OBSERVATIONS AND COMMENTS ON THE THERMAL BEHAVIOR OF 7-SILANORBORNADIENES *

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Summary

Evidence for a radical mechanism in the thermal decomposition of a 7-sila-norbornadiene is presented. It is demonstrated that 2-carboxy-7-silanorborna-dienes undergo a formal 1,5-migration of silicon to form O-silyl enol ethers. An earlier suggested rearrangement of a 7-silanorbornadiene to a silepin or silanor-caradiene is excluded. A recent report of thermal and photochemical epimeri-zation of 7-silanorbornadienes is shown to be incorrect.

Introduction

Henry Gilman's synthesis of 7-silanorbornadienes (1) and his demonstration that they thermally decompose with extrusion of the bridge as silylenes [1,2] has in the intervening seventeen years continued to stimulate interest in the use of these novel bicyclic systems. Unfortunately this method of silylene genera-tion has been hampered by the rather extreme temperatures (>250°C) generally required for decomposition. Thus, a portion of our interest has been on mani-pulation of substitution on 7-silanorbornadienes in order to obtain a silylene generator possessing less severe thermal requirements.

(1)

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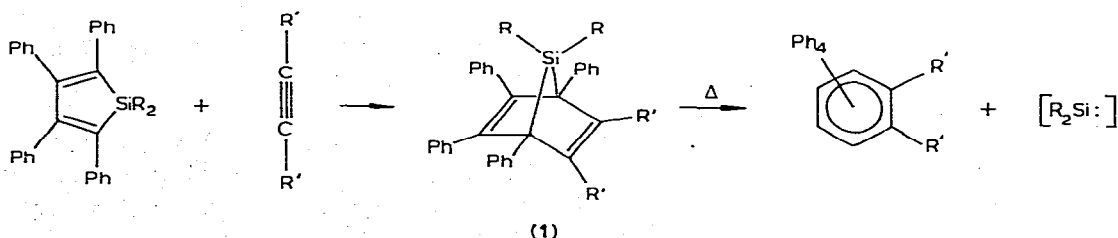
* This paper is dedicated to Professor Henry Gilman for his numerous and outstanding contributions to organosilicon chemistry from Iowa State University.

Results and discussion

The only method known for the synthesis of 7-silanorbornadienes is the Diels-Alder reaction of acetylenes and silacyclopentadienes (siloles) [1—10]. As there is some evidence that decreasing substitution on the six-membered ring of 7-silanorbornadienes results in decreased thermal stability [3—7], we chose what was at that time the least substituted silole known, 1,1-dimethyl-2,5-diphenylsilole (2) as our diene component rather than the tetraphenyl-siloles employed by Gilman. Reaction of 2 and excess perfluoro-2-butyne (25°C, CHCl$_3$, 5 days) afforded 7-silanorbornadiene 3 in 80% isolated yield as a white, crystalline solid, m.p. 100—104°C. Thermolysis of 3 at 180°C (neat, sealed tube) resulted in copious evolution of gaseous Me$_2$SiF$_2$. Precedent for this result was found in the work of Hota and Willis [11] who had reported that thermolysis of 1 (R = Me, R' = CF$_3$) produced Me$_2$SiF$_2$ and polymeric material. In contrast, recrystallization of the residue from the thermolysis of 3 afforded benzocyclobutene 4 in 45% yield [6].
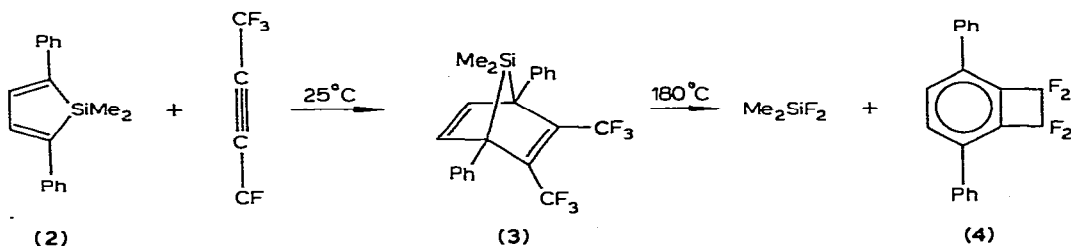
The possibility that Me$_2$SiF$_2$ was formed from fluorine abstraction by dimethylsilylene (Me$_2$Si:) was excluded by performing the decomposition of 3 in neat tolane without formation of the normal product of silylene trapping, 5. Thus, a stepwise radical pathway (Scheme 1) was examined. If the decomposition of 3 proceeds by initial homolysis of a Si—C bond, followed by intramolecular fluorine atom abstraction and loss of Me$_2$FSi$^·$, it should be possible to trap the intermediate benzyl radical 9. Indeed, when the thermolysis of 3 was conducted in the presence of N-phenyl-2-naphthylamine, a known hydrogen transfer agent [12], pentafluoroxylene 10 was obtained in 49% yield. Likewise the N-deuteroamine afforded deuterated 10. Further evidence for the intermediacy of radical 9 was obtained from the gas-phase pyrolysis of 3 (N$_2$ flow, 540°C) which produced an 87% yield of a ca. equal mixture of 11 and 12. The formation of fluorene 11 is most easily rationalized by the cyclization of radical 9. It should be noted that while these results clearly indicate a radical mechanism, they do not suggest at what stage radicals become involved. It is entirely possible that the reaction is initiated by a 1,3-silyl migration [13] to form sila-norcaradiene 7. Since silacyclopropanes are known to react rapidly with halogenated alkanes, the formation of 8 would be expected (possibly through diradical 6). At present we have no data that would allow further comment on the possible intermediacy of 7 in this reaction.

In view of our identification of benzocyclobutene 4 from the thermolysis of 3, we naturally suspected that the nonvolatile material from the thermolysis of 1 (R = Me, R' = CF$_3$) was not the polymeric material reported by Hota and Willis
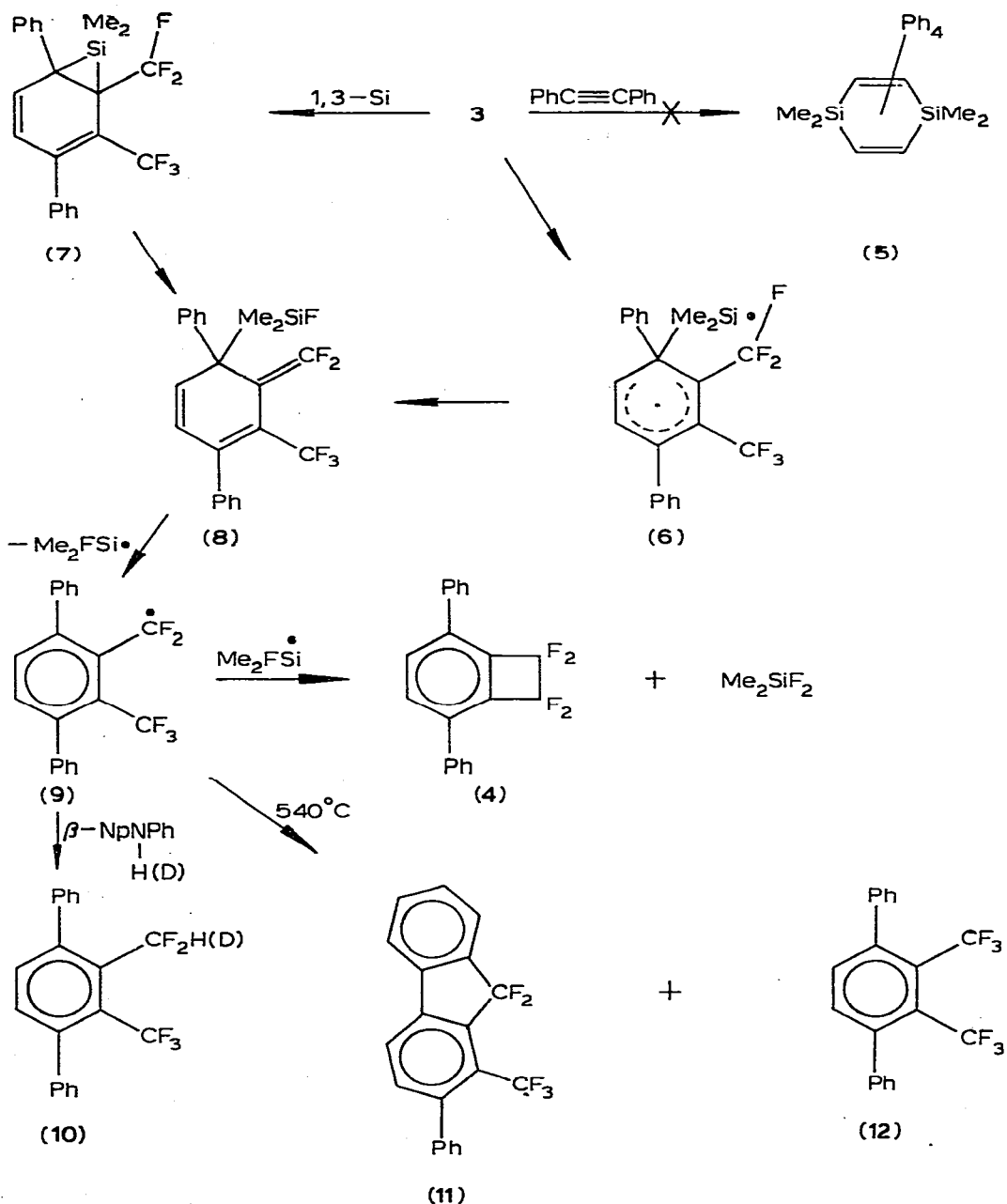
SCHEME 1

[11], but the tetraphenyl analog of **4**. Thus, we thought to undertake a reinvesti-gation of this thermolysis. However, synthesis of the 7-silanorbornadiene **13** (**1**, R = Me, R' = CF₃) by Diels-Alder reaction (100°C, 7 days) of 1,1-dimethyl-tetraphenylsilole and perfluoro-2-butyne produced an adduct (m.p. 124—126°C) with an NMR spectrum of only a singlet silicon methyl at δ 0.44 ppm and an

aromatic multiplet at δ 6.9 ppm. Although the mass spectrum revealed a molecular ion at the expected m/e 576 ($C_{34}H_{26}F_6Si$) and the ^{19}F NMR spectrum showed only a singlet absorption at 51.5 ppm downfield from $FCCl_3$, this clearly was not the same material as that reported by Hota and Willis [11] for 13. These authors reported a melting point of 143—145°C and an NMR spectrum containing two SiMe singlets at δ 0.47 and 0.61 ppm. Attempts to determine the structure of our adduct by X-ray crystallography were thwarted when the crystals were found to be twinned. Were it not for the report of Hota and Willis we would certainly have assumed that our adduct was the expected 7-silanorbornadiene 13 since: (a) thermolysis at 233°C produces Me_2SiF_2 (as reported for 13); (b) photolysis in CCl_4 produces Me_2SiCl_2 (as does 3) and o-bis(trifluoromethyl)tetraphenylbenzene; and (c) photolysis in heptane containing tolan as a trap affords disilin 5.
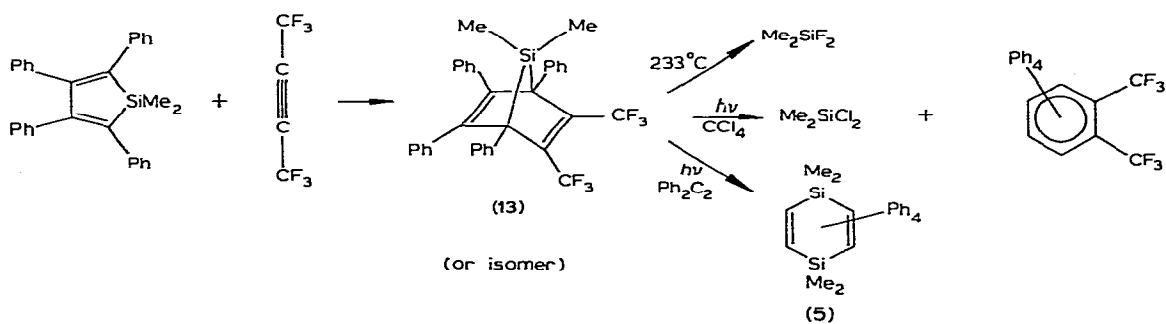

Since the unexpected interception of a reaction intermediate by the trifluoromethyl group prevented 3 or 13 from acting as a thermal silylene generator, other acetylenic dienophiles were examined. The reaction of 2 and tolane at room temperature was reported in 1971 to afford 7-silanorbornadiene 14 [14]. However, it was later demonstrated [15] that the product was actually a 1 : 1 crystal complex of tolane and 2. Thus conditions for the desired cycloaddition were sought. After considerable effort, including attempts at extreme pressure inducement, the only case where we have actually observed the formation of 14 was when the reaction was conducted in a sealed tube at 150°C for 7 days. Unfortunately the product mixture consisted of 2, 14, and 5 in a respective ratio of 4 : 1 : 8. Thus, although 14 can be isolated by chromatography, the combination of low yield and obvious thermal instability under the synthesis conditions render 14 unsuitable as a convenient thermal generator of dimethylsilylene.
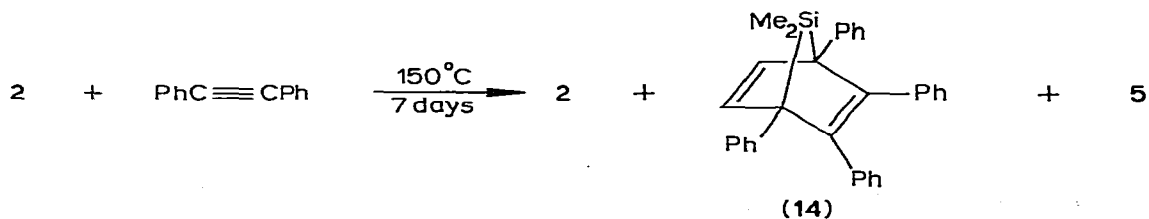

The reaction of silole 2 and dimethyl acetylenedicarboxylate (DMADC) proved to be far more complicated than expected. Indeed, addition of DMADC to a CH_2Cl_2 solution of 2 at room temperature did not yield the expected 7-sila-

norbornadiene **15** upon workup. Instead the rapid formation of a deep red color was observed, and upon solvent removal in vacuo a deep red oil remained from which only dimethyl-2,5-diphenylphthalate (**16**) could be isolated (ca. 50%).


$$2 \quad + \quad MeO_2CC \equiv CCO_2Me \xrightarrow[CH_2Cl_2]{25\ ^{\circ}C}$$

(DMADC)

(15)   (16)
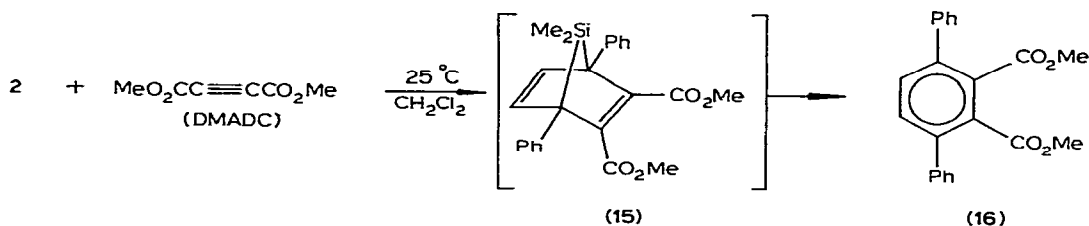
Although the origin of **16** would a priori appear to be extrusion of Me$_2$Si: from **15**, doubt was cast on this route by following the reaction by NMR. Immediately after addition of DMADC to a D$_2$CCl$_2$ solution of **2**, signals correspondent to **15** began to grow in the spectrum [singlets at δ 0.10 (SiMe), 0.55 (SiMe), 3.35 (2 CO$_2$Me), and 6.98 ppm (HC=CH)]. As the reaction proceeded a second set of signals grew in, and after two hours at room temperature the entire spectrum consisted of this second set. This ultimate NMR spectrum [δ 0.00 and 0.47 (s, SiMe$_2$), 3.60 and 3.75 (s, 2 CO$_2$Me), 6.38 and 6.42 ppm (s, vinyl)] clearly revealed that the symmetry of **15** had been destroyed in the rearrangement.

Rearrangement of Diels-Alder adducts of siloles and DMADC finds precedent in the work of Gilman. In 1964 Gilman [1,2] reported that both 7-silanorbornadienes **17** and **18** rearranged upon treatment with ethanol. Three structures were considered for the rearranged materials: **19, 20** and **21**. Siloxane **19** was eliminated from further consideration due to the absence of an absorption band uniquely assignable to an Si—O—C stretch in the 1100—850 cm^{-1} region of the IR spectra (although there were several bands in this region). Thus based on the observation that the isomerized materials showed two strong bands attributed to carbonyl stretching of two different methyl carboxylate groups (R = Me,

(17, R = Me ;
18, R = Ph)

(19a, R = Me ;
19b, R = Ph)
OR

(20a, R = Me ;
20b, R = Ph)
OR

(21a, R = Me ;
21b, R = Ph)
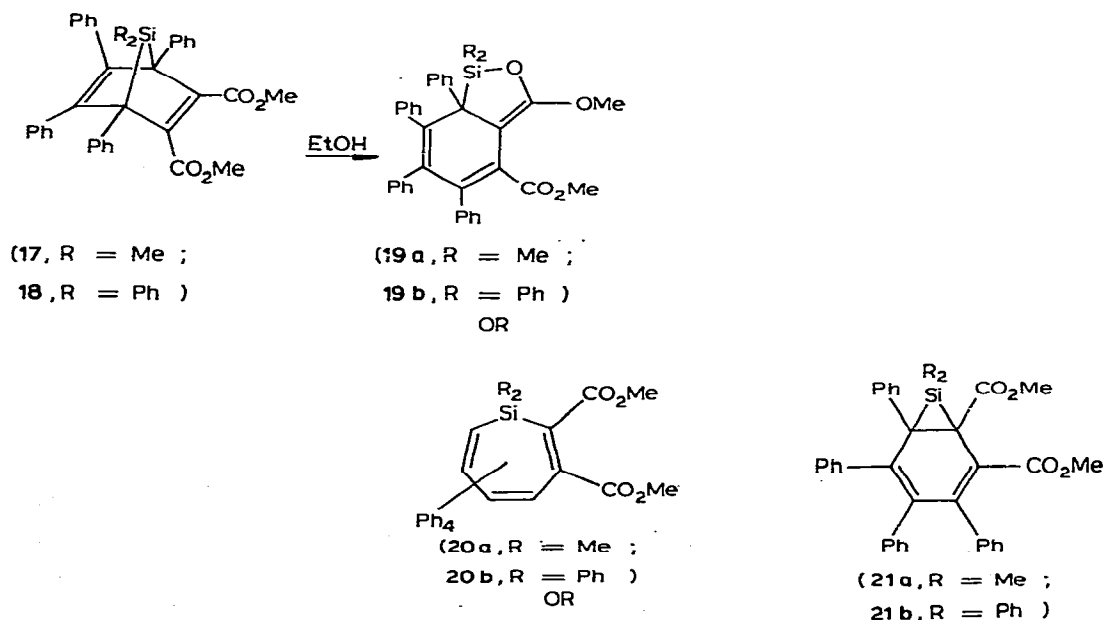
1727 and 1626 cm^{-1}; R = Ph, 1724 and 1618 cm^{-1}) it was left that the products were either silepins **20** or silanorcaradienes **21**, but a conclusive distinction could not be made.

Since it was possible that identification of our product from the isomerization of **15** would allow comment on this longstanding problem, this was attempted. The following observations were made by NMR: (a) **15** was relatively stable in D$_2$CCl$_2$ from −20 to 0°C; (b) above 0°C **15** rearranged; (c) the rate of rearrangement of **15** appeared dependent on the presence of oxygen. Thus when **15** was prepared by the addition of DMADC to a CCl$_4$ solution of **2**, rearrangement was complete after three hours. However, when all reagents were deoxygenated with argon before mixing in CCl$_4$, nearly quantitative formation of **15** was observed (NMR), and complete rearrangement occurred only after more than 16 hours at room temperature. Thus it was possible to obtain crystalline **15** (20%) by the addition of degassed DMAC to a degassed hexane solution of **2**. Although heating degassed CCl$_4$ solutions of **15** (e.g., 100°C, 12 h) resulted in clean, quantitative rearrangement, all attempts to isolate this product were unsuccessful. Chromatography on silica gel or neutral alumina afforded only phthalate **16**, and attempts to crystallize from deoxygenated solutions produced only a deep red oil which deposited **16** upon standing. Despite our inability to isolate the rearranged product from **15**, it was possible to assign the structure of **23** to this product on the basis of spectral observation made on pure solutions of *in situ* generated **23**. In addition to the aforementioned NMR spectrum, two strong bands at 1728 and 1621 cm^{-1} in the IR spectrum allow definitive assignment to structure **23**. While the band at 1728 cm^{-1} is consistent with the C═O stretch of an ester, the band at 1621 cm^{-1} is not. This latter band is typical in strength for an enol ether C═C stretch and entirely consistent in position with such bands reported for *O*-silyl-*O*-alkylketeneacetals by Lutsenko [16]. Thus, the actual products of rearrangement of the analogous tetraphenyl adducts **17** and **18** are almost certainly the ketene acetals **19a** and **19b**.
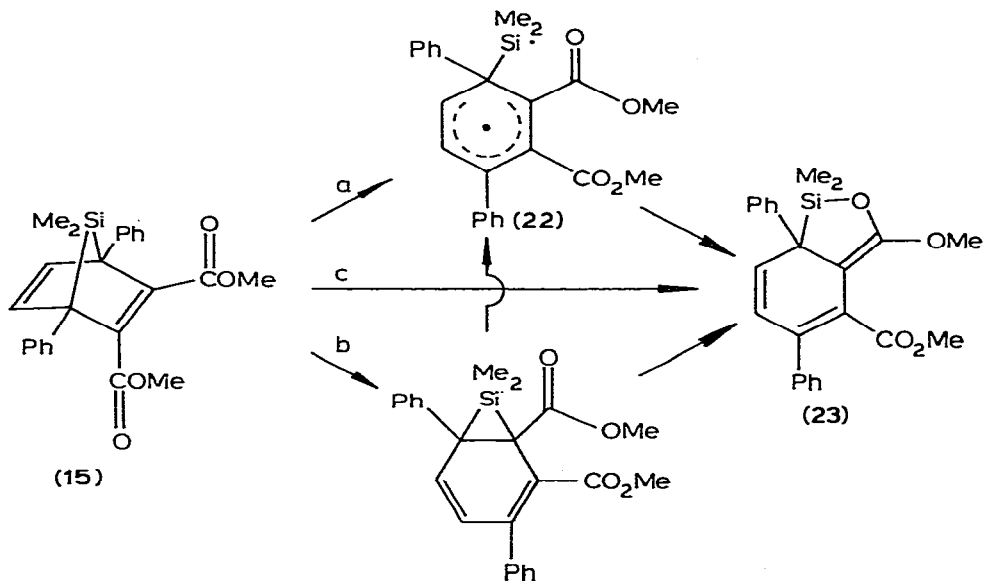

SCHEME 2

There are at least three distinct nonionic mechanisms that can be envisioned for the isomerization of **15** to **23** (Scheme 2). A stepwise radical process (Path a) initiated by Si—C bond homolysis can not be excluded, but is rendered less likely by the fact that the rearrangement is conducted in CCl₄ with no trapping of the silyl radical [17]. The same criticism can be leveled at a route (Path b) which involves initial 1,3-silyl migration to form an intermediate silanorcaradiene since silacyclopropanes are known to react instantaneously with CCl₄ [18]. Thus we favor a single 1,5-sigmatropic rearrangement of silicon to oxygen (path c). This is to our knowledge an unprecedented rearrangement, although several other 1,5-migrations of silicon have been reported [19—21]. This formal 1,5-migration of silicon from carbon to carbonyl oxygen appears to be general. When the Diels-Alder addition of butyn-3-one to silole **2** was carried out in CCl₄ at room temperature, gradual appearance in the NMR spectrum of peaks correspondent to the expected 7-silanorbornadiene, **24**, was observed [δ —0.08 and 0.35 (s, s; SiMe₂); 2.10 (s, O=C—CH₃); 6.40 ppm (m center, 3 vinyl H's)]. After about 40 hours only the signals tentatively ascribed to **24** were visible as all **2** was consumed. Removal of solvent and unreacted acetylene (in vacuo) afforded an oil whose NMR (vide supra) and mass spectra were consistent with **24**. However, the IR spectrum revealed a strong band at 1630 cm⁻¹ and no carbonyl band. Therefore it appears that **24** also rearranges through a formal 1,5-silyl migration to carbonyl oxygen and the ultimate product is enol ether **25**.

(24)   (25)
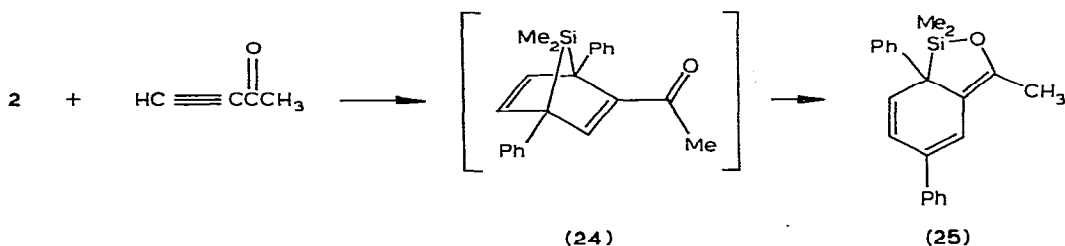
Recently, Neumann [7] reported a variety of data ostensibly demanding initial, reversible Si—C bond homolysis in the thermolysis of 7-silanorbornadienes. In particular, our attention was captured by the disclosure that 7-silanorbornadiene **15** decomposed "rapidly even at 28°C in CCl₄ or toluene" and produced an ESR spectrum consisting of "a doublet split into a quintet", whereas we had found **15** to be quite stable to decomposition under these conditions. Indeed, we find that when crystalline **15** is dissolved in degassed CCl₄ or C₆D₆, no ESR signal is observed even though slow rearrangement to **23** is observed by NMR. However, when degassed DMADC was allowed to react with **2** in degassed CCl₄, a complex ESR signal was observed that was clearly different from that reported. The origin of this signal (or, more likely, combination of signals) is not yet identified.

Another interesting observation reported [7] was that 7-silanorbornadienes with two different substituents on silicon (**26**) underwent both thermally- and photochemically-induced epimerization at silicon. This is of course consistent with opening to diradical **27**, rotation about the remaining Si—C bond, and closure to the diastereoisomer. Thus it was reported that "heating (**26a**—**26b**) in benzene or CCl₄ at 50°C or irradiation at 20°C, the latter also with **26d**, pro-

duced the other isomer (**28a—28d**). The original Me—Si NMR peak disappeared, and nearby a new one appeared . . .". It was concluded that these data indicated that a reversible one-bond cleavage takes place for 7-silanorbornadienes at relatively low temperatures.
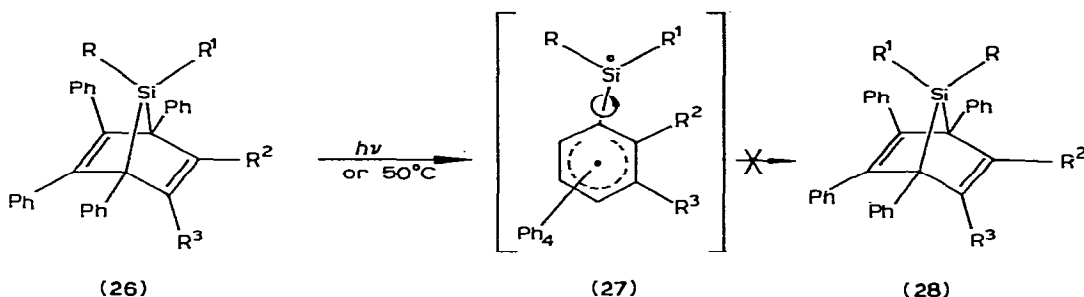
	R	R¹	R²	R³
a	Me	Cl	CO$_2$Me	CO$_2$Me
b	Me	Cl	Ph	H
c	Ph	Me	CO$_2$Me	CO$_2$Me
d	Ph	Me	Ph	H
e	Me	Me	Ph	H

Several points struck us as remarkable about these data. For example, photo-isomerization of **26** is contrary to the results of Balasubramanian and George [8], who observed rapid photo-induced decomposition of the 7,7-dimethyl analog of **26a** to afford dimethyltetraphenylphthalate in 88% yield. These authors were unable to detect radical intermediates when their photolyses were conducted in the presence of radical traps. Also remarkable is that while it is argued in ref. 7 that "CCl$_4$ enhances the thermolysis of **15** presumably by trapping the biradical **22** . . . thus preventing the back reaction", in the same paper it is claimed that thermal epimerization of **26a—26c** can take place in CCl$_4$ via this diradical without trapping. Coupling the above facts with the extreme unlikeliness of quantitative epimerization to a single diastereomer when the groups on silicon are sterically similar (e.g., **26a**) led us to reinvestigate these isomerizations.

In contrast to the results of Neumann [7], but in accord with the report of George [8], we found that photolysis of **26c, 26d,** or **26e** in benzene did not produce observable isomerization but afforded rapid extrusion of the corresponding substituted benzene. In each case, following the photolysis by NMR revealed a steady buildup of a broad unidentifiable SiCH$_3$ resonance between δ −0.2 and 1.5 ppm.
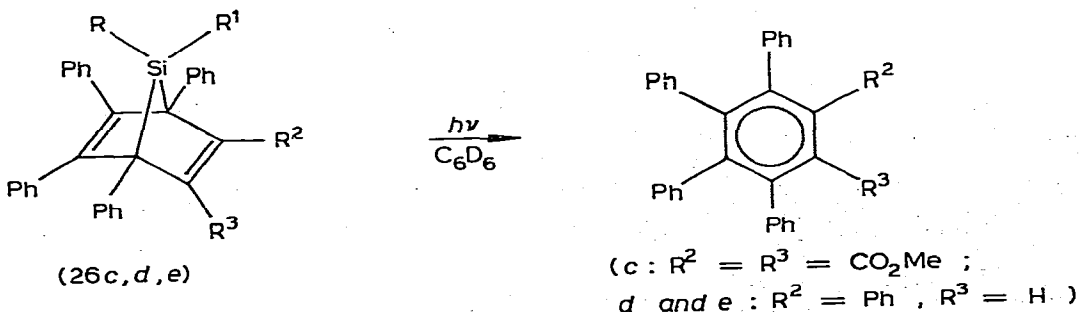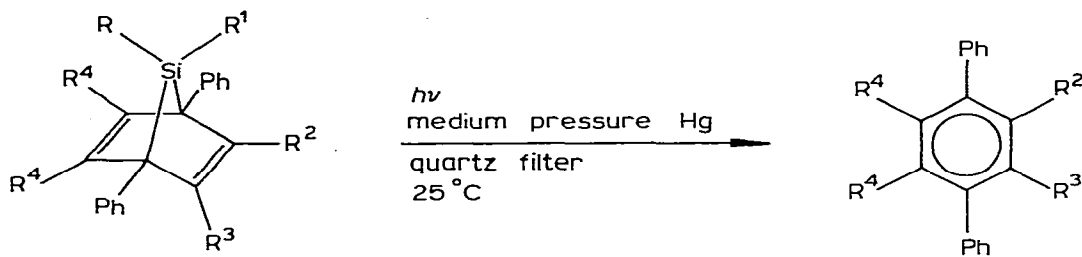

(26c, d, e)

(c : R² = R³ = CO$_2$Me ;
d and e : R² = Ph , R³ = H)

TABLE 1

PHOTOLYSIS OF 7-SILANORBORNADIENES

|	Conditions [a]	R2	R3	R4
26c	CCl$_4$, 210m C$_6$D$_6$, 220m	CO$_2$Me	CO$_2$Me	Ph
26d	CCl$_4$, 100m C$_6$D$_6$, 190m	H	Ph	Ph
26f	CCl$_4$, 6 h [b] C$_6$D$_6$, 180m	CO$_2$Me	CO$_2$Me	Ph
R, R^1 = Me, R^2, R^3 = CO$_2$Me R^4 = Ph				
15 [c]	CCl$_4$, 120m	CO$_2$Me	CO$_2$Me	H
3 [c]	CCl$_4$, 4 h	CF$_3$	CF$_3$	H

[a] All solutions deoxygenated with argon. [b] 0°C. [c] Pyrex filter.

We are also unable to reproduce the results reported [7] for photolysis of **26** in CCl$_4$. Photolysis of **26e** (SiMe$_2$) should have resulted in no observable reaction, but instead the two SiMe signals disappeared with concomitant appearance of a sharp singlet at δ 0.78 ppm. After completion of the photolysis (6 h, 0°C) solvent and volatiles were removed in vacuo and NMR analysis of the residue revealed the spectrum of pentaphenylbenzene and absence of the peak at δ 0.78 ppm. GCMS analysis of the photolysis mixture demonstrated the presence of Cl$_3$CSiClMe$_2$. This product could either arise from sequential radical abstraction and combination, or from silylene insertion into CCl$_4$. Our photolysis results are summarized in Table 1. In no case was any evidence for isomerization obtained.

Next, the thermal isomerization of 7-silanorbornadienes were reinvestigated. The reported results for epimerization at silicon at 50°C were immediately suspect since the Diels-Alder syntheses with phenylacetylene as the dienophile are normally conducted at 100°C or greater. Neumann [7] reported that thermolysis of **26c** at 50°C in CCl$_4$ or benzene resulted in disappearance of the lone SiMe signal at δ 0.71 ppm, and appearance of a new signal at δ 1.06 ppm which was assigned to the SiMe of **28c**. In our hands thermolysis of **26c** at 100°C in deoxygenated benzene-d_6 for 49 hours resulted in essentially no change. New signals consistent with <5% isomerization to ketene acetal **29** were observed at δ 0.00, 3.31 and 3.59 ppm. The isomerization to **29** was found to be accelerated by the presence of oxygen. Thus, after 29 hours at 100°C in O$_2$-saturated benzene-d_6 approximately 50% isomerization was observed. Although **29** was not isolated, the IR spectrum of the thermolysate revealed a strong band at

1620 cm^{-1} in support of the ketene acetal structure.

Thermolysis of **26c** in deoxygenated CCl_4 for 12 hours at 100°C afforded an NMR spectrum which showed <5% isomerization to **29**. The new signals appeared at δ —0.15, 3.42 and 3.96 ppm in CCl_4 solution, and in contrast to the results in benzene did not increase with continued heating. After heating at 100°C for 50 hours the peaks attributed to **29** had disappeared and were replaced by new signals at δ 1.02 and 3.42 ppm. Even after 98 hours at 100°C only about 45% of **26c** had been consumed. The new signals at δ 1.02 and 3.42 ppm are very similar to those reported [7] for the thermolysis of **26c** at δ 1.06 and 3.36 ppm. However, the possibility that epimerization was actually being observed was eliminated by the observation that in vacuo removal of the volatiles resulted in the disappearance of the peak at δ 1.02 ppm. These results are in keeping with the formation of tetraphenylphthalate **30** and MePhSiCl$_2$ which have identical chemical shifts to those observed.
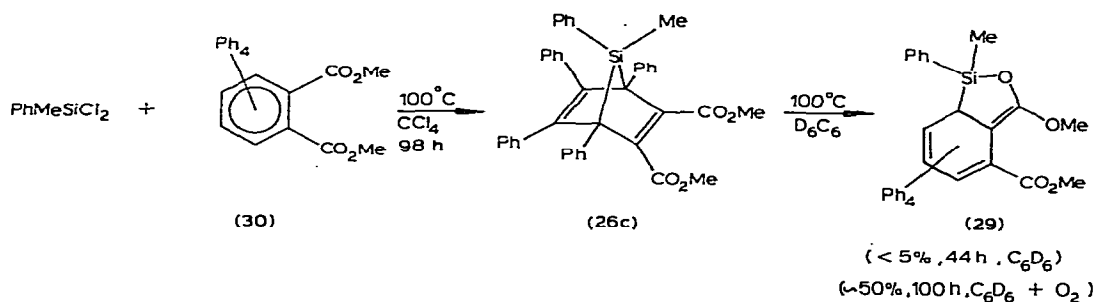
Our findings that certain reported observations interpreted as photochemical and thermal isomerizations of 7-silanorbornadienes have alternate explanations does not comment on the mechanism of silylene extrusion from these systems. It is still very possible, if not likely, that all 7-silanorbornadienes extrude silylenes through a stepwise, radical process, although the mechanism employed may be quite dependent on the nature of the substituents.

Experimental

Melting points were measured with a Thomas Hoover capillary melting point apparatus and are uncorrected. The ^{1}H NMR spectra were obtained with either a Varian A-60 or EM-360 spectrometer. All chemical shifts are reported as ppm (δ scale) using tetramethylsilane as an internal standard. The ^{13}C NMR spectra were recorded on a JEOL FX-90 FT NMR with DCCl$_3$ as an internal standard. The IR spectra were recorded with a Beckman IR-4250, IR-18A, or acculab-2 spectrometer and were calibrated with the 2000 cm^{-1} grating change. High resolution mass spectra were obtained on a MS-902 mass spectrometer and are given as m/e values. Gas chromatographic mass spectra (GCMS) were obtained on a Finnegan Model 4023 mass spectrometer. The ESR spectra were recorded on a Varian E-3 spectrometer with a field set of 3360 and a scan range of ±50 gauss.

All silacyclopentadienes (siloles) were prepared according to literature procedures and were found to have physical properties identical to those reported.

2,3-Bis(trifluoromethyl)-1,4-diphenyl-7,7-dimethyl-7-silanorbornadiene (3)

Into a thick-walled glass tube (27 × 2 cm), with a constriction for sealing, was placed 9.0 g (0.034 mol) of **2** [22] and 30 ml of chloroform (passed through neutral alumina to remove ethanol). The solution was degassed, and 17.3 g (0.107 mol) of hexafluoro-2-butyne (Peninsular Chemical Co.) were condensed into the tube at liquid nitrogen temperature. The tube was sealed and attached (electrical tape) to a rod mounted horizontally from a stirring motor. The tube was allowed to warm to room temperature, and the motor was started, rotating the tube in an acentric manner to insure complete mixing of the contents of the tube. After five days of mixing at room temperature, the tube was opened. The excess butyne was allowed to escape, and the solvent was removed in vacuo leaving a cream-colored solid. Recrystallization from pentane gave **3** (80% yield), m.p. 100—104°C, which was identified on the basis of the following spectra: NMR (CCl$_4$) δ 0.12 (s, 3 H, SiCH$_3$), 0.64 (s, 3 H, SiCH$_3$), 6.82 (s, 2 H, vinyl), 7.11 (s, 10 H, phenyl); IR (CCl$_4$) 1606, 1502, 1445, 1301, 1248, 1172, 1151, 1032, and 1010 cm^{-1}; UV (hexane) λ_{max} = 2840 Å (log ϵ = 3.187); mass spectrum (70 eV) (% rel. int.) 424 (12), 366 (28), 348 (32), 328 (75), 307 (54), 259 (100); calcd. for C$_{22}$H$_{18}$SiF$_6$ *m/e* 424.10809, found 424.11044. Elemental analysis. Found: C, 62.44; H, 4.39; Si, 6.45. Calcd. for C$_{22}$H$_{18}$SiF$_6$: C, 62.25; H, 4.27; Si, 6.62%.

Pyrolysis of **3**

A 0.77 g (1.82 mmol) sample of **3** was heated in an evacuated tube. After a few minutes at 180°C, the sample had turned dark red. The volatile product was collected in an evacuated bulb (cooled to liquid nitrogen temperature) to give a 69% yield of Me$_2$SiF$_2$ (**20**): NMR (CCl$_4$) δ 0.32 (t, J(HF) = 6 Hz); IR (gas phase) 1452, 1408, 1285, 1270, 1100, 930, and 820 cm^{-1}; mass spectrum (70 eV) (% rel. int.) 96 (18.8), 81 (100).

The NMR spectrum of the nonvolatile products indicated a number of peaks in the range 0.0 to 0.7 ppm and an aromatic multiplet in the range 6.8 to 7.7 ppm. Crystallization of the solid material from CCl$_4$/hexane gave a 45% yield of **4**, m.p. 161—162.5°C: NMR (CCl$_4$) aromatic multiplet δ 7.2—7.9; ^{19}F NMR (CCl$_4$) singlet δ 102.5 vs. CFCl$_3$; mass spectrum (70 eV) (% rel. int.) 328 (100), 307 (48). Elemental analysis. Found: C, 73.08; H, 3.68. Calcd. for C$_{20}$H$_{12}$F$_4$: C, 73.17; H, 3.68%.

Pyrolysis of **3** *in the presence of N-phenyl-β-naphthylamine*

A) A tube containing 0.41 g (0.97 mmol) of **3** and 0.22 g (0.97 mmol) of naphthylamine was evacuated and sealed. The tube was heated at 170°C for 20 minutes. The tube was then opened, the dark contents dissolved in methylene chloride and chromatographed on a silica gel column packed in pentane. Elution with pentane brought down **10** in 49% yield, m.p. 113—114°C; NMR (CCl$_4$) aromatic multiplet δ 7.35—7.45; ^{19}F NMR (CCl$_4$) (vs. FCCl$_3$) δ 49.5 (t, J(FF) = 15 Hz, CF$_3$), 106.2 and 107.1 (non-overlapping doublet of quartets, J(HF) = 50.2 Hz, J(FF) = 15 Hz, CHF$_2$); IR (CCl$_4$) 1604, 1468, 1445, 1402, 1315, 1261, 1184, 1141, 1120 and 1053 cm^{-1}; mass spectrum, calculated for C$_{20}$H$_{13}$F$_3$ *m/e* 348.09181, found 348.091802.

B) The same procedure was used as in part A except that deuterated amine

was used. Exact mass studies of the product mixture indicated that products with m/e 349 and 348 were present in the ratio of 8 : 3, respectively. High resolution mass spectrum, calculated for $C_{20}H_{12}DF_5$ m/e 349.10001, found 349.09681.

Pyrolysis of 3 in the presence of diphenylacetylene

A sample containing 0.424 g (0.1 mmol) of **3** and 1.47 g (2.6 mmol) of diphenylacetylene was placed into a glass tube, the tube was evacuated and sealed. After heating for approximately 25 minutes at 210°C, the tube was opened and the contents were sublimed to give 1.450 g (98% yield) of diphenylacetylene. The material which did not sublime was crystallized from methylene chloride/hexane to give a 31% yield of **4**.

Photolysis of 3

A solution containing 0.918 g (2.17 mmol) of **3** and 225 ml of carbon tetrachloride was irradiated, through Pyrex, with a 450 watt Hanovia medium pressure mercury arc lamp. The solution was constantly purged with nitrogen during irradiation. After four hours, the irradiation was stopped. An NMR spectrum of the resulting orange solution showed singlets at 0.77, 7.3 and 7.4 ppm. Removal of the solvent in vacuo followed by crystallization of the residue from hexane gave a 61% yield of 1,4-diphenyl-2,3-bis(trifluoromethyl)benzene (**12**): NMR (CCl_4) δ 7.3 (s), 7.4 (s); ^{19}F NMR (CCl_4) (vs. $FCCl_3$) δ 51 (s); IR (CCl_4) 1605, 1465, 1448, 1402, 1320, 1240, 1185, 1165, 1100, 1051, and 1040 cm^{-1}; mass spectrum, calculated for $C_{20}H_{12}F_6$ m/e 366.084300, found 366.083417.

Attempted synthesis of 2,3-bis(trifluoromethyl)-1,4,5,6-tetraphenyl-7,7-dimethyl-7-silanorbornadiene, 13

(The procedure of Hota and Willis [7] was used although the same results were not obtained.) To a degassed solution of 4.02 g (9.7 mmol) of 1,1-dimethyl-2,3,4,5-tetraphenylsilacyclopentadiene [2] and 20 ml dry benzene was added 3.81 g (23.4 mmol) of hexafluoro-2-butyne. The tube was evacuated, sealed and heated at 100°C for seven days. (There was very little reaction after two days.) Removal of the benzene in vacuo left a cream-colored solid from which the adduct, **13** or isomer, was crystallized: m.p. 124—126°C; 73% yield; NMR (CCl_4) δ 0.44 (s, 6 H), 6.9 (m, 20 H); ^{19}F NMR singlet 51.5 ppm downfield from $CFCl_3$; IR (CCl_4) 1020w, 1044w, 1150s, 1176s, 1242w, 1300m, 1446w, 1502w and 1604w cm^{-1}; m/e (% rel. int.) 576 (10), 518 (65), 500 (100), 480 (65). Analysis. Found: C, 70.75; H, 4.74; Si, 5.04. Calcd. for $C_{34}H_{26}SiF_6$: C, 70.82; H, 4.54; Si, 4.87%.

Pyrolysis of 13 or isomer

A 1.083 g (1.88 mmol) sample of **13** or isomer from the above experiment was sealed in an evacuated bulb equipped with a break-seal. Upon heating at 233°C the sample turned yellow and began to bubble vigorously. After 5 m of heating the sample was quite dark and heating was discontinued. The break-seal was broken and the gaseous products were collected in a cooled, evacuated bulb. The mass and IR spectra were identical to authentic Me_2SiF_2, and the weight of the gaseous product corresponded to a 90% yield of silane. Attempts to purify and identify the solid residue by chromatography and crystallization failed.

Photolysis of **13** *or isomer*

A solution of 0.099 g (0.172 mmol) **13** or isomer (vide supra) in 0.75 ml CCl$_4$ in a Pyrex NMR tube was irradiated for 19.5 h with 300 nm lamps in a Rayonet reactor. At this time only the new peaks at δ 0.77 (Me$_2$SiCl$_2$) and 7.0 were present. Removal of solvent also removed the Me$_2$SiCl$_2$, and left a white solid, m.p. 210—211°C, which was shown by spectral comparison with an authentic sample (vide infra) to be *o*-bis(trifluoromethyl)tetraphenylbenzene.

Photolysis of **13** *or isomer with tolane*

A solution containing 1.014 g (1.76 mmol) of **13** or an isomer (vide supra) and 3.14 g (17.6 mmol) of tolane in 65 ml of n-heptane was degassed with N$_2$ bubbling, and irradiated with a 200 W medium pressure mercury arc lamp (Hanovia). After 9.5 hours the solution was filtered to obtain 0.126 g (0.27 mmol) of **5**. Although more **5** could be isolated from the filtrate, separation was incomplete and little effort was made to learn the total yield of **5**.

Synthesis of 2,3-bis(trifluoromethyl)paraterephenyl (12)

A 3.85 g (18.7 mmol) sample of 1,4-diphenylbutadiene dissolved in 20 ml of HCCl$_3$ (percolated through neutral alumina) was placed in a stainless steel cylinder (80 ml volume). After addition of 6.8 g (42 mmol) of hexafluoro-2-butyne, the valve was closed and the bomb heated at 170°C for 12 hours. Chromatography on neutral alumina with hexane afforded white crystalline 2,3-bis(trifluoromethyl)-1,4-diphenylcyclohexadiene: NMR (CCl$_4$) δ 4.35 (d, 2 H), 5.6 (d, 2 H), 7.1 (s, 6 H); ^{19}F NMR (CCl$_4$) singlet at 59 ppm; IR (CCl$_4$) 1030w, 1132m, 1162s, 1202m, 1278s, 1445w and 1496w cm^{-1}. This material was mixed with sulfur and heated in an ethylene glycol solution overnight. After dilution with water and extraction with ether, **12** was crystallized from hexane: m.p. 130—132°C; IR (CCl$_4$) 1040w, 1100w, 1162s, 1187s, 1238m, 1320m, 1400w, 1448w, 1465w cm^{-1}; *m/e* 366 (100%).

Synthesis of 2,3-bis(trifluoromethyl)tetraphenylbenzene

To a degassed solution of 1.10 g (2.87 mmol) of tetraphenylcyclopentadienone and 20 ml of benzene was added 1.51 g (9.35 mmol) of hexafluoro-2-butyne. The tube was sealed and heated at 90°C for 10 days. Crystallization from hexane gave the title compound: m.p. 210—211°C; IR (CCl$_4$) 1123w, 1160s, 1181s, 1238m, 1339m, 1407w, 1443w cm^{-1}.

Synthesis of dimethyldifluorosilane

To a 3.958 g (38.4 mmol) sample of ZnF$_2$ was added dropwise with stirring a solution of 5.15 g (40 mmol) of Me$_2$SiCl$_2$ in 25 ml of CCl$_4$. After stirring for three hours the solution was filtered, and the filtrate examined by NMR to reveal only a clean triplet at δ 0.32 ($J \sim$ 6 Hz).

Reaction of **2** *with tolane*

Tolane (0.679 g, 0.0038 mol) and **2** (1.00 g, 0.0038 g) were degassed, sealed in a tube, and heated at 150°C for 7 days. Crystallization from CHCl$_3$/hexane gave 0.117 g light yellow solid spectrally identified as **5**. Removal of solvent and crystallization of the residue from acetone afforded 0.503 g (30%) of a white

solid (m.p. 175—188°C) identified as 1,2,3,4-tetraphenyl-7,7-dimethyl-7-disila-norbornadiene (14): NMR (CCl_4) δ 0.17 (s, 3 H), 0.64 (s, 3 H), 6.4—7.1 (m, 20 H), 7.41 (s, 2 H). The NMR spectrum of the crude reaction mixture was devoid of absorption between δ 0.64 and 6.40. Integration of the SiMe peaks revealed a ratio of 4 : 1 : 8 of **2** : **5** : **14**.

2,3-Dicarbomethoxy-1,4-diphenyl-7,7-dimethyl-7-silanorbornadiene (15)

A) Attempted preparation in CH_2Cl_2. To a solution of 1.14 g (4.36 mmol) of **2** and 20 ml of methylene chloride was added 0.62 g (4.36 mmol) of dimethyl acetylenedicarboxylate (DMADC) (Aldrich). After approximately five minutes of stirring at room temperature, the solution turned from yellow to red. The solvent was removed in vacuo, leaving a red oil. The resulting red oil was dissolved in a minimum amount of boiling benzene. Upon cooling a white solid was collected. Recrystallization from acetone gave white flocculent crystals of dimethyl diphenylphthalate (16) m.p. 184—186°C: NMR ($CDCl_3$) (ppm): δ 3.56 (s, 6 H), 7.33 (s, 10 H), 7.47 (s, 2 H).

B) A solution of 1.91 g (7.29 mmol) of **2** and 30 ml of hexane was degassed by the freeze-thaw method. To this solution was added, by trap-to-trap distillation, 3 ml (24 mmol) of dimethyl acetylenedicarboxylate, which was degassed by the freeze-thaw method prior to addition. The vessel was then sealed and heated slightly above room temperature to dissolve **2**. After cooling to room temperature, the reaction vessel was cooled at about —10°C for 24 hours. After cooling to 0°C, the presence of a deep red oil and some pale yellow-green crystals was noted. Careful collection of the crystals, under an atmosphere of argon in a glove bag, gave 0.6 g (1.49 mmol, 20%) of **15**: m.p. (sealed tube) 80—90°C (d), NMR (CCl_4) δ 0.15 (s, 3 H), 0.59 (s, 3 H), 3.41 (s, 6 H), 6.92 (s, 2 H), 7.18 (s, broadened at the base line, 10 H); IR (CCl_4) 3060, 3025, 2950, 1721, 1592, 1540, 1494, 1429, 1282, 1239, 1048, 721 and 690 cm^{-1}; mass spectrum (70 eV) (% rel. int.) 389 (13), 345 (19), 315 (22), 105 (47), 98 (31), 97 (25), 89 (67), 83 (90), 75 (32), 71 (23), 70 (29), 69 (44), 59 (29), 57 (48), 55 (100); calculated for $C_{24}H_{24}O_4Si$ *m/e* 404.14439, found 404.14614; calculated for $C_{23}H_{21}O_4Si$ (Parent — CH_3) 389.12091, found 389.12101.

C) In situ preparation of **15**. A solution of 0.52 g (1.98 mmol) of **2** and 10 ml of CCl_4 was deoxygenated by bubbling argon through the solution for about 15 minutes. To this solution was added 0.29 g (2.0 mmol) of freshly distilled DMADC, which was deoxygenated by bubbling argon through it for 15 minutes prior to addition. After stirring at room temperature for about 20 minutes examination of the reaction mixture by NMR showed only **15** and excess DMADC to be present. This solution was found to be adequate for subsequent reactions of **15**. However, attempts to isolate **15** by in vacuo removal of the solvent, or addition of dodecane and in vacuo removal of CCl_4, afforded a deep red oil, or a red dodecane solution, from which only dimethyl diphenylphthalate **16** could be isolated.

Isomerization of 15 to 7,7-dimethyl-3,6-diphenyl-2-carbomethoxy-9-methoxy-bicyclo[4.3.0]nona-2,4,9-triene 23

A) A CCl_4 solution of **2**, prepared in situ as described above, was placed in a NMR tube and degassed by the freeze-thaw method. The tube was then sealed

and placed in an oven thermostated at 105—110°C. After thermolysis for about 10 hours analysis by NMR showed the **15** had completely isomerized to **23** and some minor unidentified decomposition products. Based on relative peak areas **23** accounted for >80% of the products formed. The identification of **23** was made on the basis of its spectral data: NMR (CCl_4) δ 0.01 (s, 3 H), 0.50 (s, 3 H), 3.55 (s, 3 H), 3.79 (s, 3 H), 6.41 (AB quartet, $J = 10$ Hz, 2 H), 7.39 (broad multiplet, 10 H); IR (CCl_4) 3060, 3022, 2942, 1728, 1621, 1595, 1442, 1431, 1256, 1130, 1050, 853, and 695 cm^{-1}. Continued thermolysis of this solution led to the gradual decomposition of **23** and the formation of dimethyl diphenyl-phthalate.

A repeat of this reaction in $DCCl_3$ afforded the following ^{13}C NMR spectrum for **23**: (ppm relative to TMS) δ —3.17, —3.39, 51.54, 55.50, a plethora of signals between 125.06 and 130.48, 139.79, 145.10, 159.24 and 169.81. After standing under vacuum at 0°C for 18 months this solution was found to be unchanged, however, exposure to the air resulted in the rapid decomposition of **23** giving dimethyl diphenylphthalate.

ESR experiments

A) A solution of 0.064 g (0.24 mmol) of **2** and CCl_4 was placed in an NMR tube and degassed by the freeze-thaw method. DMADC, 0.015 g (0.11 mmol), was degassed by evacuation at 28°C and 0.02 Torr, and then trap-to-trap distilled into the NMR tube. After sealing the tube, analysis by ESR revealed an unsymmetrical signal that appeared to be a mixture of at least two radicals. No definitive identification of the radicals present could be made.

B) A solution of silanorbornadiene **15**, isolated as previously described, and CCl_4 was placed in a septum-sealed NMR tube under an atmosphere of argon. Analysis by ESR showed no radical signal. After 72 hours at 0°C under argon about 10% of **15** was found, by NMR, to have rearranged to **23**. However, no ESR signal was observed during this period. Further isomerization (ca. 25%) of **15** to **23** was found after 18 hours at room temperature in the dark. Analysis of this sample by ESR showed no observable radical signal. Oxygen was then bubbled through the tube to observe the effect of O_2 upon the isomerization. After standing under O_2 for 1 hour at room temperature in the dark, **15** was found by NMR to have completely decomposed, giving dimethyl diphenyl-phthalate and unidentifiable silicon containing products. Repetition of this experiment in benzene-d_6 also failed to produce an ESR signal.

Photolysis of 15

A CCl_4 solution of **15** prepared in situ in a Pyrex NMR tube was irradiated with a medium pressure Hg lamp at room temperature. After irradiation for 120 minutes a large amount of precipitate was found. NMR analysis of this suspension revealed a new Si—CH$_3$ signal at δ 0.79. Based on the relative peak areas of **15** and the new signal at δ 0.79 approximately 50% of **15** had decomposed. The precipitate, following isolation by filtration, was found to be dimethyl-1,4-diphenylphthalate by comparison of its NMR with that of authentic dimethyl-1,4-diphenylphthalate. Based on NMR chemical shifts, the new Si—CH$_3$ signal at δ 0.79 was identified as dimethyldichlorosilane.

7,7,9-Trimethyl-3,6-diphenyl-7-sila-8-oxa-bicyclo[4.3.0]nona-2,4,9-triene (25)

A solution of 0.54 g (2.1 mmol) of silole **2** and 6 ml of CCl_4 was deoxygenated by bubbling argon through the solution for 15 minutes at room temperature. To this solution was added 0.44 g (6.4 mmol) of 3-butynone, with continuous argon bubbling. Argon bubbling was maintained for 15 minutes after the addition of 3-butynone to assure complete deoxygenation. After stirring for 44 hours at room temperature in the dark under an atmosphere of argon, analysis by NMR revealed only the presence of **25**, excess 3-butynone, and small amounts of decomposition products. Based on relative peak areas of the $Si-CH_3$ absorptions **25** accounted for >85% of the products formed. In vacuo removal of the volatiles afforded a brown-red oil identified as **25**: NMR (CCl_4) δ −0.08 (s, 3 H), 0.35 (s, 3 H), 2.10 (s, 3 H), 6.35 (broad d, 2 H), 6.48 (broad s, 1 H), 7.10 (broad multiplet, 10 H); IR (CCl_4) 3065, 3040, 2965, 1660, 1630, 1598, 1495, 1447, 1380, 1255, 1210, 1027, 845, and 690 cm^{-1}; mass spectrum (70 eV) (% rel. int.) 330 (70), 329 (49), 315 (35), 272 (21), 271 (27), 257 (28), 253 (100), 241 (48), 77 (52), 75 (71); calculated for $C_{22}H_{22}OSi$ *m/e* 330.14400, found 330.14320. Attempted purification of **25** by column chromatography (neutral alumina, CCl_4 elution) afforded 2′,5′-diphenylacetophenone: NMR (CCl_4) δ 1.96 (s, 3 H), 7.55 (s, broadened at the base line, 13 H); IR (CCl_4) 3060, 3025, 2970, 1689, 1600, 1470, 1445, 1350, 1250, 1215, and 690 cm^{-1}.

1,2-Dicarbomethoxy-3,4,5,6,7-pentaphenyl-7-methyl-7-silanorbornadiene (26c)

A solution of 1.008 g (2.12 mmol) of 1,2,3,4,5-pentaphenylmethylsilole (**23**) and 15 ml of CCl_4 was placed in a septum-sealed round bottom flask equipped with a magnetic stirring bar. The reaction vessel was then deoxygenated by bubbling argon through the solution for 15 minutes. After the addition of 0.578 g (4.07 mmol) of DMADC the reaction was stirred at room temperature for 18 hours. The volatiles were then removed in vacuo, and the resulting residue was crystallized from CH_2Cl_2/hexane to afford 0.8069 g (1.31 mmol, 62% yield) of **26c**, m.p. (sealed tube) 208—211°C, which was identified on the basis of the following spectra: NMR (CCl_4) δ 0.69 (s, 3 H), 3.6 (s, 6 H), broad absorption from 6.3 to 7.7 with the major signal centered at 6.81 (25 H); IR (CCl_4) 3104, 3070, 3000, 1730, 1600, 1431, 1232, 1060, 860, and 700 cm^{-1}; mass spectrum (70 eV) (% rel. int.) 618 (2), 603 (23), (602 (49), 560 (44), 558 (87), 540 (32), 498 (13), 434 (21), 172 (16), 168 (35), 152 (45), 57 (100), 56 (87), calculated for $C_{41}H_{34}O_4Si$ *m/e* 618.22265, found 618.22377.

1,2,3,4,5,7-Hexaphenyl-7-methyl-7-silanorbornadiene (26d)

A mixture of 1.0 g (2.1 mmol) of 1,2,3,4,5-pentaphenylmethylsilole and 0.56 g (5.46 mmol) of phenylacetylene, in an evacuated sealed tube, was heated at 140°C for 12 hours. After thermolysis the tube was opened and the volatiles were removed in vacuo. The resulting residue was then crystallized from CH_2Cl_2/hexane to afford 0.862 g (1.49 mmol) of **26d**, m.p. 203—206°C, which was identified on the basis of the following spectra: NMR (CCl_4) δ 0.65 (s, 3 H), broad absorption between 6.2 and 7.9 with the major absorption at 6.9 (31 H); IR (CCl_4) 3055, 3020, 1600, 1490, 1440, 1425, 1245, 1100, 1070, 1025, 905, 855, and 690 cm^{-1}; mass spectrum (70 eV) (% rel. int.) 578 (32), 485 (11),

458 (24), 105 (15), 86 (40), 84 (65), 57 (61), 56 (58), 49 (100); calculated for $C_{43}H_{34}Si$ m/e 578.24299, found 578.24136.

1,2,3,4,5-Pentaphenyl-7,7-dimethyl-7-silanorbornadiene (26e)

A mixture of 0.753 g (1.82 mmol) of 2,3,4,5-tetraphenyldimethylsilole (2) and 0.54 g (5.26 mmol) of phenylacetylene, in an evacuated sealed tube, was heated at 140°C for ten hours. After thermolysis the tube was opened and the volatiles were removed in vacuo. The resulting residue was crystallized from CH_2Cl_2/hexane to afford 0.577 g (1.12 mmol, 61% yield) of 26e, m.p. 145.5—147.5°C, that was identified on the basis of the following spectra: NMR (CCl_4) δ 0.35 (s, 3 H), 0.63 (s, 3 H), broad absorption between 6.2 and 7.2 with the major absorption centered at 6.95 (26 H); IR (CCl_4) 3070, 3038, 2960, 1600, 1495, 1443, 1245, 1074, 1030, 905, 877, 855, 840, and 690 cm^{-1}; mass spectrum (70 eV) (% rel. int.) 516 (100), 501 (31), 458 (39), 439 (27), 423 (31), 380 (31), 365 (15), 136 (25), 102 (13); calculated for $C_{38}H_{32}Si$ m/e 516.22734, found 516.22612.

Photolysis of 26c

A) A solution of 26c and CCl_4 was placed in a quartz NMR tube which was sealed with a rubber septum and deoxygenated by bubbling argon through the tube for 15 minutes. The tube, which was placed in a large container of H_2O, was then irradiated with a 450 W Hanovia lamp through a quartz filter. After irradiation for 210 minutes, analysis by NMR revealed that 26c had completely disappeared. New peaks were observed in the NMR at δ 0.90 (singlet), 3.31 (singlet), 6.7 (broad singlet) and 6.95 (broad singlet). The photolysate was dissolved in hot 50/50 CCl_4/hexane, which after cooling afforded pale yellow-brown crystals (m.p. 251—255°C) identified as dimethyl tetraphenylphthalate 30 on the basis of the following spectra: NMR (CCl_4) δ 3.3 (s, 6 H), broad absorption between 6.3 and 7.2 with major absorptions at 6.7 and 7.0 (20 H); IR (CCl_4) 3065, 3040, 2960, 1734, 1605, 1496, 1438, 1345, 1245, 1174, 1068, and 695 cm^{-1}. This spectral data was found to be identical to that of an authentic sample of 30.

B) A solution of 26c and benzene-d_6 was placed in a quartz NMR tube which was sealed with a rubber septum and deoxygenated by bubbling argon through the tube for 15 minutes. The photolysis was conducted as described for 26c in CCl_4. After irradiation for 220 minutes at room temperature analysis of the photolysate by NMR showed that the Si—CH$_3$ singlet of 26c had completely disappeared. A broad, unidentifiable, hump between δ 0.2 and 1.1 was observed in the NMR plus a new singlet at δ 3.3. Chromatography of the photolysate on neutral alumina with CCl_4 elution affords a white, crystalline product, which was identified as dimethyl tetraphenylphthalate (30) on the basis of its NMR and IR spectra.

Photolysis of 26d

A) The photolysis of 26d in CCl_4 was conducted in the same manner as for 26c (vide supra). After irradiation for 100 minutes NMR analysis of the photolysate showed that 26d had completely disappeared. The Si—CH$_3$ signal for 26d had disappeared and was replaced by a new Si—CH$_3$ signal at δ 0.96. In vacuo

removal of the volatiles resulted in disappearance of the peak at δ 0.96. The signal at δ 0.96 is consistent with phenylmethyldichlorosilane. The residue was then chromatographed on neutral alumina with CCl_4 elution to afford a white, crystalline, solid, m.p. 248–249°C, which was identified as pentaphenylbenzene on the basis of its melting point and NMR spectra: NMR (CCl_4) δ 6.73 (broad singlet), 7.01 (singlet), 7.25 (singlet). This NMR spectrum was found to be identical to that of authentic pentaphenylbenzene.

B) The photolysis of **26d** in benzene-d_6 was conducted in the same manner as for **26c**. After irradiation for 190 minutes at room temperature the singlet Si—CH_3 absorption for **26d** was found by NMR to have collapsed to a broad hump between δ —0.1 to 1.5. Chromatography of the photolysate on neutral alumina with CCl_4 elution afforded pentaphenylbenzene which was identified on the basis of its melting point (m.p. 247–248°C) and NMR spectrum.

Photolysis of **26e**

A) The procedure for the photolysis of **26e** in CCl_4 was the same as that employed for **26c** with one exception, **26e** was photolyzed at 0°C. After irradiation for six hours, NMR analysis of the photolysate showed that the Si—CH_3 signals of **26e** had completely disappeared, and were replaced by a new signal at δ 0.78. This new signal is consistent with dimethyldichlorosilane. GCMS analysis of the photolysate revealed the presence of dimethyldichlorosilane; GCMS (% rel. int.) 132 (0.5), 130 (4), 128 (5), 117 (15), 115 (65), 113 (100), 95 (4), 95 (4), 93 (4); and trichloromethyldimethylchlorosilane; GCMS (% rel. int.) 195 (0.22), 177 (1.5), 175 (1.4), 135 (8), 133 (8), 115 (16), 113 (23), 95 (34), 93 (100), 65 (20), and 63 (21). After in vacuo removal of the volatiles from the photolysate, crystallization of the resulting residue afforded a brown solid, m.p. 234–237°C. This solid was identified as pentaphenylbenzene by comparison of its NMR spectrum with that of authentic pentaphenylbenzene.

B) The procedure for the photolysis of **26e** in benzene-d_6 was the same as that used for the **26c**. Analysis of the reaction by NMR, after irradiation for three hours, showed that the two singlet, Si—CH_3, absorptions of **26e** had collapsed to a broad hump between δ —0.1 and 1.3. Chromatography of the photolysate on neutral alumina gave a white, crystalline, solid, m.p. 239–241°C, which was identified as pentaphenylbenzene on the basis of its NMR spectrum.

Thermolysis of **26c**

A) A solution of **26c** and CCl_4 was placed in a septum-sealed NMR tube, and deoxygenated by bubbling argon through the tube for about 15 minutes. The solution was then heated at 100°C, and the progress of the reaction was monitored by NMR. After heating for three hours new signals at δ —0.15, 3.42, and 3.96 were observed. These signals continued to grow with continued thermolysis. Thus, after heating for 12 hours, about 5% of **26c** was observed to have decomposed, affording the new NMR signals. Further thermolysis did not result in a continued increase in the signals at δ —0.15, 3.42 and 3.96. Instead, after 24.75 hours of heating the signals at δ —0.15 and 3.96 had decreased in intensity with a concomitant increase in the signal of δ 3.42, and the appearance of a new signal at δ 1.02. After heating at 100°C for 50 hours only the signals at δ 1.02 and 3.42 were observed in addition to unreacted starting material. Based

on the relative peak areas of the Si—CH_3 peak of **26c** and the new peak at δ 1.02, about 20% of **26c** had decomposed. After heating for 98 hours about 45% of **26c** had decomposed. The signal of δ 1.02 was found not to be due to isomerized **26c** when in vacuo removal of the volatiles (0.02 Torr, 60°C) caused this signal to completely disappear. Thus, NMR analysis of this residue showed on signals due to **26c** and the peak at δ 3.42, which based on chemical shifts was attributed to the carbomethoxy methyls of dimethyl tetraphenylphthalate (**30**).

B) A solution of **26c** and benzene-d_6 was placed in a septum-sealed NMR tube and deoxygenated by bubbling argon through the solution for about 15 minutes. The solution was then heated at 100°C. NMR analysis after 24.5 hours revealed only signals due to **26c**. NMR analysis, after 48.75 hours at 100°C, revealed the presence of new signals at δ 0.00, 3.31, and 3.59, which based on relative peaks areas of the Si—CH_3 resonance for **26c** and the signal at δ 0.00 represented <5% decomposition of **26c**. Oxygen was then bubbled through the tube for ca. 5 minutes. In the presence of O_2 thermolysis, at 100°C, resulted in a gradual decrease in the intensity of NMR signals of **26c** and an increase in the intensity of the signals at δ 0.00, 3.31, and 3.59. NMR analysis, after heating in the presence of O_2 for 29 hours, showed that ca. 50% of **26c** had decomposed. After thermolysis for 102 hours in the presence of O_2 only about 10% of **26c** remained, on the basis of relative Si—CH_3 peak areas. Based on the NMR and IR spectra, the product of the reaction was tentatively identified as bicycloenol ether **29**. NMR (C_6D_6) δ 0.00, 3.31, 3.59 (all singlets, relative areas 1 : 1 : 1), broad absorption between δ 6.70 and 7.90 (relative area not determined); IR (C_6D_6) 3060, 3030, 2950, 1725, 1620, 1595, 1490, 1440, 1430, 1293, 1225, 1200, 1135, 1110, 1057, 1025, 840, and 691 cm^{-1}.

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