

CHEMISTRY OF ORGANOSILICON COMPOUNDS

CXXIII *. NEW PHOTOCHEMICAL AND THERMAL DEGRADATION REACTIONS OF VINYLDISILANES TO VINYLSILANES THROUGH (η^3 -1-SILAPROPENYL)TRICARBONYLIRON COMPLEXES

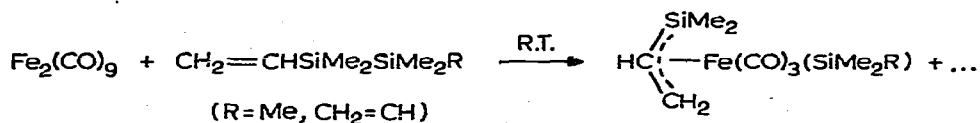
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Summary

Vinylsilanes (II) of the type $R^1CH=CR^2SiMe_2SiMe_3$ (a, $R^1 = Ph$, $R^2 = H$; b, $R^1 = H$, $R^2 = Me$; c, $R^1 = R^2 = H$) and $(R^1CH=CHSiMeR^3)_2$ (d, $R^1 = Ph$, $R^3 = Me$; e, $R^1 = H$, $R^3 = Ph$) undergo a novel degradation reaction to give the corresponding vinylsilanes, $R^1CH=CR^2SiMe_3$ and $(R^1CH=CH)_2SiMeR^3$, respectively, under photochemical or thermal conditions in the presence of a stoichiometric amount of pentacarbonyliron. Two α -styryldisilanes (IIf, $CH_2=CPhSiMe_2SiMe_3$ and IIg, $[CH_2=CPhSiMe_2]_2$) undergo similar degradation reactions, but gave β -styrylsilanes. In the presence of additional benzophenone, IIb, IIc, and IIf gave (*E*)- $Me_3SiCH=CRSiMe_2OCHPh_2$ (b, $R = Me$; c, $R = H$; f, $R = Ph$) under either photochemical or thermal conditions, but IIa gave $Ph\bar{C}=CHSiMe_2OCHPh_2$ under photochemical, or $Ph_2CHSiMe_3$ under thermal conditions as main product. Mechanisms involving η^3 -1-silapropenyltricarbonyliron intermediates are proposed, and indeed separately prepared (η^3 -1-silapropenyl)(trimethylsilyl)tricarbonyliron gave the same products under similar conditions.

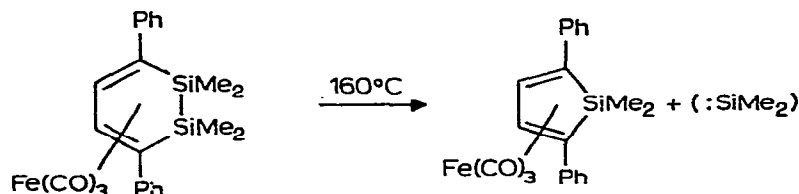
Introduction

In a recent paper [1], we reported the preparation of (η^3 -1-silapropenyl)tricarbonyliron complexes by the reaction of enneacarbonyldiiron with vinyl-disilanes. More recently, we have found that (η^4 -1,2-disilacyclohexadiene)tricar-



* For part CXXII see ref. 25.

bonylirons undergo a facile ring contraction on thermolysis to give (η^4 -silacyclopentadiene) tricarbonyliron complexes [2], where similar (η^3 -1-silapropenyl)-iron complexes were proposed as intermediates.

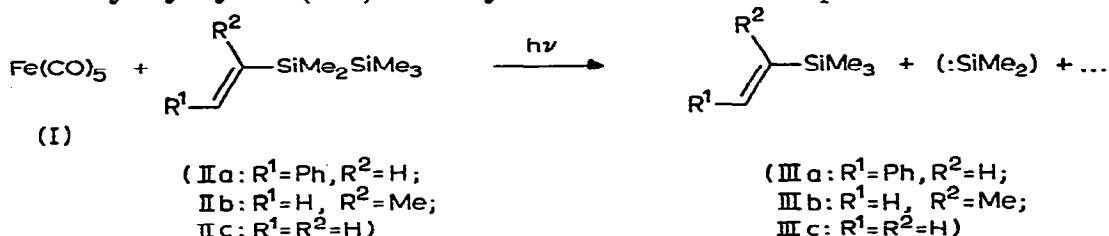


In the course of further studies on the reaction of carbonyliron compounds with vinylsilanes, we have found that such a silylene extrusion reaction is general. We report here that vinyldisilanes give the corresponding vinylsilanes in moderate yields either on irradiation or on thermolysis in the presence of pentacarbonyliron.

Results and discussion

Photochemical reactions of pentacarbonyliron with vinyldisilanes

A solution of pentacarbonyliron (I) and *trans*-pentamethyldisilanylstyrene (IIa) in hexane was irradiated for 3 h with a 450 W high-pressure mercury arc lamp through a Pyrex filter at room temperature under argon. During the irradiation, the color of the reaction mixture changed from yellow to dark brown. The dark brown reaction mixture was separated by TLC on silica gel to give *trans*-trimethylsilylstyrene (IIIa) in 38% yield as the sole volatile product.



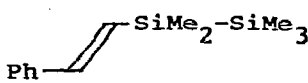
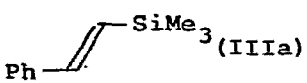
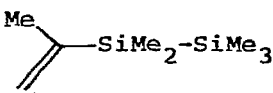
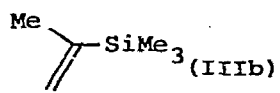
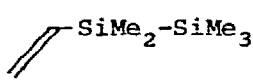
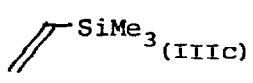
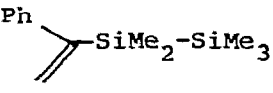
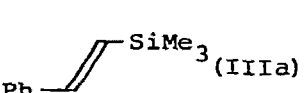
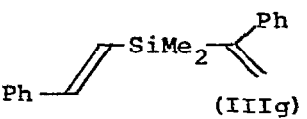
The fate of the silylene unit is not clear, but it results in the formation of uncharacterized polymeric materials. When the resulting reaction mixture was irradiated further after adding triphenylphosphine, the yield of IIIa increased to 46% yield. It is well known that the photochemical reaction of an olefin-iron complex with triphenylphosphine liberates the olefin ligand from the complex [3].

Similarly, isopropenylpentamethyldisilane (IIb) and vinylpentamethyldisilane (IIc) are found to react with I under the same conditions to give IIIb and IIIc, respectively. 1,2-Divinylsilylanes, as well as monovinylsilylanes, react with I to give the corresponding divinylsilylanes. The results are summarized in Table 1.

Interestingly, the reaction of α -styrylpentamethyldisilane (IIf) with I gives only IIIa in 47% yield.

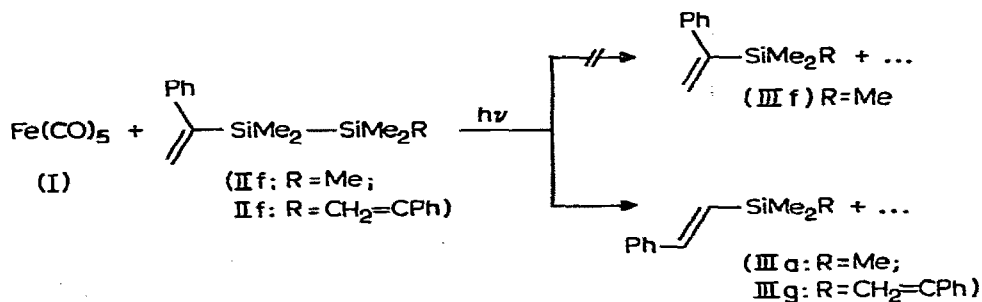
Since α -styryltrimethylsilyl (III f) did not react with I under the reaction conditions, IIIa cannot have been formed by isomerization of III f. Similarly, 1,2-di- α -styryltetramethyldisilane (IIg) gave *trans*- β -styryl- α -styryldimethylsilyl

Table 1 Photochemical Reactions of Vinyldisilanes with (I)

Vinyldisilane	Solvent	Vinylsilane	Yield (%)
 (IIa)	Hexane	 (IIIa)	46 ^a
 (IIb)	xylene	 (IIIb)	64 ^b
 (IIc)	xylene	 (IIIc)	47 ^b
$\left(\text{Ph}-\text{CH}=\text{CH}-\text{SiMe}_2 \right)_2$ (II d)	hexane	$\left(\text{Ph}-\text{CH}=\text{CH}-\text{SiMe}_2 \right)_2$ (III d)	45 ^a
$\left(\text{CH}_2=\text{CH}-\text{SiPhMe} \right)_2$ (II e)	hexane	$\left(\text{CH}_2=\text{CH}-\text{SiPhMe} \right)_2$ (III e)	19 ^a
 (II f)	hexane	 (III a)	47 ^a
$\left(\text{Ph}-\text{CH}=\text{CH}-\text{SiMe}_2 \right)_2$ (II g)	hexane	 (III g)	42 ^a

a) Yield of isolated materials. b) Yield was determined by GLC.

(IIIg) on irradiation in the presence of I in 42% yield.



The photochemical reaction of II f with I has been carried out under various

Table 2 Photochemical Reactions of (I) with (II_f)

mmol		Solvent	Conditions		Yield (%) ^a
(I)	(II _f)		Filter	Time(h)	
0	0.41	hexane	Pyrex	3	0
0.06	0.44	hexane	Pyrex	3.5	72 ^b
0.23	0.45	hexane	Pyrex	1.5	50 ^b
0.44	0.43	hexane	Pyrex	3	40
0.70	0.43	hexane	Pyrex	3	41
1.24	0.41	hexane	Pyrex	2	41
0.46	0.41	hexane	Pyrex	2.5	47 ^c
0.70	0.45	hexane	—	2	34
0.45	0.42	benzene	Pyrex	3	34
0.46	0.42	THF	Pyrex	2	44

a) Yield of isolated material.

b) Based on starting (I).

c) After the post-treatment.

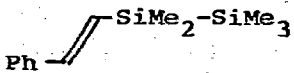
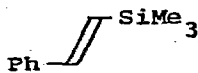
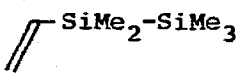
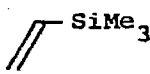
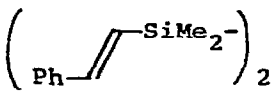
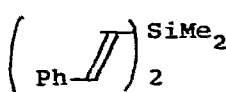
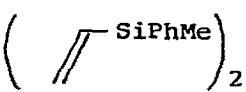
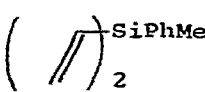
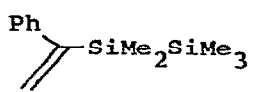
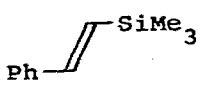
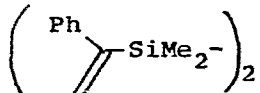
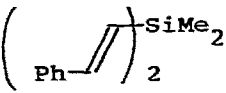
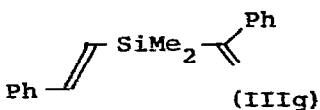
conditions. The results are summarized in Table 2, which shows that an equimolar amount of I is required for the reaction to be completed, that is, I does not catalyze the silylene extrusion reaction. The reaction was not affected by nature of the solvent employed, so that the silylene extrusion reaction proceeded similarly in benzene and THF. Although vinylsilanes undergo photochemical 1,2-[4a] and 1,3-shifts [4a,b] of a silyl group, no indication of rearrangement was observed under the reaction conditions. Presumably, light absorption occurs only in pentacarbonyliron.

Thermal reactions of pentacarbonyliron (I) with vinylsilanes

The thermal reaction of I with II at 160°C occurs similarly to give the corresponding vinylsilanes. When a solution of I and II_a in hexane was heated at 160°C for 24 h under an argon atmosphere in a small high-pressure vessel, III_a was obtained in 72% yield as the sole volatile product.

The results of the thermal reaction are summarized in Table 3. In contrast to the photochemical reaction, the yield of III_c is significantly lower and III_e could

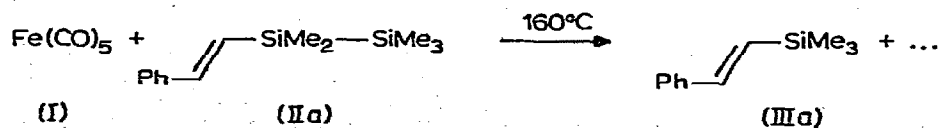
Table 3 Thermal Reactions of (I) with (II)

Vinyldisilane	Vinylsilane	Yield ^a (%)
 (IIa)	 (IIIa)	72
 (IIc)	 (IIIc)	8 ^b
 (IIId)	 (IIIId)	59
 (IIe)	 (IIIe)	0
 (IIIf)	 (IIIIf)	59
 (IIIg)	 (IIIId)	37
	 (IIIIf)	14

a) Yield of isolated materials.

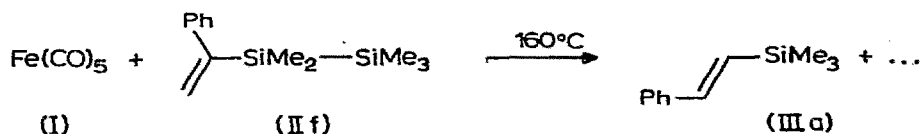
b) Determined by GLC.

not be isolated. Under these reaction conditions, unsubstituted vinylsilanes such

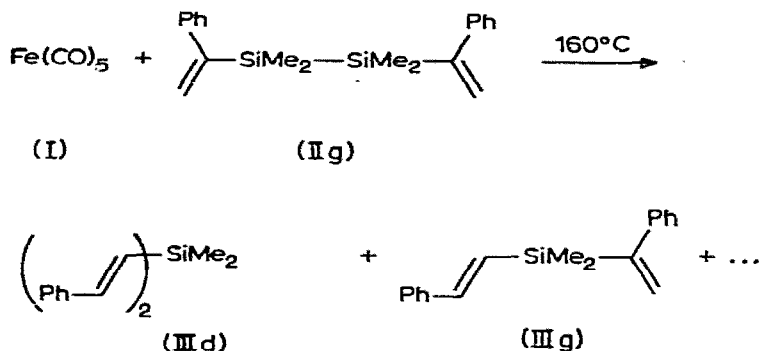


as IIIc and IIIe are found to undergo oligomerization. Therefore, the low yields in these cases could partly be due to the oligomerization.

The thermal reaction of I with II f gave III a in 59% yield, similar to the corresponding photoreaction.



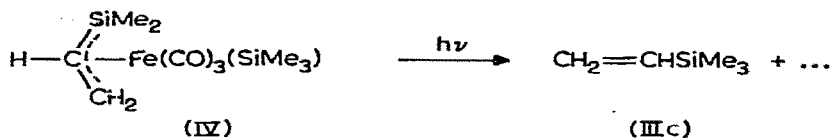
However, the reaction of I with II g gave III d (37%) and III g (14%). Since only III g was obtained in the corresponding photochemical reaction, III g was thought to undergo isomerization under the thermal conditions. Di- α -styryldimethylsilane is found to isomerize to III g (63% yield) when it is heated at 160°C for 25 h in the presence of I. This fact indicates that thermal isomerization of α -styryl to β -styryl on silicon is possible under these conditions. However, isomerization of isolated III g to III d in the presence of I proceeds very slowly. Therefore, the difference in product distribution between photochemical and thermal conditions is unclear.



Although an active iron species "Fe(CO)₄" is known to be generated from enneacarbonyldiiron at low temperature [5], the reaction of enneacarbonyldiiron with II f gives only a trace amount of III a at 80°C for 16 h. Apparently, a more elevated temperature is required for the thermal formation of vinylsilanes from the corresponding vinyldisilanes.

Photochemical reaction of (η^3 -1-silapropenyl)(trimethylsilyl)tricarbonyliron

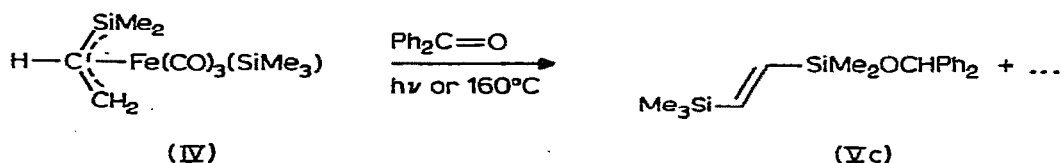
Irradiation of (η^3 -1-silapropenyl)(trimethylsilyl)carbonyl iron (IV) in hexane gave vinyltrimethylsilane (III c) in 42% yield. Since the yield of III c is compara-



ble to the photochemical reaction of II c with I, the existence of η^3 -1-silapropenyl complexes such as IV is strongly suggested as an intermediate.

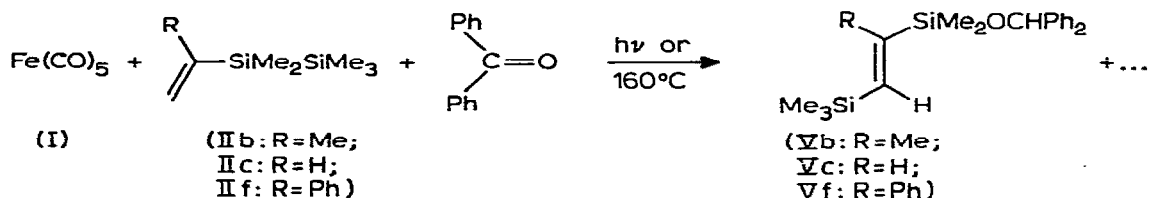
It is also interesting to note that (η^3 -1-silapropenyl)(trimethylsilyl)tricarbonyliron (IV) reacts with benzophenone either on irradiation or on thermolysis to

give (*E*)-1-(diphenylmethoxy)dimethylsilyl-2-trimethylsilylethylene (Vc).



Photochemical and thermal reactions of II and I in the presence of benzophenone

Since IV was found to react photochemically with benzophenone, it was interesting to examine the photochemical and thermal reactions of I with II in the presence of benzophenone in an attempt to trap the intermediate. A solution of I, II and benzophenone in hexane was irradiated with a 450 W high-pressure mercury arc lamp through a Pyrex filter for 3 h at room temperature. A similar solution was also heated at 160°C in a small high-pressure vessel for 29–30 h. Vinyldisilanes (IIb, IIc and IIf) gave (*E*)-1-(diphenylmethoxy)dimethylsilyl-2-trimethylsilylethylene derivatives (V) in 20–50% yields in these



reactions. The results are summarized in Table 4. The structures of V were determined on the basis of various spectroscopic data. The proton NMR spectrum of Vf shows two Si—CH₃ signals at δ -0.27 (9 H, s) and 0.03 (6 H, s) ppm, a C—H signal at 5.60 (1 H, s) ppm, a vinyl proton signal at 6.25 (1 H, s) ppm and phenyl proton signals at 6.54–7.14 (15 H, m) ppm. As compared with the spectra of (*E*)- and (*Z*)-1-phenyl-1-methoxydimethylsilyl-2-trimethylsilylethylene [6], the stereochemical relation between two silyl groups of Vf was determined to be *E*-configuration. The proton NMR spectrum of Vb shows an allylic-CH₃ signal at δ 1.76 (3 H, d, *J* = 1.5 Hz) ppm and a vinyl proton signal at 6.03 (1 H, q, *J* 1.5 Hz) ppm in addition to the signals due to the silyl and phenyl groups. In the spectra of (*E*)- and (*Z*)-1-methyl-2-trimethylsilylethylene [7], the allylic coupling constant was observed to be *J* 1.4 Hz for the *E*-isomer, and this type

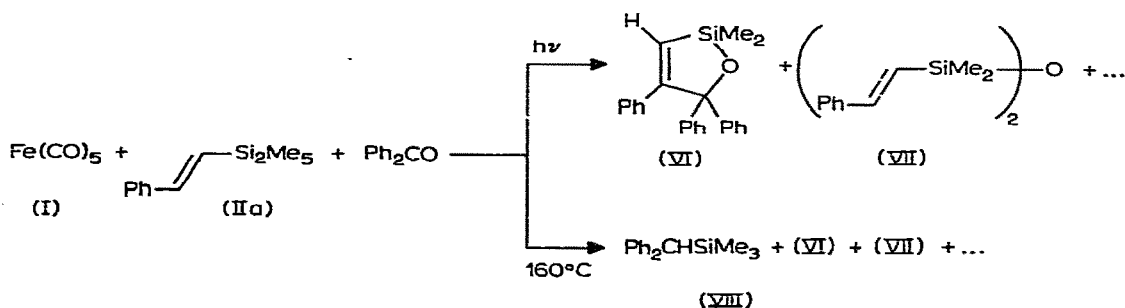
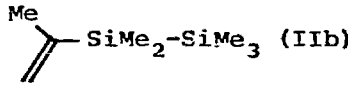
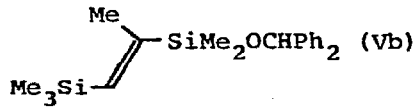
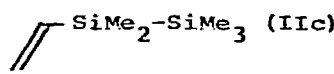
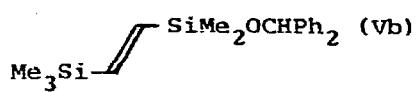
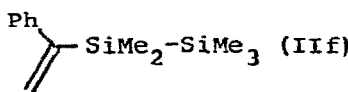
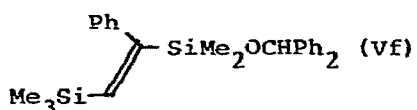


Table 4 Photochemical and Thermal Reactions of (I) with (II) in the Presence of Benzophenone

Vinylsilane	Reaction Condition	(V)	Yield ^a (%)
 (IIb)	hν	 (Vb)	25
 (IIc)	hν	 (Vb)	29
	160°C	(Vb)	16
 (IIf)	hν	 (Vf)	47
	160°C	(Vf)	27

^aYield of isolated materials.

of coupling constant was not detected for the *Z*-isomer. A similar observation was reported for (*E*)- and (*Z*)-1-methyl-2-pentamethyldisilanylene ethylene [8]. Thus, the stereochemistry between these two silyl groups in Vb is assigned to be also *E*-configuration.

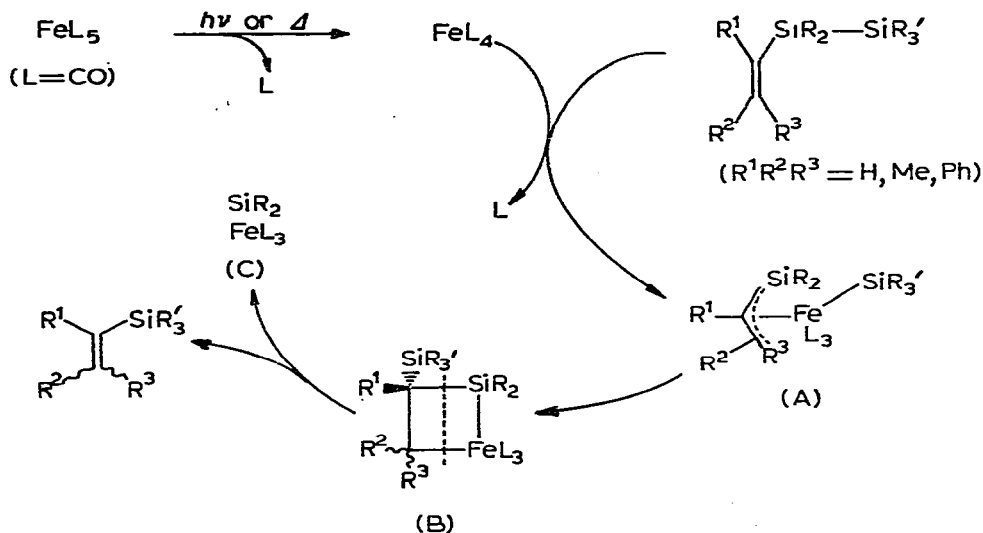
The reaction of I with IIc in the presence of benzophenone gives Vc either on photolysis or on thermolysis. However, in contrast with these vinylsilanes, in the presence of benzophenone, IIa gives different types of products in the reaction with I.

The mechanism of the reactions

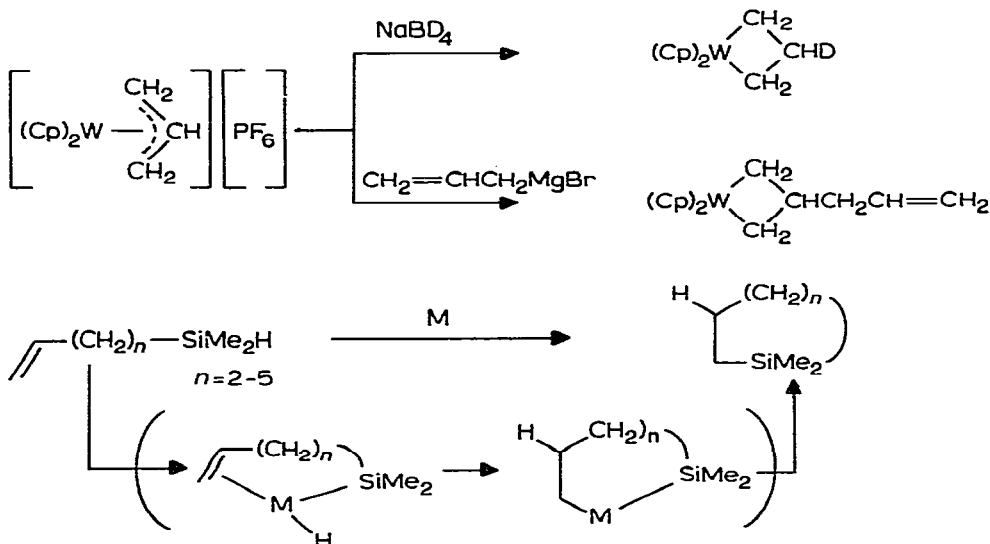
The reaction mechanisms are not necessarily unequivocal but the present knowledge of the reaction mode of the transition-metal catalyzed reactions of olefins and the Si-Si bond leads us to suggest the mechanisms shown in Scheme 1.

Under photochemical and thermal conditions, pentacarbonyliron is known to generate an active species, "Fe(CO)₄" [9], which, in the second step, reacts with II to form an η³-1-silapropenylyron complex (A). The intermediate (A) isomerizes to a metallasilacyclobutane (B) by migration of the SiR₃' group. Similar transformation of a π-allyl complex to a metallacyclobutane complex has been reported in the reaction of an π-allyltungsten complex [10], and intramolecular π → σ transformation involving a silicon-transition metal bond has been also

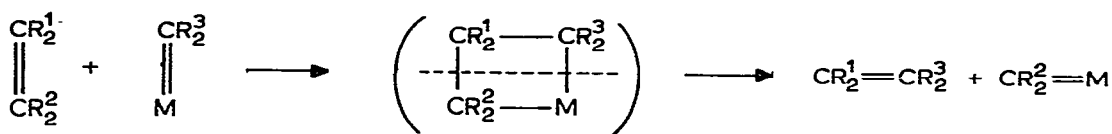
SCHEME 1. The mechanism of the reaction of I with II.



suggested in transition metal-catalyzed intramolecular hydrosilylation [11].

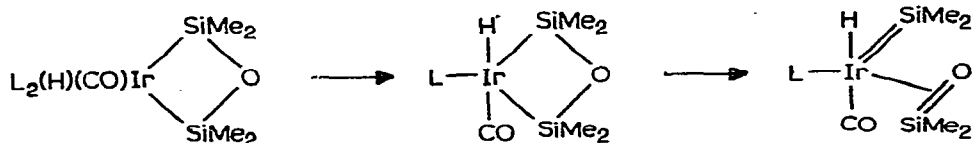


The metallasilacyclobutane may cause ring cleavage to give an olefin and a silylene complex (C). This step is analogous to the scission of metallacyclobutane intermediates in the proposed mechanism for olefin metathesis [12].

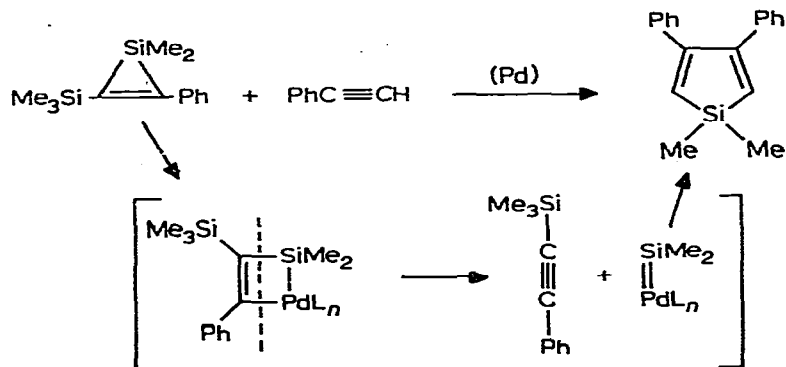


Recently, Greene and Curtis have reported that cyclometalladisiloxane is an

effective catalyst for siloxane metathesis which undergoes similar ring cleavage of the cyclometalladisiloxane [13].

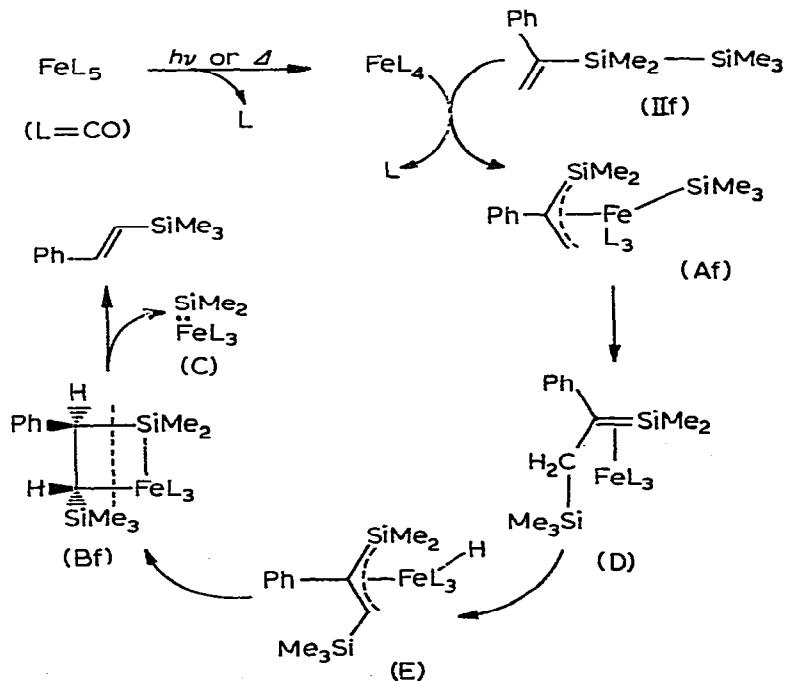


We have also suggested similar ring cleavage in the reaction of a silacyclopropene with phenylacetylene catalyzed by palladium complex [6a].



By ring cleavage of B, the silylene complex C forms together with the olefin. We have reported recently an example of such a silylene complex [14].

SCHEME 2. The mechanism of the reaction of I with II f.

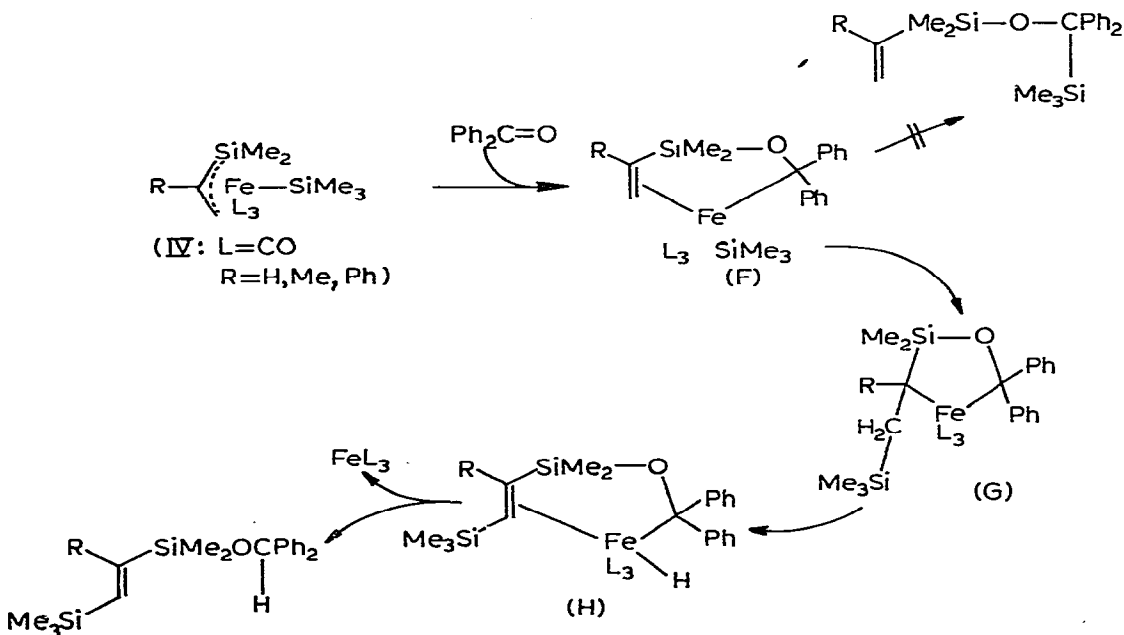


In the case of IIf (see Scheme 2), a trimethylsilyl group on (Af) is forced to migrate to the terminal carbon to give D due to the steric hindrance between phenyl and trimethylsilyl groups. The silaethene complex D formed gives another η^3 -1-silapropenyliron complex (E) by β -elimination. As described above, E should give *trans*-trimethylsilylstyrene via metallasilacyclobutane (Bf).

The stereochemistry observed in the product may be accounted for the structure of the metallasilacyclobutane B, which is determined by the process for formation of B. The substituent groups on the neighboring carbon atoms are forced into the *E*-configuration owing to steric hindrance. Therefore, the silylene extrusion reactions of I with II give the corresponding *trans*-olefins stereospecifically.

A possible mechanism of the reaction of I with II in the presence of benzophenone is shown in the Scheme 3.

SCHEME 3. A mechanism of the reaction of I with II in the presence of benzophenone.

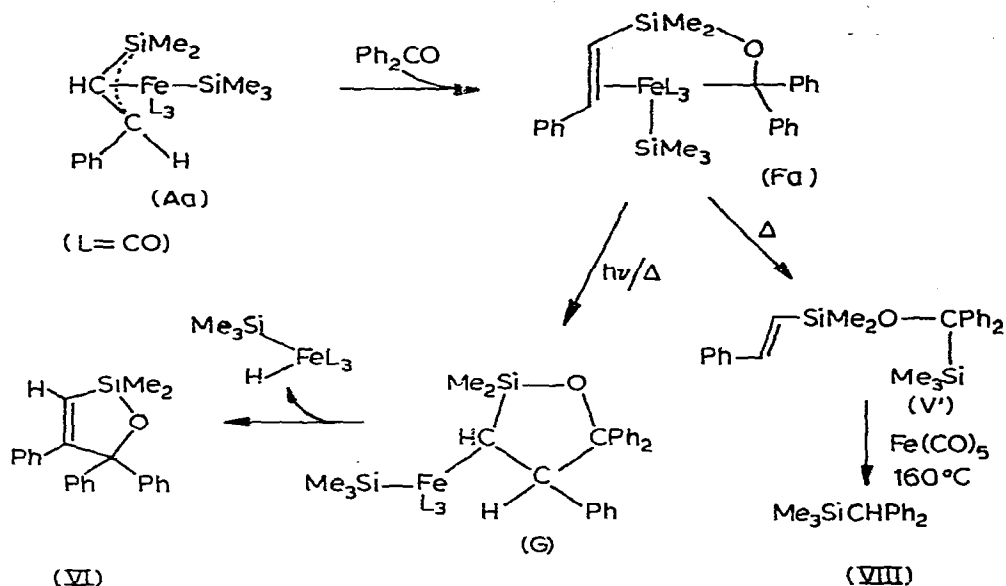


(η^3 -1-Silapropenyl)(trimethylsilyl)tricarbonyliron (IV) reacts with benzophenone to give F, and subsequently the silyl group on F migrates from iron to the vinyl carbon to give G. G is transformed to a hydride complex H by β -elimination, which yields the product by reductive elimination.

The photochemical reaction of IIa with I in the presence of benzophenone gives VI and VII in 24 and 12% yield, respectively, together with minor unidentified products. On the other hand, the thermal reaction of IIa gives VIII in 32% yield as a major product together with VI and VII. Formation of these products are also rationalized by the reaction of η^3 -1-silapropenyltricarbonyliron as shown in Scheme 4.

Fa is presumably forced to isomerize to G because of steric hindrance between the phenyl and trimethylsilyl groups. In the photochemical reaction, G gives VI by β -elimination of a hydride complex. Under the thermal conditions, the main product was VIII, presumably through V' which can be reduced to give VIII un-

SCHEME 4. The mechanism of the reaction of I with IIa in the presence of benzophenone.



der the reaction conditions. This process is proved by a separate experiment, and a similar reduction of alkoxydisilanes is also observed in the thermal reaction of (diphenylmethoxy) (phenyl)dimethylsilane with pentacarbonyliron (see Experimental).

Experimental

Materials

Enneacarbonyliron was prepared from pentacarbonyliron according to the procedure reported by King [15].

Solvents, hexane, xylene, benzene and THF, were dried over metallic sodium and distilled before use.

Vinylpentamethyldisilane (IIc) [16,17] and isopropenylpentamethyldisilane (IIb) [18] were prepared by established procedures. Other vinyldisilanes were prepared as follows.

α -Styrylpentamethyldisilane (IIf). To a Grignard solution prepared from 3.00 g (0.12 g-atom) of magnesium and 20.0 g (0.11 mol) of α -bromostyrene in ether was added 10.0 g (0.06 mol) of chloropentamethyldisilane. After the addition was completed, the reaction mixture was refluxed for 10 h, and the mixture was then hydrolyzed with water and worked up in the usual way. Distillation gave 8.0 g (0.034 mol, 57% yield) of α -styrylpentamethyldisilane: b.p. 75–80°C/3 mmHg; n_D^{23} 1.5005; mass spectrum (rel. int. %): M^+ 234 (31.6), m/e 73 (100); IR (neat): 2950, 1245, 830 cm^{-1} ; NMR (CCl_4): δ (ppm) 0.00 (9 H, s, Si- CH_3), 0.23 (6 H, s, Si- CH_3), 5.55 (1 H, d, J 3.0 Hz, =C- H), 5.90 (1 H, d, J 3.0 Hz, =C- H), 7.25–7.50 (5 H, m, Ph). Anal. Found: C, 66.77; H, 9.39. $\text{C}_{13}\text{H}_{22}\text{Si}_2$ calcd.: C, 66.59; H, 9.46%.

1,2-Di(α -styryl)tetramethyldisilane (IIg). Similarly, the reaction of 1,2-dichlo-

rotetramethyldisilane (9.4 g, 0.05 mol) with a Grignard reagent prepared from 3.0 g (0.12 g-atom) of magnesium and 20.0 g (0.11 mol) of α -bromostyrene gave 11.0 g (0.034 mol, 68% yield) of 1,2-di- α -styryltetramethyldisilane; b.p. 114–115°C/0.5 mmHg; D_D^{23} 1.5640; mass spectrum (rel. int. %): M^+ 322 (7.8), m/e 135 (100); IR (neat): 2950, 1245, 930, 840, 790, 700 cm^{-1} ; NMR (CCl_4): δ (ppm) 0.13 (12 H, s, Si- CH_3), 5.50 (2 H, d, J 3.0 Hz, =C- H), 5.80 (2 H, d, J 3.0 Hz, =C- H), 7.00–7.40 (10 H, m, Ph). Anal. Found: C, 74.63; H, 8.38. $\text{C}_{20}\text{H}_{26}\text{Si}_2$ calcd.: C, 74.46; H, 8.12%.

trans-Styrylpentamethyldisilane (IIa). The reaction of chloropentamethyldisilane (10.0 g, 0.06 mol) with a Grignard reagent prepared from 2.00 g (0.08 g-atom) of magnesium and 11.0 g (0.06 mol) of *trans*-bromostyrene gave 9.2 g (0.038 mol, 63% yield) of *trans*-styrylpentamethyldisilane; b.p. 73–78°C/0.7 mmHg; n_D^{23} 1.4990; mass spectrum (rel. int. %) M^+ 234 (25.5), m/e 73 (100); IR (neat): 2950, 1245, 830, 790 cm^{-1} ; NMR (CCl_4): δ (ppm) 0.09 (9 H, s, Si- CH_3), 0.21 (6 H, s, Si- CH_3), 6.47 (1 H, d, J 19.0 Hz, =C- H), 6.92 (1 H, d, J 19.0 Hz, =CPh- H), 7.25–7.55 (5 H, m, Ph). Anal. C, 66.31; H, 9.70. $\text{C}_{13}\text{H}_{22}\text{Si}_2$ calcd.: C, 66.59; H, 9.46%.

1,2-Di-*trans*-styryltetramethyldisilane (IIc). Similarly, the reaction of 1,2-dichlorotetramethyldisilane (7.1 g, 0.038 mol) with a Grignard reagent prepared from 2.2 g (0.09 g-atom) of magnesium and 14.0 g (0.07 mol) of *trans*-bromostyrene gave 8.0 g (0.025 mol, 66% yield) of 1,2-di-*trans*-styryltetramethyldisilane; b.p. 138–141°C/0.5 mmHg; m.p. 58.0–58.5°C; mass spectrum (rel. int. %) M^+ 322 (4.2), m/e 218 (100); IR (KBr): 2950, 1245, 990, 840, 790 cm^{-1} ; NMR (CCl_4): δ (ppm) 0.23 (12 H, s, Si- CH_3), 6.40 (2 H, d, J 19.0 Hz, =C- H), 6.95 (2 H, d, J 19.0 Hz, =CPh- H), 7.00–7.50 (10 H, m, Ph). Anal. Found: C, 74.65; H, 8.40. $\text{C}_{20}\text{H}_{26}\text{Si}_2$ calcd.: C, 74.46; H, 8.12%.

1,2-Dimethyl-1,2-diphenyldivinylsilane (IIe). To a Grignard reagent prepared from 12.0 g (0.2 mol) of magnesium and vinyl chloride in THF was added 62.0 g (0.2 mol) of 1,2-dichloro-1,2-dimethyldiphenyldisilane. The mixture was refluxed for 15 h and it was then hydrolyzed. Distillation through a short column packed with glass helices gave 47.7 g (0.16 mol, 80% yield) of IIe; b.p. 158–161°C/5 mmHg; n_D^{23} 1.5815; mass spectrum (rel. int. %): M^+ 294 (3.0), m/e 121 (100); IR (neat): 3020, 2950, 1240, 1105, 995, 940, 760 cm^{-1} ; NMR (CCl_4): δ (ppm) 0.40 (6 H, s, Si- CH_3), 5.40–6.20 (6 H, m, $\text{CH}_2=\text{CH}$), 7.10–7.50 (10 H, m, Ph). Anal. Found: C, 73.51; H, 7.42. $\text{C}_{18}\text{H}_{22}\text{Si}_2$ calcd.: C, 73.40; H, 7.53%.

Authentic samples of vinylsilanes were prepared by methods described in literatures: *trans*-trimethylsilylstyrene [19], vinyltrimethylsilane [20], isopropenyltrimethylsilane [21], di-*trans*-styryltrimethylsilane [22], and divinylmethylphenylsilane [20].

Preparation of (η^3 -1,1-dimethyl-1-silapropenyl)(trimethylsilyl)tricarbonyliron (IV)

Enneacarbonyldiiron (200.0 mg, 0.55 mmol), vinylpentamethyldisilane (IIc) (230.0 mg, 1.45 mmol) and benzene (10 ml) were placed in a 20 ml two-necked flask equipped with a mechanical stirrer under an argon atmosphere. The yellow-orange suspension was stirred at room temperature for 17 h under an argon atmosphere. The solvent and volatile materials were evaporated and the residue

was distilled under reduced pressure ($\sim 10^{-3}$ mmHg) to give a yellow-brown oil. A hexane solution of the oil was purified by TLC on silica gel. After elution with hexane, the solution was evaporated to give a residual oil which was fractionated with a short column to give (η^3 -1,1-dimethyl-1-silapropenyl)(trimethylsilyl)tricarbonyliron (IV) in 61% yield (100.0 mg, 0.34 mmol); b.p. 45.0°C/0.005 mmHg; n_D^{16} 1.5065; mass spectrum (rel. int. %): M^+ 298(2.9), m/e 270 (4.9), 242 (6.8), 214 (21.6), 158 (23.9), 143 (21.0), 85 (54.4), 73 (100); IR (neat) 2940m, 2880sh, 2025s, 1995vs, 1975vs, 1400w, 1315m, 1245s, 1195m, 830s, 795s cm^{-1} ; $^1\text{H NMR}$ (CS_2): δ (ppm) 0.15 (3 H, s, Si- CH_3), 0.27 (9 H, s, Si- CH_3), 0.38 (3 H, s, Si- CH_3), 2.29 (1 H, dd, J 15.0, 10.0 Hz, H^1), 2.68 (1 H, d, J 15.0 Hz, H^2), 3.17 (2 H, d, J 10.0 Hz, H^3); $^{13}\text{C NMR}$ (CS_2 , TMS = 0): δ (ppm) -3.0, -1.0, 0.0, 43.0, 46.0, 212.0; UV (hexane) λ_{max} (nm): 212.0 ($\epsilon = 20500$), 221.0 (sh, $\epsilon = 17400$), 236.0 (sh, $\epsilon = 12600$), 270.0 (sh, $\epsilon = 7000$). Anal. Found: C, 40.43; H, 5.86. $\text{C}_{10}\text{H}_{18}\text{O}_3\text{Si}_2\text{Fe}$ calcd.: C, 40.27; H, 6.08%.

Photochemical reactions of pentacarbonyliron (I) with vinyldisilanes (II)

A solution of I (86.2 mg, 0.44 mmol) and IIa (103.2 mg, 0.44 mmol) in hexane (8 ml) was deoxygenated by bubbling a stream of argon and irradiation for 2 h with a 450 W high pressure mercury arc lamp through a Pyrex filter at room temperature under an argon atmosphere. The color of the reaction mixture changed from yellow to dark-brown during the reaction. After evaporation of volatile materials, the dark residue was subjected to TLC on silica gel. IIIa was isolated in 38% yield (40.0 mg, 0.17 mmol).

Similarly, other vinyldisilanes gave the corresponding vinylsilanes in the reaction with I as shown in Table 1. These products were identified by comparison of GLC and NMR spectra with those of authentic samples.

The structure of (α -styryl) (β -styryl)dimethylsilane (IIIg) was determined on the basis of the following physical data; an oil; n_D^{26} 1.5660; mass spectrum (rel. int. %): M^+ 264 (74.0), m/e 145 (100); IR (neat): 3050, 2950, 1600, 1250, 840 cm^{-1} ; NMR (CDCl_3): δ (ppm) 0.28 (6 H, s, Si- CH_3), 5.66 (1 H, d, J 2.5 Hz, =C- H), 5.91 (1 H, d, J 2.5 Hz, =C- H), 6.45 (1 H, d, J 19.0 Hz, =C- H), 6.99 (1 H, d, J 19.0 Hz, =C- H), 7.23 (10 H, brs, Ph). Anal. Found: C, 81.51; H, 7.43. $\text{C}_{18}\text{H}_{20}\text{Si}$ calcd.: C, 81.76; H, 7.62%.

Thermal reactions of pentacarbonyliron (I) with vinyldisilanes (II)

A typical example is shown for IIa: a solution of I (137.0 mg, 0.70 mmol) and IIa (103.2 mg, 0.44 mmol) in hexane (10 ml) was deoxygenated by bubbling a stream of argon and heating at 160°C for 24 h under an argon atmosphere in a small high-pressure vessel. A black solid, presumably iron powder, deposited from the reaction mixture and a pale-yellow solution was obtained. The mixture was filtered and concentrated under reduced pressure. The residue was subjected to TLC on silica gel and 49.5 mg (0.28 mmol, 72% yield) of *trans*-trimethylsilylstyrene (IIIe) was isolated.

Thermal reactions of pentacarbonyliron (I) with 1,2-di- α -styryltetramethyldisilane (IIg)

In a similar manner, a mixture of IIg (102.0 mg, 0.316 mmol) and I (0.1 ml) dissolved in hexane (10 ml) was heated at 160°C for 26 h. From the reaction

mixture, 6.6 mg of IIg, 11.0 mg (14.2%) of IIIg and 29.0 mg (37.2%) of IIId were separated by preparative TLC.

Isomerization of di- α -styryldimethylsilane

A mixture of 100 mg (0.378 mmol) of di- α -styryldimethylsilane (I) (0.1 ml) was heated at 160°C for 25 h. From the mixture, 55.4 mg of di- α -styryldimethylsilane was recovered and 27.7 mg (63%) of IIIg was separated.

Irradiation of IV

A solution of IV (90.0 mg, 0.30 mmol) and hexane (24.0 mg, 0.23 mmol) as an internal standard for GLC analysis in xylene (8 ml) was irradiated with a 450 W high-pressure mercury arc lamp through a Pyrex filter for 3 h at room temperature. By GLC analysis of the reaction mixture, vinyltrimethylsilane was obtained in 42% yield (by GLC: column, 30% Apiezon L, 50°C, H₂ gas).

Photochemical and thermal reactions of IV with benzophenone

A solution of IV (150.0 mg, 0.50 mmol) and benzophenone (140.0 mg, 0.77 mmol) in hexane (8 ml) was irradiated through a Pyrex filter for 3 h at room temperature under an argon atmosphere. After evaporation of the solvent, the residue was subjected to TLC on silica gel and 65.0 mg (0.19 mmol, 38% yield) of (*E*)-1-(diphenylmethoxy)dimethylsilyl-2-trimethylsilylethylene (Vc) was isolated together with minor unidentified products.

Vc: n_D^{24} 1.15189; mass spectrum (rel. int. %): M^+ 340 (7.5), m/e 167 (100); IR (neat): 2930, 1245, 1080, 1055, 830 cm^{-1} ; NMR (CDCl₃): δ (ppm) -0.05 (9 H, s, Si-CH₃), 0.08 (6 H, s, Si-CH₃), 5.61 (1 H, s, CPh₂-H), 6.17 (1 H, d, J 21.0 Hz, =C-H), 6.44 (1 H, d, J 21.0 Hz, =C-H), 7.13 (10 H, brs, Ph). Anal. Found: C, 70.25, H, 8.47. C₂₀H₂₈OSi₂ calcd.: C, 70.53; H, 8.29%.

Similarly, when a solution of IV (150.0 mg, 0.50 mmol) and benzophenone (140.0 mg, 0.77 mmol) in hexane (10 ml) was heated at 160°C for 26 h under an argon atmosphere in a small high-pressure vessel, 56.0 mg (0.17 mmol, 33% yield) of Vc was obtained.

Reaction of pentacarbonyliron (I) with isopropenylpentamethyldisilane (IIb) in the presence of benzophenone

A solution of I (133.0 mg, 0.68 mmol), IIb (105.0 mg, 0.61 mmol) and benzophenone (120.0 mg, 0.66 mmol) in hexane (8 ml) was irradiated for 3 h with a 450 W high-pressure mercury arc lamp through a Pyrex filter under argon atmosphere at room temperature. After evaporation of volatile materials, the residue was separated by TLC on silica gel. 54.0 mg (0.15 mmol, 25% yield) of (*E*)-1-trimethylsilyl-2-(diphenylmethoxy)dimethylsilylpropene (Vb) was isolated together with minor unidentified products.

Vb: an oil; n_D^{26} 1.5230; mass spectrum (rel. int. %): M^+ 354 (4.1), m/e 167 (100); IR (neat): 3070, 3030, 2950, 1245, 1080, 1060, 830 cm^{-1} ; NMR (CCl₄): δ (ppm) 0.08 (15 H, s, Si-CH₃), 1.76 (3 H, d, J 1.5 Hz, =C-CH₃), 5.63 (1 H, s, CPh₂-H), 6.03 (1 H, q, J 1.5 Hz, =C-H), 7.22 (10 H, brs, Ph). Anal. Found: C, 70.95; H, 8.39. C₂₁H₃₀OSi₂ calcd.: C, 71.12; H, 8.53.

Reaction of pentacarbonyliron (I) with vinylpentamethyldisilane (IIc) in the presence of benzophenone

When a solution of I (134.0 mg, 0.69 mmol), IIc (100.0 mg, 0.63 mmol) and benzophenone (130.0 mg, 0.71 mmol) in hexane (8 ml) was irradiated through a Pyrex filter for 3 h under an argon atmosphere at room temperature, 63.0 mg (0.19 mmol, 29% yield) of (*E*)-1-(diphenylmethoxy)dimethylsilyl-2-trimethylsilylethylene (Vc) was obtained.

When a solution of I (0.3 ml, 2.10 mmol), IIc (330.0 mg, 2.09 mmol) and benzophenone (405.0 mg, 2.23 mmol) in benzene (30 ml) was heated at 160°C for 29 h under an argon atmosphere in a small high-pressure vessel, Vc was obtained in 16% yield (110.0 mg, 0.33 mmol) together with minor unidentified products.

Reaction of pentacarbonyliron (I) with α -styrylpentamethyldisilane (IIf) in the presence of benzophenone

When a solution of I (82.3 mg, 0.42 mmol), IIf (95.9 mg, 0.41 mmol) and benzophenone (130.0 mg, 0.71 mmol) in hexane (8 ml) was irradiated through a Pyrex filter for 3 h under an argon atmosphere at room temperature, 82.0 mg, (0.20 mmol, 47% yield) of (*E*)-1-(diphenylmethoxy)dimethylsilyl-2-trimethylsilylstyrene (Vf) was obtained.

Vf: an oil; n_D^{20} 1.5530; mass spectrum (rel. int. %) M^+ 416 (22.5), m/e 167 (100); IR (neat): 3070, 3030, 2950, 1600, 1250, 1090 cm^{-1} ; NMR (CDCl_3): δ (ppm) -0.27 (9 H, s, Si-CH₃), 0.03 (6 H, s, Si-CH₃), 5.60 (1 H, s, CPh₂-H), 6.25 (1 H, s, =C-H), 6.54-7.14 (15 H, m, Ph). Anal. Found: C, 74.87; H, 7.78. $\text{C}_{26}\text{H}_{32}\text{OSi}_2$ calcd.: C, 74.94; H, 7.74%.

When a solution of I (135.0 mg, 0.70 mmol), IIf (99.0 mg, 0.42 mmol) and benzophenone (130.0 mg, 0.71 mmol) in hexane (10 ml) was heated at 160°C for 30 h under an argon atmosphere in a small high-pressure vessel, 43.5 mg (0.11 mmol, 27% yield) of Vf and 6.0 mg (0.034 mmol, 9% yield) of IIa were obtained.

Reaction of pentacarbonyliron (I) with trans-styrylpentamethyldisilane (IIa) in the presence of benzophenone

When a solution of I (85.0 mg, 0.43 mmol), IIa (102.0 mg, 0.43 mmol) and benzophenone (135.0 mg, 0.73 mmol) in hexane (8 ml) was irradiated for 3 h through a Pyrex filter, 36.0 mg (0.11 mmol, 24% yield) of 1,1-dimethyl-3,3,4-triphenyl-1-sila-2-oxacyclopent-4-ene (VI) and 17.0 mg (0.05 mmol, 12% yield) of *trans, trans*-1,7-diphenyl-3,3,5,5-tetramethyl-3,5-disila-4-oxahepta-1,6-diene (VII) were obtained together with minor unidentified products.

VI; white crystals; m.p. 106.0-107.0°C; mass spectrum (rel. int. %): M^+ 342 (100); IR (neat): 3040, 1250, 1020, 880 cm^{-1} ; NMR (CCl_4): δ (ppm) 0.29 (6 H, s, Si-CH₃), 6.05 (1 H, s, =C-H), 6.54-7.14 (15 H, m, Ph). Anal. Found: C, 80.48; H, 6.54. $\text{C}_{23}\text{H}_{20}\text{OSi}$ calcd.: C, 80.65; H, 6.47%.

VII, an oil: n_D^{25} 1.5473; mass spectrum (rel. int. %) M^+ 338 (38.0), m/e 219 (100); IR (neat): 1250, 1050, 850 cm^{-1} ; NMR (CCl_4): δ (ppm) 0.16 (12 H, s, Si-CH₃), 6.23 (2 H, d, J 20.0 Hz, =C-H), 6.82 (2 H, d, J 20.0 Hz, =C-H), 6.95-7.34 (20 H, m, Ph). Anal. Found: C, 70.70; H, 7.94. $\text{C}_{20}\text{H}_{26}\text{OSi}_2$ calcd.: C, 70.95; H, 7.74%.

When a solution of I (135.0 mg, 0.70 mmol), IIa (100.0 mg, 0.43 mmol) and benzophenone (134.0 mg, 0.74 mmol) in hexane (10 ml) was heated at 160°C for 29 h under an argon atmosphere in a small high-pressure vessel, 32.7 mg (0.14 mmol, 32% yield) of (diphenylmethyl)trimethylsilane (VIII) (m.p. 75.0–75.5°C) [23], 16.5 mg (0.05 mmol, 11% yield) of VI and 24.0 mg (0.07 mmol, 17% yield) of VII were obtained.

Reaction of phenyldimethylsilane with benzophenone in the presence of penta-carbonyliron (I)

A solution of phenyldimethylsilane (100.0 mg, 0.74 mmol), benzophenone (143.0 mg, 0.79 mmol) and I (148 mg, 0.76 mmol) in hexane (8 ml) was irradiated through a Pyrex filter for 3 h at room temperature. By TLC on silica gel, 88.0 mg (0.28 mmol, 38% yield) of (diphenylmethoxy) (phenyl)dimethylsilane (IX; n_D^{20} 1.5709) [24] was obtained.

When a solution of phenyldimethylsilane (98.0 mg, 0.72 mmol), benzophenone (145.0 mg, 0.79 mmol) and I (0.2 ml, 1.40 mmol) in hexane (10 ml) was heated at 160°C for 24 h, 74.0 mg (0.23 mmol, 32% yield) of IX and 20.0 mg (0.12 mmol, 17% yield) of diphenylmethane were isolated.

A solution of I (135.0 mg, 0.70 mmol) and IX (74.0 mg, 0.23 mmol) in hexane (10 ml) was heated at 160°C for 24 h in a small high-pressure vessel. By TLC on silica gel, 11.8 mg (0.07 mmol, 30% yield) of diphenylmethane and 23.0 mg (0.14 mmol, 60% yield) of *syn*-tetraphenylethane were isolated.

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