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PHOTOLYSIS OF ORGANOPOLYSILANES. PREPARATION AND PHOTOLYSIS OF SILYLPHENYLPROPYNES AND SILYLPHENYLPROPADIENES

MITSUO ISHIKAWA, HIROSHI SUGISAWA, LÁSZLÓ FÁBRY * and MAKOTO KUMADA

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Kyoto 606 (Japan)

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Summary

The synthesis and photochemistry of 1-silyl- and 1-disilanyl-3-trimethylsilyl-3-phenylpropynes, and 1-silyl- and 1-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes is described. The UV-irradiation of the 1-silyl- and 1-disilanyl-3-trimethylsilyl-3-phenylpropynes with a high-pressure mercury lamp resulted in formation of equilibrium mixtures consisting of the silylphenylpropynes and silylphenylpropadienes. In these photochemical reactions, the equilibrium favored the formation of the silylphenylpropadienes. Irradiation of 1-disilanyl-1,3-bis-(trimethylsilyl)-3-phenylpropadienes afforded exclusively 1,1-bis(trimethylsilyl)-3-disilanyl-3-phenylpropadienes, while the corresponding monosilyl derivatives were photochemically stable under the conditions used.

Introduction

Recently, we reported that photolysis of (pentamethyldisilanyl)phenylacetylene leads to the formation of 1,1-dimethyl-2-trimethylsilyl-3-phenyl-1-silacycloprop-2-ene and 1,1-dimethyl-3-trimethylsilyl-3-phenyl-1-silapropadiene [1—4]. During the course of our investigations into the photochemical formation of the reactive silicon species from the silyl-substituted alkynes, we have found that 1-silyl- and 1-disilanyl-3-trimethylsilyl-3-phenylpropynes undergo novel photochemical transformations, leading to the corresponding silyl-substituted phenylpropadiene derivatives. Also, we have found a new type of photochemical isomerization of 1-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes in which an interchange of the disilanyl group with the trimethylsilyl group is involved.

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* On leave from Eötvös Loránd University, Budapest (Hungary).

Results and discussion

Synthesis of silyl-substituted phenylpropynes and phenylpropadienes

All of the compounds used for photolysis experiments reported here were synthesized by the method developed by West and his co-workers for preparing similar compounds [5].

The reaction of 1-phenylpropyne with 1 molar equivalent of butyllithium/*N*,*N*,*N'*,*N'*-tetramethylethylenediamine (BuLi/TMEDA) in hexane followed by reaction of the resulting product with chloropentamethyldisilane, gave 1-pentamethyldisilanyl-3-phenylpropyne (I) in 45% yield, in addition to a 13% yield of 1,3-bis(pentamethyldisilanyl)-3-phenylpropyne (VI). Similar reaction of lithiate phenylpropyne with various chlorosilanes afforded the corresponding silyl substituted compounds, II—V, in 63, 76, 46 and 46% yields, respectively (Schen 1).

SCHEME 1

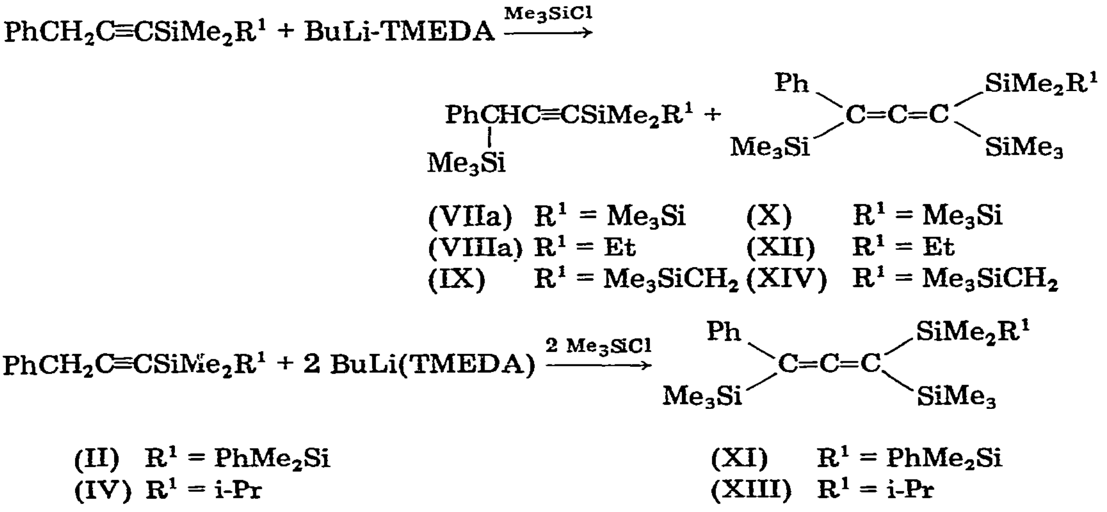
$$\mathrm{PhC{\equiv}CCH_3 + BuLi(TMEDA) \rightarrow PhCH_2C{\equiv}CLi(TMEDA) \xrightarrow{R^1Me_2SiCl}}$$

$$\mathrm{PhCH_2C{\equiv}CSiMe_2R^1}$$

(I) $R^1 = Me_3Si$
(II) $R^1 = PhMe_2Si$
(III) $R^1 = Et$
(IV) $R^1 = i\text{-}Pr$
(V) $R^1 = Me_3SiCH_2$

Treatment of compounds I, III and V with 1.2 molar equivalents of BuLi/TMEDA and then with trimethylchlorosilane gave, in each case, a pair of the further-silylated derivatives of phenylpropyne and phenylpropadiene: VIIa and X; VIIIa and XII; and IX and XIV (Scheme 2).

SCHEME 2

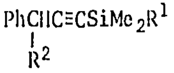


(VIIa) $R^1 = Me_3Si$ (X) $R^1 = Me_3Si$
(VIIIa) $R^1 = Et$ (XII) $R^1 = Et$
(IX) $R^1 = Me_3SiCH_2$ (XIV) $R^1 = Me_3SiCH_2$

(II) $R^1 = PhMe_2Si$ (XI) $R^1 = PhMe_2Si$
(IV) $R^1 = i\text{-}Pr$ (XIII) $R^1 = i\text{-}Pr$

TABLE 1

YIELDS, SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR



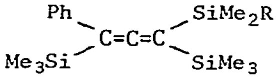
$Ph\underset{R^2}{\underset{|}{C}}HC{\equiv}CSiMe_2R^1$

Compound		Yield (%)	B.p. °C (torr)	n_D^{20}	Found (calcd.) (%)	
					C	H
I	R^1=Me_3Si, R^2=H	45^a	94-95(3)	1.5105	67.95(68.22)	9.20(9.00)
II	R^1=$PhMe_2Si$, R^2=H	63^a	140-142(2)	1.5580	73.67(73.96)	8.10(7.84)
III	R^1=Et, R^2=H	76^a	87-90(3)	1.5060	76.88(77.16)	9.21(8.97)
IV	R^1=iso-Pr, R^2=H	46^a	76(3)	1.4930	77.75(77.71)	9.33(9.32)
V	R^1=Me_3SiCH_2, R^2=H	46^a	86-88(2)	1.5010	69.01(69.15)	9.56(9.29)
VI	R^1=Me_3Si, R^2=$Me_3SiSiMe_2$	13^a	132-135(3)	—	60.30(60.56)	9.71(9.63)
VIIa	R^1=R^2=Me_3Si	22^b	110-113(3)	1.5070	64.01(64.07)	9.64(9.49)
VIIIa	R^1=Et, R^2=Me_3Si	12^b	115-120(3)	1.5103	69.72(70.00)	9.83(9.55)
IX	R^1=Me_3SiCH_2, R^2=Me_3Si	24^b	107-110(2)	1.4975^c	65.23(64.98)	9.94(9.69)

[a] Isolated yield. [b] Determined by GLC. [c] n_D^{25}.

TABLE 2

YIELDS, SOME PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR



$Ph(Me_3Si)C=C=C(SiMe_2R)(SiMe_3)$

Compound		Yield (%)[a]	B.p. °C (torr)	n_D^{20}	Found (calcd.) (%)	
					C	H
X	R=Me_3Si	21	127-130(2)	1.5328	61.25(61.46)	9.97(9.80)
XI	R=$PhMe_2Si$	23	152-158(2)	1.5610	66.41(66.30)	9.16(8.90)
XII	R=Et	14	130-132(3)	1.5275	65.55(65.82)	10.16(9.88)
XIII	R=iso-Pr	46	141-142(3)	1.5285	66.80(66.59)	10.22(10.06)
XIV	R=Me_3SiCH_2	18	129-132(2)	1.5195	62.08(62.30)	10.26(9.96)

[a] Isolated yield.

The reaction of dilithio derivatives of II and IV with trimethylchlorosilane gave XI and XIII, respectively. 1-Silyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes (X—XIV) could easily be isolated from the reaction mixture by fractional distillation. However, 1-silyl-3-trimethylsilyl-3-phenylpropynes (VIIa, VIIIa and IX) could not be obtained in pure form by distillation. The distillates were always contaminated with small amounts of their respective isomers, 1-silyl-1-trimethylsilyl-3-phenylpropadienes (10—15%) and traces of unidentified substances. The formation of these isomers can be expected from isomerization of the monolithiated derivatives, followed by reaction with trimethylchlorosilane [5]. Therefore, compounds VIIa, VIIIa and IX were isolated in the pure state by preparative GLC.

The structure of new compounds, I—XIV, was confirmed by elemental analyses and IR, mass and ^1H NMR spectroscopic studies (Tables 1—3).

Photolysis of silyl-substituted phenylpropyne

Photolysis of 1-silyl-3-trimethylsilyl-3-phenylpropynes by irradiation with ultraviolet light afforded their respective isomers, 1-silyl-1-trimethylsilyl-3-phenylpropadienes. In these reactions, neither silacyclopropenes nor silapropadienes, which were produced in the photolysis of (pentamethyldisilanyl)phenylacetylene [1], were detected. Thus, when a solution of 1-pentamethyldisilanyl-3-trimethylsilyl-3-phenylpropyne (VIIa) was irradiated with a high-pressure mercury lamp for 4 h in the presence or absence of methanol, and the resulting product was analyzed by GLC, two peaks having an area ratio of 5/95 were observed. The combined yield was 85%. The reaction was very clean and no other products were detected. The structure of the main product was determined to be 1-pentamethyldisilanyl-1-trimethylsilyl-3-phenylpropadiene (XVI) by ^1H NMR spectroscopy (Table 5). A strong band at 1910 cm^{-1} in its IR spectrum clearly indicated that it must have an allenic structure. The retention time on GLC of the minor product was exactly the same as that of starting VIIa under

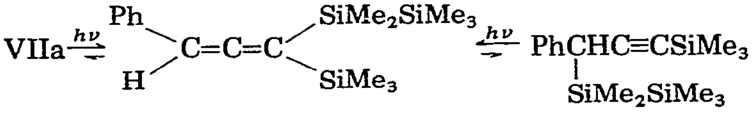
TABLE 3

IR, MASS AND ^{1}H NMR DATA FOR COMPOUNDS (I-XIV)

Compound	$\nu C\equiv C$ or $\nu C=C$	M^+	Chemical shifts (δ, ppm) (in CCl_4)
I	2180	246	0.12(Me_3Si, s, 9H), 0.21(Me_2Si, s, 6H), 3.62 (H_2CPh, s, 2H), 7.1-7.4(ring protons, m, 5H)
II	2185	308	0.18(Me_2Si, s, 6H), 0.39(Me_2Si, s, 6H), 3.60 (H_2CPh, s, 2H), 7.1-7.5(ring protons, m, 10H)
III	2185	202	0.14(Me_2Si, s, 6H), 0.5-1.2(C_2H_5, m, 5H), 3.60(H_2CPh, s, 2H), 7.1-7.3(ring protons, m, 5H)
IV	2185	216	0.12(Me_2Si, s, 6H), 0.9-1.1(iso-Pr, m, 7H), 3.60(H_2CPh, s, 2H), 7.1-7.3(ring protons, m, 5H)
V	2190	260	-0.15($SiCH_2Si$, s, 2H), 0.07(Me_3Si, s, 9H), 0.19(Me_2Si, s, 6H), 3.57(H_2CPh, s, 2H), 7.1-7.4(ring protons, m, 5H)
VI	2165	376	0.04(Me_3Si, s, 9H), 0.10(Me_2Si, s, 6H), 0.13 (Me_3Si, s, 9H), 0.22(Me_2Si, s, 6H), 3.26(HCPh, s, 1H), 7.0-7.3(ring protons, m, 5H)
VIIa	2170	318	0.05(Me_3Si, s, 9H), 0.14(Me_3Si, s, 9H), 0.21 (Me_2Si, s, 6H), 3.14(HCPh, s, 1H), 7.1-7.4 (ring protons, m, 5H)
VIIIa	2175	274	0.05(Me_3Si, s, 9H), 0.15(Me_2Si, s, 6H), 0.5-1.2(C_2H_5, m, 5H), 3.21(HCPh, s, 1H), 7.0-7.3 (ring protons, m, 5H)
IX	2180	332	-0.13($SiCH_2Si$, s, 2H), 0.05(Me_3Si, s, 9H), 0.08(Me_3Si, s, 9H), 0.21(Me_2Si, s, 6H), 3.11 (HCPh, s, 1H), 7.0-7.2(ring protons, m, 5H)
X	1890	390	0.19(Me_3Si, s, 9H), 0.33(Me_3Si, s, 9H), 0.35 (Me_2Si, s, 6H), 0.38(Me_3Si, s, 9H), 7.0-7.4 (ring protons, m, 5H)
XI	1890	452	0.12(Me_3Si, s, 9H), 0.18(Me_2Si, s, 6H), 0.21 (Me_3Si, s, 9H), 0.30 and 0.32(Me_2Si, 6H), 7.0-7.4(ring protons, m, 10H)
XII	1892	346	0.14(Me_2Si, s, 6H), 0.17(Me_3Si, s, 9H), 0.22 (Me_3Si, s, 9H), 0.6-1.1(C_2H_5, m, 5H), 6.9-7.2 (ring protons, m, 5H)
XIII	1890	360	0.10(Me_2Si, s, 6H), 0.17(Me_3Si, s, 9H), 0.23 (Me_3Si, s, 9H), 0.8-1.1(iso-Pr, m, 7H), 6.9-7.3(ring protons, m, 5H)
XIV	1895	404	-0.08($SiCH_2Si$, s, 2H), 0.02(Me_3Si, s, 9H), 0.18(Me_3Si and Me_2Si, s, 15H), 0.22(Me_3Si, s, 9H), 6.9-7.2(ring protons, m, 5H)

various conditions. The mass spectrum of this compound showed the presence of the parent ion at 318, corresponding to the calculated molecular weight for VIIa. Furthermore, its IR spectrum showed a strong absorption band at 2170

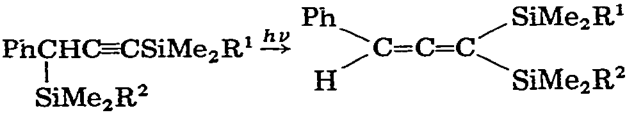
cm^{-1} due to the stretching vibration of a carbon—carbon triple bond. However, the ^1H NMR spectrum obviously indicated that it consisted of two compounds in a ratio of 1/3. The chemical shift of the minor component was consistent with that of VIIa. The proton resonances for the more abundant isomer, however, showed four signals at δ 0.05, 0.18, 0.20 and 3.21 with relative intensities of 9/9/6/1, attributed to two different Me_3Si protons, Me_2Si and HCPh protons, respectively, in addition to the phenyl ring protons which overlapped with those of VIIa. On the basis of these results we assigned the more abundant isomer to be 1-trimethylsilyl-3-pentamethyldisilanyl-3-phenylpropyne (VIIb). The same GLC area ratio (5/95) as above was obtained from the photolysis of pure XVI under identical conditions, implying that equilibrium was reached in the photolysis.



(XVI) (VIIb)

Similar photolysis of 1,3-bis(pentamethyldisilanyl)-3-phenylpropyne (VI) afforded an equilibrium mixture consisting of VI and 1,1-bis(pentamethyldisilanyl)-3-phenylpropadiene (XV) in 84% combined yield (Scheme 3). In this case, the ratio of VI/XV in the equilibrium mixture was determined to be 13/87 by GLC analysis. The ^1H NMR spectrum of XV showed two singlets at δ 0.06 and 0.23 ppm due to Me_3Si protons and Me_2Si protons, respectively, indicating that the two pentamethyldisilanyl groups are magnetically equivalent. The IR spectrum of XV showed an intense absorption due to the allenic structure at 1908 cm^{-1}.

SCHEME 3



(VI, VIIa, VIIIa, IX) (XV) $R^1 = R^2 = Me_3Si$

(XVI) $R^1 = Me_3Si$, $R^2 = Me—$

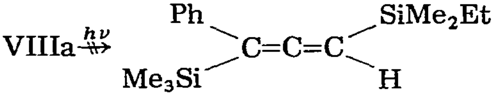
(XVII) $R^1 = Et$, $R^2 = Me—$

(XVIII) $R^1 = Me_3SiCH_2$, $R^2 = Me—$

Such a photochemical isomerization is not confined to disilanyl derivatives such as VI and VIIa, but is a general reaction for 1,3-bis(silyl)-3-phenylpropynes. Thus, 1-ethyldimethylsilyl-3-trimethylsilyl-3-phenylpropyne (VIIIa) was largely transformed into 1-ethyldimethylsilyl-1-trimethylsilyl-3-phenyl-propadiene (XVII) under similar conditions, in addition to small amounts of a mixture of VIIIa and 1-trimethylsilyl-3-ethyldimethylsilyl-3-phenylpropyne (VIIIb). The ratio of XVII/(VIIIa + VIIIb) in the equilibrium mixture was 97/3 by GLC. The proton chemical shift of VIIIb was consistent with that of an authentic sample.

Similarly, photolysis of 1-(trimethylsilylmethyl)dimethylsilyl-3-trimethylsilyl-3-phenylpropyne (IX) afforded an equilibrium mixture consisting of IX and 1-(trimethylsilylmethyl)dimethylsilyl-1-trimethylsilyl-3-phenylpropadiene (XVIII) in a ratio of 13/87. In this case, recovered IX from the equilibrium mixture did not contain any isomeric products. Presumably, the rate of migration of the (trimethylsilylmethyl)dimethylsilyl group would be extremely small compared with that of the trimethylsilyl group.

It is noteworthy that in the present system, $PhCH(SiMe_2R^2)C{\equiv}CSiMe_2R^1$, a 1,3-hydrogen shift from the benzylic carbon to the unsaturated carbon atom does not occur. Only the silyl group can migrate to give the propadiene structure. Careful GLC analysis of the equilibrium mixture obtained from the photolysis of VIIIa showed no peak corresponding to 1-ethyldimethylsilyl-3-trimethylsilyl-3-phenylpropadiene (XIX). Furthermore, compound XIX was found to be photochemically stable under the conditions used. The photolysis conditions,



(XIX)

TABLE 4

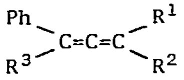
PHOTOLYSIS OF SILYL-SUBSTITUTED PHENYLPROPYNES AND PHENYLPROPADIENES

Compound g (mmole)		Time (h)	Solvent[a] (ml)	Product ratio in the equilibrium mixture	Total yield (%)
VI	0.0196 (0.052)	3.5	5.5	XV/VI (87/13)	84
XV	0.0365 (0.097)	4.5	16.0	XV/VI (87/13)	81
VIIa	0.0249 (0.078)	8.0	8.0	XVI/(VIIa + VIIb) (95/5)	83
XVI	0.0429 (0.135)	1.5	10.0	XVI/(VIIa + VIIb) (95/5)	97
VIIIa	0.0212 (0.077)	8	8.0	XVII/(VIIIa + VIIIb) (97/3)	83
XVII	0.0271 (0.099)	5.0	16.0	XVII/(VIIIa + VIIIb) (97/3)	100
IX	0.0328 (0.099)	10	10.0	XVIII/IX (87/13)	99
XVIII	0.0210 (0.063)	18	10.0	XVIII/IX (88/12)	92
X	0.0250 (0.075)	23	10.0	XX	62
XI	0.564 (1.25)	77	100	XXI	37

[a] Hexane.

TABLE 5

REFRACTIVE INDICES AND ANALYTICAL DATA FOR



Compound				n_D^{20}	Found (calcd.) (%)	
	R^1	R^2	R^3		C	H
XV	$Me_3SiSiMe_2$	$Me_3SiSiMe_2$	H	1.5372	60.73(60.56)	9.52(9.63)
XVI	$Me_3SiSiMe_2$	Me_3Si	H	1.5429	63.78(64.07)	9.37(9.49)
XVII	$EtMe_2Si$	Me_3Si	H	1.5383	70.21(70.00)	9.70(9.55)
XVIII	$Me_3SiCH_2SiMe_2$	Me_3Si	H	1.5305[a]	64.80(64.98)	9.84(9.69)
XX	Me_3Si	Me_3Si	$Me_3SiSiMe_2$	1.5275[a]	61.46(61.46)	9.72(9.80)
XXI	Me_3Si	Me_3Si	$PhMe_2SiSiMe_2$	1.5533	66.30(66.30)	8.93(8.90)

[a] n_D^{25}.

TABLE 6

IR, MASS AND ^{1}H NMR DATA FOR PHOTOREARRANGED PRODUCTS (XV-XXI)

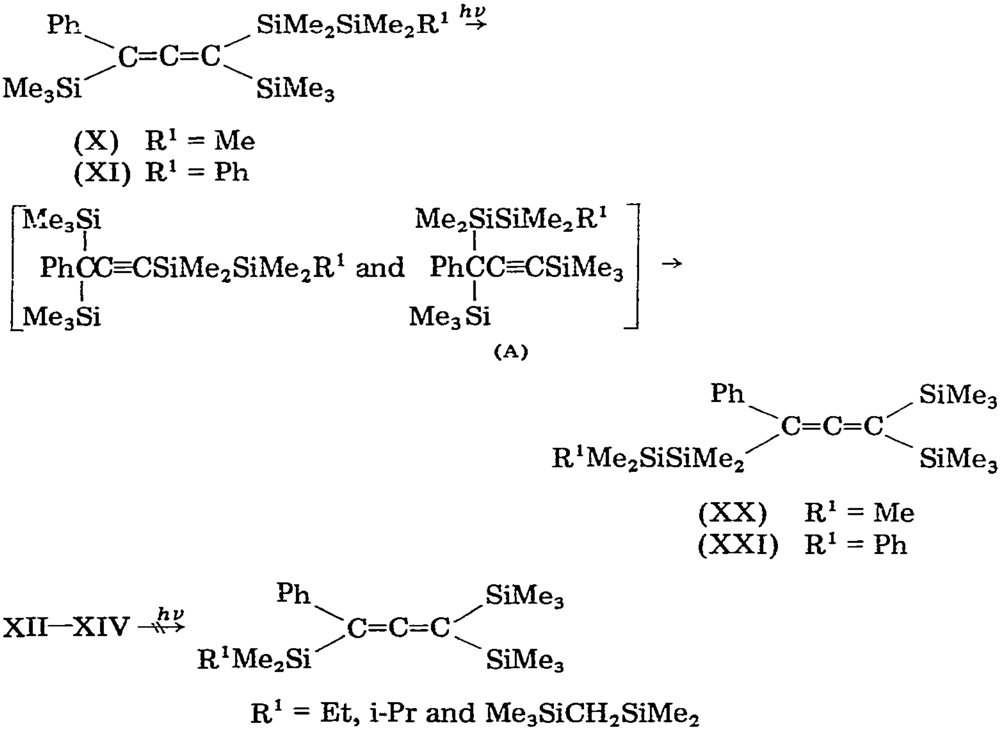
Compound	νC=C=C (cm^{-1})	M^+	Chemical shifts (δ, ppm) (in CCl_4)
XV	1908	376	0.06(Me_3Si, s, 18H), 0.23(Me_2Si, s, 12H), 5.41(HC, s, 1H), 6.9-7.3(ring protons, m, 5H)
XVI	1910	318	0.07(Me_3Si, s, 9H), 0.19(Me_3Si, s, 9H), 0.23(Me_2Si, s, 6H), 5.44(HC, s, 1H), 6.9-7.3(ring protons, m, 5H)
XVII	1915	274	0.16(Me_2Si, s, 6H), 0.18(Me_3Si, s, 9H), 0.5-1.1(C_2H_5, m, 5H), 5.46(HC, s, 1H), 7.0-7.3(ring protons, m, 5H)
XVIII	1918	332	-0.07($SiCH_2Si$, s, 2H), 0.04(Me_3Si, s, 9H), 0.19(Me_3Si, s, 9H), 0.22(Me_2Si, s, 6H), 5.45(HCPh, 1H), 6.9-7.2(ring protons, m, 5H)
XX	1890	390	0.05(Me_3Si, s, 9H), 0.19(Me_3Si, s, 18H), 0.26(Me_2Si, s, 6H), 7.1-7.4(ring protons, m, 5H)
XXI	1895	452	0.14(Me_3Si, s, 18H), 0.20(Me_2Si, s, 6H), 0.29(Me_2Si, s, 6H), 6.9-7.3(ring protons, m, 10H)

ratios of products in equilibrium mixtures and total yields are given in Table 4. The analytical, ^{1}H NMR, IR and mass spectral data for photolysis products are listed in Tables 5 and 6.

Photolysis of 1-disilanyl-1,3-bis(trimethylsilyl)propadiene

The photochemical behaviour of 1-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes is of considerable interest, because a photochemically induced intramolecular interchange of the disilanyl group with the silyl group is involved. Thus, photolysis of 1-pentamethyldisilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadiene (X) in hexane with a high-pressure mercury lamp afforded 1,1-bis(trimethylsilyl)-3-pentamethyldisilanyl-3-phenylpropadiene (XX). However, the rate of isomerization in this system was slower than that of the silylphenylpropyne system. Prolonged irradiation of the 1-disilanyl-3-phenylpropadiene led to complete transformation into the 3-disilanyl isomer. Under similar photolysis, 1-(2'-phenyltetramethyldisilanyl)-1,3-bis(trimethylsilyl)-3-phenylpropadiene (XI) was converted to an isomer, 1,1-bis(trimethylsilyl)-3-(2'-phenyltetramethyldisilanyl)-3-phenylpropadiene (XXI). In this case, small amounts of compounds arising from cleavage of the silicon—silicon bond, followed by hydrogen abstraction were produced. Photolysis of X in the presence of methanol gave the same result as above, indicating that a silicon—carbon double-bond intermediate arising from a 1,3-shift of the silyl group as observed in the photolysis of alkenyldisilanes [6] is not involved in the present photolysis (Scheme 4).

SCHEME 4



Interestingly, only 1-disilanyl-substituted 1,3-bis(silyl)propadienes underwent such photochemical Si—Si/Si interchange. The corresponding monosilyl-substituted derivatives, XII—XIV, did not isomerize under the conditions used. For this reason, one might consider the possibility that the steric hindrance between a trimethylsilyl group and the disilanyl group on the same carbon atom would be important for the interchange. However, 1-(trimethylsilylmethyl)dimethylsilyl-1,3-bis(trimethylsilyl)-3-phenylpropadiene (XIV) was photochemical ly stable.

Further studies will be required in order to better understand the mechanism of this type of photochemical Si—Si/Si interchange. It is likely that the key step is the formation of 3-disilanyl-1,3-bis(trimethylsilyl)-3-phenylpropyne (A). Indeed, the intermediate (maximum yield, ca. 2%) which is consistent with the molecular weight of A was always detected by GLC-mass spectrometry during the photolysis of X, together with products, X and XX. This species disappeared completely at the end of the isomerization.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen. Photolysis was performed using a 100-W high-pressure mercury lamp surrounded by a quartz cooling jacket. Identification of the products by GLC was done by using two different columns (30% Silicone grease SE-30 on Chromosorb W and 30% Apiezon grease on Celite 545).

Proton NMR spectra were determined with a JEOL Model JNM-MH-100 spectrometer using carbon tetrachloride solutions containing cyclohexane as an internal standard. IR spectra of thin liquid films were determined using a Hitachi Model GPI-3 grating spectrometer. Mass spectra were obtained on a JEOL Model JMS-D 300 equipped with a JMA-2000 data processing system. Ionizing voltage was 24 eV for all compounds. An Aerograph Model 90-P gas chromatograph with a thermal conductivity detector was used for separating the reaction products. Most of the products were easily separated as colorless liquids by using a 20′ × 3/8″ column containing Silicone grease (30%) on Chromosorb W.

1-Silyl-substituted 3-phenylpropynes

The following is typical of the procedures used. In a 200-ml three-necked flask fitted with a stirrer, dropping funnel, and condenser was placed a mixture of 7 g (0.060 mol) of 1-phenylpropyne and 7 g (0.060 mol) of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in 15 ml of hexane. To this was added 43 ml of 1.4 *M* butyllithium/hexane solution (1 mol equiv.) with dry ice/acetone cooling. The reaction mixture was warmed up to room temperature and then refluxe for 15 min. To this brown solution was added 10.5 g (0.063 mol) of chloropentamethyldisilane in 20 ml of hexane. The reaction mixture was refluxed for 30 min and hydrolyzed with water. The organic layer was separated and the water layer was extracted with ether. The organic layer and ether extracts were combined and washed with water, and dried over potassium carbonate. The solvents were distilled off and the residue was fractionally distilled under reduce pressure to give 6.6 g (45% yield) of 1-pentamethyldisilanyl-3-phenylpropyne (I) and 2.9 g (13% yield) of 1,3-bis(pentamethyldisilanyl)-3-phenylpropyne (VI).

Compounds II—V were prepared similarly. The figures in parentheses refer to the quantities (g) used of 1-phenylpropyne, TMEDA, and chlorosilane, respectively: II (5.0, 5.0, 9.9), III (7.0, 7.0, 7.4), IV (7.0, 7.0, 8.3) and V (7.0, 7.0, 10.9). The results are given in Table 1.

1-Silyl-3-trimethylsilyl-3-phenylpropynes and 1-silyl-1,3-bis(trimethylsilyl)-3-phenylpropadienes

In a 100-ml three-necked flask was placed a solution of 6.1 g (0.025 mol) of I and 2.9 g (0.025 mol) of TMEDA in 20 ml of hexane. To this was added 1 molar equivalent of 1.4 *M* butyllithium/hexane solution (18 ml) with dry ice/acetone cooling. After the mixture was refluxed for 5 min, 3.2 g (0.030 mol) of trimethylchlorosilane in 10 ml of hexane was added at room temperature, and the mixture was hydrolyzed with water. The organic layer was fractionally distilled under reduced pressure to give 2.6 g of crude VIIa, b.p. 110—113°C/3 torr and 1.8 g (21% yield) of X, b.p. 127—130°C/2 torr. Pure VIIa was isolated by preparative GLC. A similar method was used for preparation of VIIIa and XII (III 8.5 g, TMEDA 4.9 g, and Me_3SiCl 4.6 g), and IX and XIV (V 7.0 g, TMEDA 3.2 g, and Me_3SiCl 3.3 g).

1-(2'-Phenyltetramethyldisilanyl)-1,3-bis(trimethylsilyl)-3-phenylpropadiene (XI)

In a 100-ml three-necked flask was placed a solution of 2.2 g (0.019 mol) of 1-phenylpropyne and 2.2 g (0.019 mol) of TMEDA in 15 ml of hexane. To this was added slowly 1 molar equivalent of 1.5 *M* butyllithium/hexane solution (12 ml) with dry ice/acetone cooling. The mixture was heated to reflux for 15 min and then treated with 4.2 g (0.018 mol) of 1-chloro-2-phenyltetramethyldisilane in 10 ml of hexane at room temperature. The mixture was again cooled down to —78°C and 2 molar equivalents of 1.2 *M* butyllithium/hexane solution (30 ml) was added to it. This dark brown solution was refluxed for 15 min and then treated with 5.8 g (0.054 mol) of trimethylchlorosilane in 10 ml of hexane. The mixture was hydrolyzed with water and the organic layer was dried over potassium carbonate. Distillation gave 2.0 g (23% yield) of XI.

1-Isopropyldimethylsilyl-1,3-bis(trimethylsilyl)-3-phenylpropadiene (XIII)

To a hexane solution of 2.2 g (0.010 mol) of IV was added 2 molar equivalents of 1.2 *M* butyllithium/hexane solution (17 ml) at room temperature. After refluxing the mixture for 15 min, 2.6 g (0.024 mol) of trimethylchlorosilane was added at room temperature. The mixture was hydrolyzed with water and dried over potassium carbonate. Distillation gave 1.7 g (46% yield) of XIII.

1-Trimethylsilyl-3-ethyldimethylsilyl-3-phenylpropyne (VIIIb)

To a solution of 6.2 g (0.033 mol) of 1-trimethylsilyl-3-phenylpropyne [5] in 15 ml of hexane was added 21 ml of 1.6 *M* butyllithium/hexane solution with dry ice/acetone cooling. The mixture was refluxed for 30 min and 6.1 g (0.05 mol) of ethyldimethylchlorosilane was added at room temperature. The mixture was hydrolyzed with water and the organic layer was dried over potassium carbonate. Distillation afforded 2.0 g (22% yield) of VIIIb, b.p. 100°C/2 torr; IR (cm^{-1}) 2185 (ν(C≡C); NMR (δ) —0.01 and 0.03 (Me_2Si, 6H), 0.19 (Me_3Si, s, 9H), 0.5—1.1 (C_2H_5, m, 5H), 3.16 (HCPh, s, 1H) and 7.0—7.3 (ring protons, m, 5H) (Found: C, 70.30; H, 9.84. $C_{16}H_{26}Si_2$ calcd.: C, 70.00; H, 9.55%).

1-Ethyldimethylsilyl-3-trimethylsilyl-3-phenylpropadiene (XIX)

To a solution of 2.1 g of a mixture consisting of VIIIa and XVII in a ratio of 3/1 and 0.4 g (3 mmol) of TMEDA in 2 ml of hexane was added 3 ml of 1.2 *M* butyllithium/hexane solution. The mixture was refluxed for 30 min and hydrolyzed with water. Distillation of the dried organic layer afforded 2.0 g of a colorless liquid consisting of VIIIa, XVII and XIX in a ratio of 4/3/4. Pure XIX was isolated by preparative GLC. IR (cm^{-1}) 1912; NMR (δ) 0.22 (Me_2Si, s, 6H), 0.25 (Me_3Si, s, 9H), 0.5—1.2 (C_2H_5, m, 5H), 4.76 (HC=C, s, 1H) and 7.0—7.3 (ring protons, m, 5H) (Found: C, 70.08; H, 9.77. $C_{16}H_{26}Si_2$ calcd.: C, 70.00; H, 9.55%).

Photolysis of 1-silyl-3-trimethylsilyl-3-phenylpropynes

For the purpose of isolating products from photolysis reactions, crude 1-silyl-3-trimethylsilyl-3-phenylpropynes obtained by fractional distillation were used as starting materials. A solution of 0.906 g of VIIa including 15% of XVI in 100 ml of dry hexane was photolyzed upon irradiation with a high-pressure mercury lamp for 11 h. The solvent was evaporated and the residue was distilled under reduced pressure to give a volatile product boiling up to 200°C/2 torr. GLC analysis of the distillate showed peaks having an area ratio of 5/95. Both peaks were separated by preparative GLC. The mass, IR and proton NMR data for the isolated products are listed in Table 3.

The ratio of the silyl-substituted propynes to propadienes in the equilibrium mixture for photolysis of compounds, VI—IX, XV and XVIII, was determined by using pure compounds isolated by GLC. In a carefully dried ca. 10-ml quartz tube was placed a solution of an exactly weighed sample of VI—IX, XV or XVIII and a known quantity of cetane (as internal standard) in hexane. The solution was purged with dry nitrogen and the tube was sealed with a serum cap. It was then irradiated externally with a high-pressure mercury lamp with a quartz filter at room temperature. The reaction product was analyzed by GLC. The conditions and results are given in Table 4.

Photolysis of 1-pentamethyldisilanyl-1,3-bis(trimethylsilyl)-3-phenylpropadiene (X)

A solution of 0.4313 g (1.11 mmol) of X in 100 ml of dry methanol was irradiated with a high-pressure mercury lamp for 41 h. At this stage, 100% of the starting X was photolyzed. The solution was concentrated by evaporation and the residue was distilled under reduced pressure to give a volatile product boiling up to 220°C at 3 torr. GLC analysis of the distillate using cetane as an internal standard revealed that 1,1-bis(trimethylsilyl)-3-pentamethyldisilanyl-3-phenylpropadiene (XX) was produced in 46% yield. Compound XX was isolat by GLC.

Photolysis of 1-(2'-phenyltetramethyldisilanyl)-1,3-bis(trimethylsilyl)-3-phenylpropadiene (XI)

A mixture of 0.5640 g (1.25 mmol) of XI and 0.1461 g (0.58 mmol) of cetane in 100 ml of hexane was irradiated for 77 h. At this point, the conversion of the starting XI was 100%. The solvent was evaporated off, and the residue was analyzed by GLC, turning out to be 1,1-bis(trimethylsilyl)-3-(2′-phenyltetramethyldisilanyl)-3-phenylpropadiene XXI (37% yield) and two products (19% combined yield, IR 2130, 2900; mass spectrum *m/e* 318 (M^+); Mol. wt. calcd. for $C_{17}H_{30}Si_3$: 318.69) which could not be separated by preparative GLC.

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