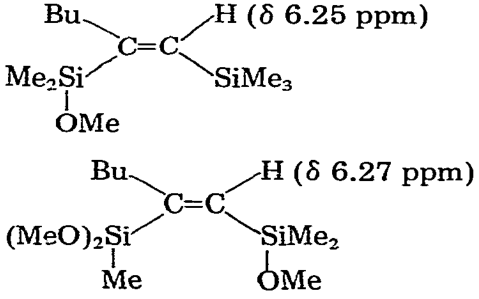
Attempted GLC isolation of the (*E*)-isomer of IIc from its mixture with the (*Z*)-isomer was unsuccessful, but comparison (NMR) of a 50(*Z*) : 50(*E*) mixture, which was isolated by preparative GLC as a fraction enriched in (*E*)-isomer (see Table 1, Run 4), with pure sample of the (*Z*)-isomer was possible. Thus, the mixture sample showed the olefinic proton due to the (*E*)-isomer at δ 5.92 ppm, while that due to (*Z*)-isomer occurred at δ 6.19 ppm. The high field shift of the olefinic proton in the (*E*)-isomer has been previously established in the case of 1,2-bis-silylstyrenes. A similar trend also was observable for the (*Z*)- and (*E*)-isomers of bis-silylethenes (see below and Table 3).

Further supporting evidence for the (*Z*)-stereochemistry was obtained from an examination of the IR spectra of the double silylation products from acetylene (HC≡CH) and dimethoxytetramethyldisilane (Ic). In this case, pure (*E*)- and (*Z*)-1,2-bis(methoxydimethylsilyl)ethene (IIh) were isolated from the mixture. The IR spectrum of the (*E*)-isomer showed a band at 1010 cm^{-1}, while the spectrum of the (*Z*)-isomer had no absorption in this region, but did have a band at 700 cm^{-1} which is due to (*Z*)-configuration [7].

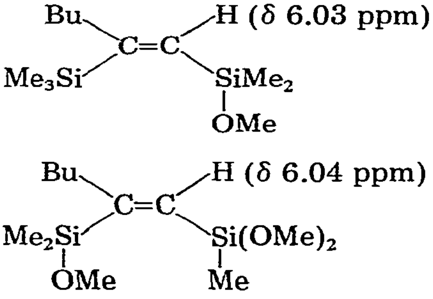
From the above results, together with the results of the previous double silylation [1—3,5,6], the structures of the other double silylation products were assigned to be of the (*Z*)-configuration (see eq. 2).

Regarding the structures of the products derived from unsymmetrical disilanes (Ib and Id) and 1-hexyne, the NMR spectra of (*Z*)-IIb and -IId showed that the presence of two kinds of the olefinic protons, so that each of the (*Z*)-compounds was composed of two types of regioisomer, the α- and β-form. On the other hand, the olefinic protons for (*Z*)-IIa, -IIc and -IIe, produced in the reactions of 1-hexyne with symmetrical disilanes, appeared at δ 6.23, 6.19 and 6.13 ppm, respectively (see Table 3), indicating that the increasing methoxy substitution on silicon affects the chemical shifts for these olefinic protons, moving them to higher fields. It is reasonable to consider that the chemical shifts of the olefinic protons were affected by the organosilyl group attached to the same carbon (β-position) rather than the vicinal one (α-position). Thus, the regioisomer which showed the proton chemical shift at higher field (6.03 ppm) was assigned to the β-structure and the isomer at lower field (6.25 ppm) the α-structure:

α-form

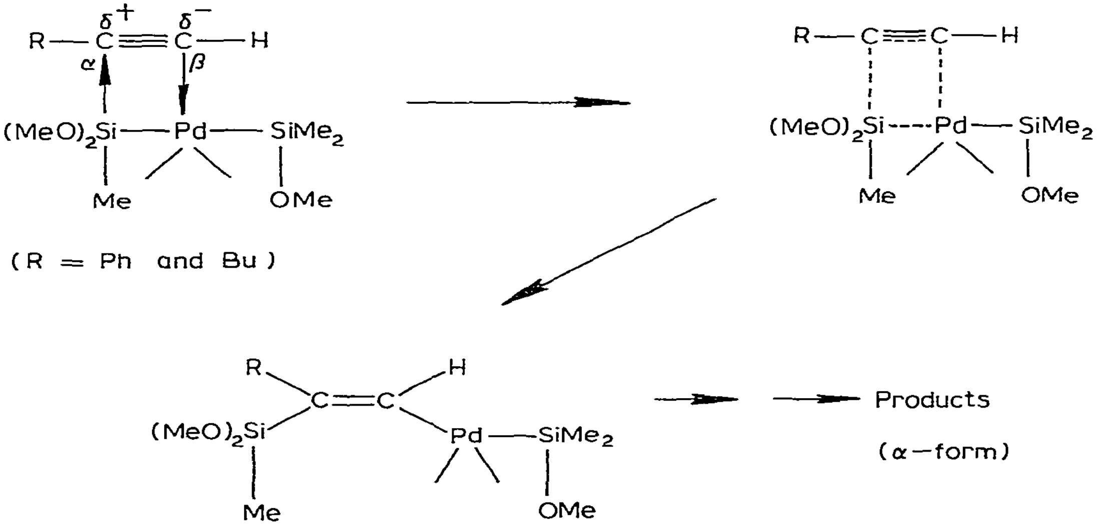


β-form



Further, the signal intensities of the protons indicated that (*Z*)-IIb contained the α-form and β-form in a ratio of 71/29, (*Z*)-IId in a ratio of 84/16. The similar trend of the olefinic proton chemical shifts between the α-form and β-form has been shown in the chemical shifts of the double silylation product pairs of phenylacetylene with unsymmetrical disilanes [5].

The regioselectivity of the double silylation described above is of interest. For example, the reaction of 1-hexyne with Id gave 1-dimethylmethoxysilyl-2-dimethoxymethylsilylhex-1-ene predominantly along with the minor regioisomer. Thus, the present double silylation using unsymmetrical disilanes proceeded to give the products in which the silyl moiety possessing more methoxy group occupies the α-position rather than β-position, as is shown in the case of the double silylations of phenylacetylene with unsymmetrical disilanes (Ib and Id). Although the directive effects of methoxy group(s) are not fully understood at the present time, the electron densities on the two carbons in the substituted acetylene also might play an important role. An indicating parameter for the electron-density distribution is available from their carbon-13 NMR chemical shifts by which the density of β-carbon is shown to be higher than that of α-carbon in both 1-hexyne and phenylacetylene * [8]. This is consistent with the mechanism which was proposed for the double silylation in the previous reactions [5]:



Experimental

All boiling points are uncorrected. IR spectra were recorded using neat liquid films with a Hitachi EPI-G3 spectrometer, and ^{1}H NMR spectra were measured on a Varian A-60D spectrometer in CCl_4 solution with TMS as

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* Also, the ^{13}C NMR spectrum for $(MeO)_2MeSiSiMe_2(OMe)$ (Id) showed that the electron density of the silicon bearing two methoxy groups appears to be higher than that of another silicon. Therefore, it is likely that the addition of the higher electron-density silicon to the α-carbons in the acetylenes would occur to predominantly give the corresponding α-form products.

internal standard. Mass spectral analyses were conducted using a JEOL JMS-07 spectrometer. GLC analyses were performed using an Ohkura Model 1700 gas chromatograph equipped with a 1 or 2 m × 4 mm Teflon column packed with Silicone KF-96 and SF-96 (15—20%) on Celite 545-AW (column temp. 120—190°C; He carrier; an external standard, n-alkane selected from C_{12}—C_{18}).

Materials

All the methoxymethyldisilanes used were prepared via methoxylation of the corresponding chlorodisilanes according to the method reported previously [9]. Acetylene gas was commercially available and purified by passing it through a Dry-Ice acetone trap and then a calcium chloride drying tube. 1-Hexyne was also commercially available and distilled before use. Trimethylsilylacetylene was obtained by the literature methods [10]. Palladium(0) complex, $Pd(PPh_3)_4$, was prepared as described in the literature [11].

Addition of methoxymethyldisilanes to 1-hexyne and trimethylsilylacetylene in the presence of the Pd^0 complex catalyst

The method used for the addition reaction to give (*Z*)-1,2-bis(methoxydimethylsilyl)hex-1-ene is representative. Under argon, a mixture of *sym*-dimethoxytetramethyldisilane (Ic, 1.8 g, 10 mmol), 1-hexyne (0.4 g, 5 mmol) and $Pd(PPh_3)_4$ (58 mg, 5×10^{-2} mmol; 1 mol% relative to the acetylene used) was heated at 75°C (oil bath) with magnetic stirring for 1.5 h. The yield of the product, 1,2-bis(methoxydimethylsilyl)hex-1-ene [IIc; a 89/11 mixture of (*Z*)- and (*E*)-isomers], was determined by GLC to be 64% (3.2 mmol), in which correction was made for thermal conductivity of the product using an external standard. Isolation of the product from the reaction mixture was carried out by preparative GLC or by distillation under reduced pressure [b.p. 106°C/20 mmHg; a 89/11 mixture of (*Z*)- and (*E*)-isomer].

Similarly, the reaction was carried out in an evacuated Carius tube in which the identical starting materials and the catalyst as described above were mixed and sealed. The yield of the product [IIc; a 84/16 mixture of (*Z*)- and (*E*)-isomers] formed after 24 h at 130°C was 76% (3.8 mmol).

Addition of methoxymethyldisilanes to acetylene in the presence of the Pd^0 complex

A mixture of *sym*-dimethoxytetramethyldisilane (Ic, 3.5 g, 20 mmol), the palladium(0) complex (0.2311 g; 1 mol% based on the disilane used) and toluene (10 ml) was heated at 110°C for 25 h, while acetylene gas was bubbled through the solution. After cooling, the resulting mixture was analyzed by GLC; no disilane remained in the mixture. Two products were formed. These were isolated by preparative GLC. From the elemental analysis and IR and NMR spectra, the minor product, which has a shorter retention time than the major one, was identified as (*E*)-1,2-bis(methoxydimethylsilyl)ethene, the major one as (*Z*)-1,2-bis(methoxydimethylsilyl)ethene (*Z*/*E* ratio, 95/5). On distillation, the reaction mixture gave a mixture of the (*Z*)- and (*E*)-isomers of IIh; b.p. 95°C/20 mmHg; 1.3 g (32% based on Ic used); (*Z*)/(*E*) isomer ratio, 87/13, and a 0.8 g residue mixture.

Similarly, acetylene gas was bubbled into a solution containing *sym*-dimethyltetramethoxydisilane (Ie, 4.2 g, 20 mmol) and the palladium complex (0.2311 g; 1 mol%) in xylene (10 ml) at 110°C for 7 h. GLC analysis of the reaction mixture showed that all of the disilane used has been consumed at this time. Distillation afforded, after separation of small amount of a forefun, IIi b.p. 87°C/20 mmHg; 1.1 g (22% based on Ie used) and 1.1 g of residue.

Attempted isomerization of (Z)-1,2-bis(dimethylmethoxysilyl)hex-1-ene (IIc) to the (E)-isomer

According to the method described in the previous paper [5], a mixture of (*Z*)-IIc (2 mmol) [88% (*Z*) and 12% (*E*)], dimethoxytetramethyldisilane (Ic) (2 mmol) and $Pd(PPh_3)_4$ (5 mg) was heated with stirring at 90°C for 20 h and then at 110°C for 19 h under argon. The (*Z*)/(*E*) isomer ratio remained essentially unchanged (86/14) after this treatment.

A similar attempt to isomerize an identical sample of the mixture [88% (*Z*) and 12% (*E*)] was made in the absence of the disilane (Ic), but the (*Z*)/(*E*) isomer ratio remained unchanged.

On the other hand, mixing a sample of (*Z*), (*E*)-IIc with one drop of water gave a new peak in the GLC trace, while the original one corresponding to the (*Z*)-isomer decreased greatly, From the elemental and spectral analyses, the new peak compound, isolated by preparative GLC, was identified as the cyclic siloxane (III).

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