

The exploratory far-UV photochemistry of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene and 2-trimethylsilylbicyclo[2.2.1]hept-2-ene

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Abstract

1-Methyl-1-silabicyclo[2.2.1]hept-2-ene was synthesized in 27% yield by chloramine-T oxidation of a mixture of C-2/C-3 phenylselenide derivatives of 1-methyl-1-silabicyclo[2.2.1]heptane. The phenylselenides in turn were produced in 8% yield by Gif^{III} oxidation of 1-methyl-1-silabicyclo[2.2.1]heptane. The 214 nm photolysis of the rigid 1-silanorbornene in MeOH or (CH₃)₃COH resulted in [1,3-C] migration to afford 3-alkoxy-3-methyl-3-silabicyclo[4.1.0]heptanes with quantum yields of 0.053 (methoxy derivative) and 0.062 (*tert*-butoxy derivative). The efficiency for photoprotonation was estimated to be $\Phi < 0.01$ for methanol and negligible for *tert*-butyl alcohol. [1,3-C] photorearrangement was also observed upon 214 nm irradiation of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene in pentane and (CH₃)₃COH, but the major photoprocess appeared to be reversible [1,2-Si] migration to give a carbene intermediate, which underwent CH insertion to form 3-trimethylsilylnortricyclene. Competing [1,2-C] shift of the carbene accounted for the formation of trimethylsilylmethylenebicyclo[2.1.1]hexane. In pentane the respective quantum yields of the two carbene-derived products were 0.0062 and 0.0019. In CH₃OH(D) as the solvent, photoprotonation was a minor photoprocess that produced 2-trimethylsilylnorbornane via hydride transfer. Photoprotonation assumed greater importance in CF₃CH₂OH and resulted in desilylation to norbornene ($\Phi = 0.0091$) and alcohol addition to give a mixture of three alcohol addition products ($\Phi = 0.0053$); the formation of carbene-derived products was relatively less efficient ($\Phi = 0.0095$).

Keywords: Silicon; 1-Silanorbornene; 2-Silylnorbornene; Photochemistry; Synthesis; Rearrangement

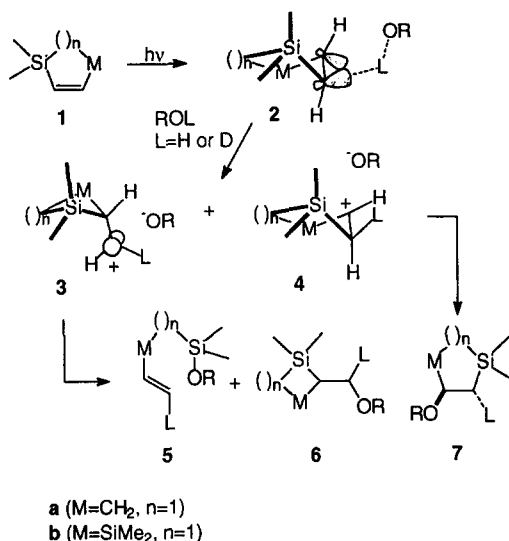
1. Introduction

Mono- and disilacyclopentenes **1** undergo photochemical addition of alcohols to give adducts attributable to the intermediacy of β -silyl carbocations (Scheme 1) [1,2]. Evidence suggests that these β -silyl cations arise through protonation of strained ground state *trans*-mono- and disilacyclopentenes **2** produced via *E,Z* photoisomerization of **1**. The final products **6b** and **7** are then formed through capture of cations **3** and **4** by alcohols, whereas cations **3** are believed to be the principal intermediates in the β -cleavage to **5**. Labeling studies of **1a,b** with deuterated alcohols show that the latter β -cleavage process is *trans*-stereospecific [1,2]

such that deuterium is incorporated *trans* to Si at the terminal position of the double bond of **5a,b**. In the case of **1a**, trapping of **4a** is also known to produce **7a** with a high degree of *trans*-diastereoselectivity [1]. As the diastereoselective formation of **7a** varies with alcohol concentration, while β -cleavage to **5a** remains *trans*-stereospecific, two different cation intermediates appear to be involved in the photoalcoholyses.

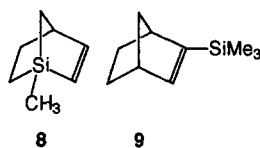
In this paper we consider an alternate mechanism for photoalcoholysis in which the σ, π^* excited state of the silacycloalkene could undergo protonation by alcohols as a consequence of enhanced basicity of the π system upon promotion of a σ electron [2]. In order to differentiate this excited state proton transfer process from that involving a ground state *trans*-silacycloalkene, we investigated the photochemistry of two rigid bicyclic silacycloalkenes, 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) [3] and 2-trimethylsilylbicyclo-

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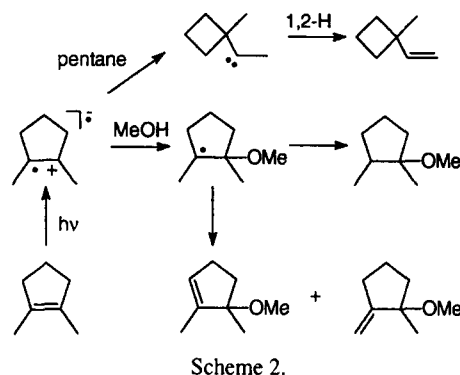


Scheme 1.

[2.2.1]hept-2-ene (9). In these silyl-ethylenes both the σ, π^* and π, π^* excited states are expected to be accessible to short UV light. While the σ, π^* transition underlies the strong π, π^* absorption in the case of monosilyl-ethylenes [1,4,5], it appears as a distinct shoulder to the red in disilyl-ethylenes and disilacycloalkenes [2] and shifts to longer wavelengths upon successive silylation of the double bond in persilylated ethylenes [2,4,5]. In addition to the σ, π^* and π, π^* excited states, one must also consider the potential role of the $\pi, 3s$ (Rydberg) state in photoreactivity, since this excited state dominates the photochemistry of hydrocarbon cyclopentenes (vide infra), and Rydberg-like photoisomerizations are observed among disilacycloalkenes [2,6].



Hydrocarbon cyclopentenes do not undergo photoalcoholyses [7] by a mechanism initiated by proton transfer. Although alcohol photoaddition is observed among the more heavily alkylated derivatives such as 1,2-dimethylcyclopentene [7,8], the mechanism involves nucleophilic addition of the alcohol to the radical cation-like $\pi, 3s$ (Rydberg) state (Scheme 2). The resultant radicals then disproportionate to form the final products. Rydberg states of alkenes also rearrange to carbenes via [1,2-C] and [1,2-H] migration [7–12]. Alkyl migration results in formation of 1-methyl-1-vinylcyclobutane upon irradiation of 1,2-dimethylcyclopentene in pentane (Scheme 2) [8], and methylenecyclobutane and bicyclo[2.1.0]pentane appear to be formed from an anal-



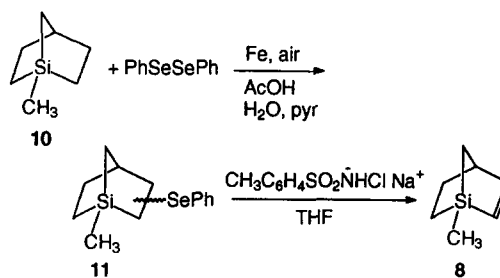
Scheme 2.

ogous cyclobutylmethylene intermediate upon photolysis of cyclopentene [13,14]. In the case of cyclopentene, deuterium labeling of both the C₃ and C₄ positions indicates that [1,2-H] migration does not compete with [1,2-C] migration in the Rydberg state [13]. Norbornene, however, undergoes both [1,2-C] and [1,2-H] shifts in the $\pi, 3s$ (R) state [14,15]. If the Rydberg state is destabilized relative to the π, π^* excited state by an electron deficient substituent at the double bond [16], [1,3-C] photorearrangements predominate, as exemplified by 2-trifluoromethyl [17] and 2-cyano derivatives of bicyclo[2.2.1]hept-2-ene [18]. The reversal in energy of π, π^* and $\pi, 3s$ (R) states can also be achieved by phenyl conjugation, but with 2-phenylbicyclo[2.2.1]hept-2-ene, the lowest energy π, π^* excited state undergoes alcohol addition to give the Markovnikov ether product, apparently as a result of polarization of the π, π^* state by the phenyl group [19]. No photoalcoholysis reactions involving proton transfer have been observed for the shorter-lived π, π^* singlet excited state of phenylcyclopentene [7,19].

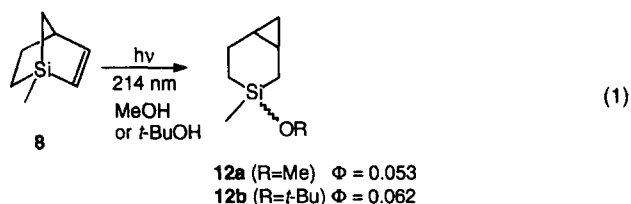
2. Results

2.1. Synthesis of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (8)

Our synthesis of the previously unknown 1-silanorbornene **8** from 1-silanorbornane **10** (Scheme 3) is based on Gif^{III} oxidation of inactivated CH₂ groups to



Scheme 3.



ketones by iron powder plus acetic acid with oxygen as the oxidizing species in aqueous pyridine [20,21]. The intermediate phenylselenide derivative **11** was obtained by a variation [21a] which utilized PhSeSePh to trap the putative Fe–C σ complex formed upon insertion of an Fe^V oxo species into the alkane CH bond. Subsequent selenoxide elimination then furnished 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) under mild conditions (*vide infra*). Free radical chlorination of 1-chloro-1-silanorbornane followed by dehydrochlorination was considered as an alternate route to **8**. However, mild heating of 1,3-dichloro-1-silabicyclo[2.2.2]octane had previously been reported to result in cleavage to 1,1-dichloro-4-vinyl-1-silacyclohexane [22]. Our attempts to dehydrohalogenate an exo/endo mixture of monochloro derivatives of 1-methyl-1-silanorbornane **10** using DBU in dry CCl₄, LDA in THF at –35 °C, and KO^tBu in triglyme and 18-crown-6 failed to give **8**. The product mixtures were usually complex, although GC-MS analyses suggested that cleavage of the bicyclic ring had occurred under these strongly basic conditions.

The Gif^{III} oxidation [21a] of 1-methyl-1-silabicyclo[2.2.1]heptane **10** gave a 70:22:5:3 mixture of four isomeric phenylselenides in 8% yield after silica gel chromatography to remove unreacted **10**, diphenyldiselenide, and a product of coupling of 1-methylsilanorbornane with pyridine. Attempted removal of the diphenyldiselenide by sodium borohydride reduction caused decomposition of **11** under the basic conditions employed. To avoid reduced yields of phenylselenides **11**, conversions of **10** were kept low, usually less than 25%. This required monitoring of the reaction by GC-MS, because induction periods for the Gif^{III} oxidations varied from run to run. By conducting five parallel reactions, each with 2 mmol of **10** as prescribed by the literature [21a], combined yields of 0.78 mmol (220 mg) of **11** were obtained after chromatography. Five repeti-

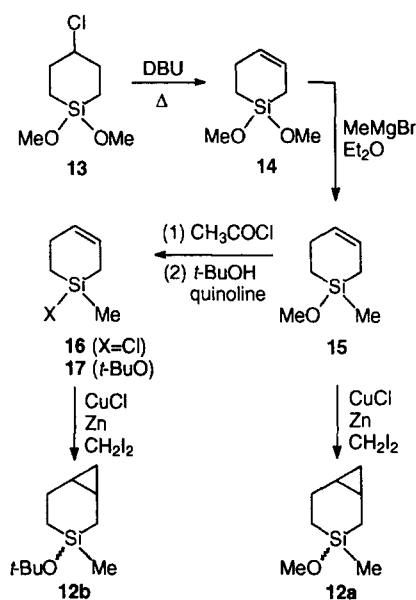
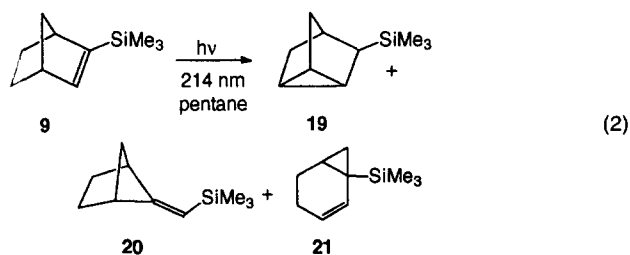
tions then gave sufficient material to conduct the subsequent phenylselenide oxidative-elimination on a ca. 1 g scale. 1-Methyl-1-silanorbornane **10** was obtained by reaction of methyllithium with 1-chloro-1-silanorbornene, which in turn was synthesized by minor modifications of the multistep route reported by Sommer and Bennett over 30 years ago [23,24].

Chloramine-T oxidation [25] of the mixture of phenylselenides **11** resulted in elimination of the *N*-tosylselenimide to give the bridgehead silanorbornene **8** in 27% isolated yield (0.97 mmol, 120 mg) after preparative GC purification. MCPBA oxidation was not attempted because of reports that sila-Pummerer rearrangement competes with the syn elimination of α -silyl selenoxides [26–28].

1-Methyl-1-silanorbornene **8** displayed two alkenyl protons in the ¹H NMR spectrum. The upfield proton at the C₂ position of the double bond appeared as a doublet, coupled by 10.5 Hz to the downfield C₃ proton, which was a doublet of doublets due to an additional 4.7 Hz coupling with the proton at the bridgehead position.

2.2. Photolyses of 1-methyl-1-sila[2.2.1]hept-2-ene (**8**)

Photolysis of 10^{–2} M (0.3 mmol) **8** in deoxygenated methanol at 214 nm with a 15 W zinc lamp produced 37% of 3-methoxy-3-silabicyclo[4.1.0]heptane (**12a**, R = Me) and ca. 4% of an unidentified isomeric methanol adduct, in addition to 57% unreacted **11** (Eq. (1)). Adduct **12a** was isolated by preparative GC from a high conversion run and found to be a 57:43 mixture of epimers by ¹H NMR spectroscopy. Since the epimeric mixture proved to be inseparable by GC on several columns, the mixture was characterized by comparison



Scheme 4.

Table 1

Product yields for 214 nm photolyses of 2-trimethylsilylnorbornene **9** in pentane and alcohols

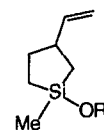
Solvent	Products (%)						
	Unreacted 9	19	20	21	22	24	25
Pentane	77	15	4	2	2		
^t BuOH	57	27	4	2	5		
MeOH ^a	57	21	3	nd ^b	4	3	3
CF ₃ CH ₂ OH	34	20	3	tr ^c	4	12 ^d	26

^a Photoreduction product **23** was produced in 7% yield. ^b Not detected by ¹H,¹³C NMR spectroscopy. ^c Trace detected by GC-MS analysis. ^d Ca. 1.1:1.5:1.0 ratio of isomers.

of ¹H,¹³C NMR spectral data to an independently synthesized sample of epimeric **12a** (Scheme 4).

Irradiation of 10⁻² M **8** in *tert*-butyl alcohol as the solvent gave *tert*-butyl silyl ether **12b** as the sole photoproduct in 24% yield as a 65:35 ratio of epimers along with 73% of unreacted **8**. In this case the epimers were partially separable, and pure minor epimer and enriched major epimer were obtained by preparative GC of a run taken to high conversion. Our initial assignment of the product structure as **12b** was based on NMR spectroscopic analysis of the pure minor epimer, whose ¹H NMR spectrum showed an upfield multiplet centered at δ -0.09, suggestive of one of the methylene protons of the cyclopropane ring. From the heterocorrelated 2D spectrum this proton could be seen to correspond to the highest field methylene carbon at δ 11.33 in the ¹³C (APT) spectrum. The appearance of the δ -0.09 multiplet (ddd) as a quartet was due to $J_{\text{gem}} \approx J_{\text{vic}} \approx 5$ Hz. The small geminal coupling is well-precedented in bicyclo[4.1.0]alkane ring systems [29]. In addition, ¹³C NMR (off-resonance decoupled) $J_{\text{C-H}} \approx 163$ Hz was similar to the $J_{\text{C-H}} \approx 157$ Hz of the cyclopropyl methine carbons at δ 7.87 and 13.31; these couplings were also larger than the $J_{\text{C-H}}$ of 112–127 Hz of the remaining downfield methylene carbons of the six-membered ring. The ¹H,¹³C NMR spectral data of the enriched major epimer of **12b** were obtained by subtraction of peaks due to the minor epimer. However, the relative stereochemistry of each epimer was not assigned. The structures of epimeric **12b** were proven by independent synthesis (Scheme 4).

Control experiments showed that silanorbornene **8** was stable in methanol and in *tert*-butyl alcohol for 5 days in the dark. In contrast, **8** completely reacted with 2,2,2-trifluoroethanol to give an alcohol adduct according to GC-MS analyses. After preparative GC isolation, this adduct was identified by ¹H,¹³C NMR spectroscopy as trifluoroethoxysilane **18**.

**18** (R = OCH₂CF₃)

Quantum yields for epimeric products **12a,b** were determined at low conversions (1–3%) utilizing uranyl oxalate actinometry [30,31]. The data summarized in Eq. (1) represent the average of duplicate runs in methanol and *tert*-butyl alcohol as solvents.

2.3. Photolyses of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (**9**)

The 214 nm photochemistry of 2-trimethylsilylnorbornene **9** in alcohols was studied for comparison with 1-silanorbornene **8**. We also investigated the photochemistry in pentane, in order to distinguish proton transfer from photorearrangement pathways. 2-Trimethylsilylnorbornene **9** [32] was synthesized by metallation of norbornene utilizing butyllithium and potassium *tert*-butoxide followed by reaction of the alkenyl potassium intermediate with chlorotrimethylsilane [33,34].

Preparative scale 214 nm photolyses of 0.1 M **9** in pentane gave trimethylsilylnortricyclene **19** as the major product along with trimethylsilylmethylenebicyclo[2.1.1]hexane **20**, 1-trimethylsilyl-2-norcarene **21** (Eq. (2)), and another minor isomeric product, allene **22**. Chemical yields and quantum yields are summarized in Tables 1 and 2. The photoproducts were isolated by preparative GC, and nortricyclene **19** [32] and norcarene **21** [35] were identified by comparison of ¹H,¹³C NMR spectral data with samples synthesized by literature

Table 2

Quantum yields ^a for 214 nm photolyses of 2-trimethylsilylnorbornene **9** in pentane and alcohols

Solvent	Products (Φ)						
	19	20	21	22	23	24	25
Pentane	0.0062	0.0019	0.0022	0.00031			
^t BuOH	0.0042	0.00058	0.00059	0.00055			
MeOH	0.0075	0.00069	nq ^b	0.00065	0.0035 ^c	tr ^d	tr ^d
CF ₃ CH ₂ OH	0.0087	0.00085	tr ^d	0.00082	nd ^e	0.0053 ^f	0.0091

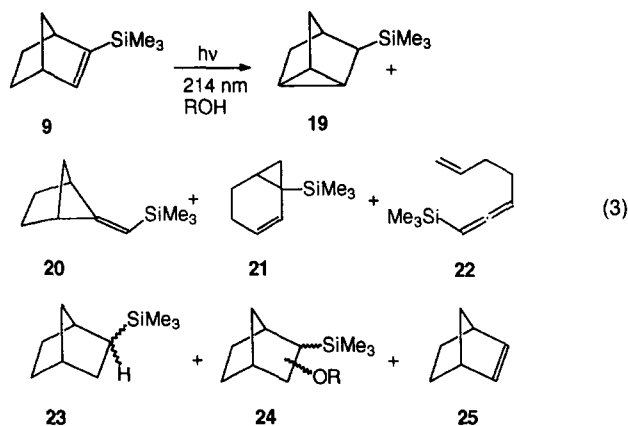
^a Average of two determinations at less than 5% conversion; average deviation was less than 10%. ^b Not quantified, obscured by product **23**.

^c Includes an undetermined amount of **21**. ^d Trace. ^e Not detected. ^f Ca. 1.2:1.8:1.0 ratio of isomers.

methods. The bicyclic compound **20** was characterized spectroscopically. The ^1H NMR spectrum of **20** resembled that reported for methylenebicyclo[2.1.1]hexane [15], and ^{13}C NMR spectral data were consistent with its assigned structure.

One of the minor isomeric photoproducts was isolated by preparative GC after a high conversion photolysis and identified spectroscopically as 1-trimethylsilyl-1,2,6-heptatriene (**22**). The previously unknown allene **22** displayed a peak at δ 209.82 corresponding to the central allenic carbon and additional peaks for vinyl carbons at δ 114.76 and δ 138.31 in the ^{13}C NMR spectrum. A characteristic pattern of a vinyl group was also present in the ^1H NMR spectrum.

Secondary photolysis of norcarene **21** could be responsible for a significant fraction of allene **22** observed in photolyses of norbornene **9**. Even at relatively low conversions, the mole percent vs. time profile (Fig. 1) showed a tendency for the yield of allene **22** to increase at the expense of norcarene **21**. Furthermore, 214 nm photolysis of norcarene **21** in pentane resulted in fragmentation to allene **22** with a $\Phi = 0.024$ at 1% conversion, which is 80-fold higher than the apparent quantum yield for formation of **22** from **9** (Table 2). An unidentified photolabile isomer was also formed from norcarene **21** with a quantum yield of 0.074, along with two minor products. This unidentified photoisomer was also observed in photolysates of **9** at low conversions by GC-MS. The photofragmentation of norcarene **21** to allene **22** is possibly analogous to the formation of 1,2,6-heptatriene from the parent bicyclo[4.1.0]hept-2-ene [36]. The parent norcarene also undergoes [1,3-C] migration to bicyclo[3.2.0]hept-2-ene and norbornene



and cyclopropane ring opening and [1,2-H] migration to isomeric 1,3- and 1,4-cycloheptadienes and 1-methylenecyclohex-3-ene.

The photochemistry of trimethylsilylnorbornene **9** in *tert*-butyl alcohol was similar to that observed for photolyses in pentane. No *tert*-butyl alcohol adducts of **9** were observed by GC-MS analyses of the photolysates. Chemical yields and quantum yields are summarized in Tables 1 and 2.

Photolyses of **9** at 214 nm in methanol gave nortricyclene **19**, methylenebicyclohexane **20**, allene **22**, and additionally, 2-trimethylsilylbicyclo[2.2.1]heptane **23** (mainly *exo*, Eq. (3)). Minor amounts of norbornene **25** and three methanol addition products of **9** ($\text{R} = \text{CH}_3$, Eq. (3)) were detected by GC-MS analyses. The chemical yields are summarized in Table 1. Silylnorbornane **23** was isolated as an inseparable mixture with nortricyclene **19**. The stereochemistry of trimethylsilylnorbornane **23** [32] was mainly *exo* from comparison of ^1H , ^{13}C NMR data with an independently synthesized sample (Experimental). From the NMR data we could not rule out the presence of as much as 20% *endo* isomer of **23**. The major stereoisomer must be *exo*, however, based on additional comparisons with the ^1H , ^{13}C NMR spectral data of authentic *endo*-**23** [32], which was independently synthesized. Norcarene **21** was not detected by GC-MS, possibly because of its proximity in retention time to **23**, and it was not detected by ^1H , ^{13}C NMR in the mixture of **19** plus **23** isolated by preparative GC from the photolysate. A control showed that norcarene **21** was stable in the dark in methanol.

The 214 nm irradiation of **9** in trifluoroethanol gave nortricyclene **19** as the major product, minor amounts of isomers **20** and **22**, norbornene **25**, and three trifluoroethanol solvent addition products **24** in a 1.1:1.5:1.0 ratio according to GC-MS analyses ($\text{R} = \text{CH}_2\text{CF}_3$, Eq. (3)). Norcarene **21** and norbornane **23** were not detected. A control showed **21** to be stable in the dark in trifluoroethanol. Nortricyclene **19** and norbornene **25**

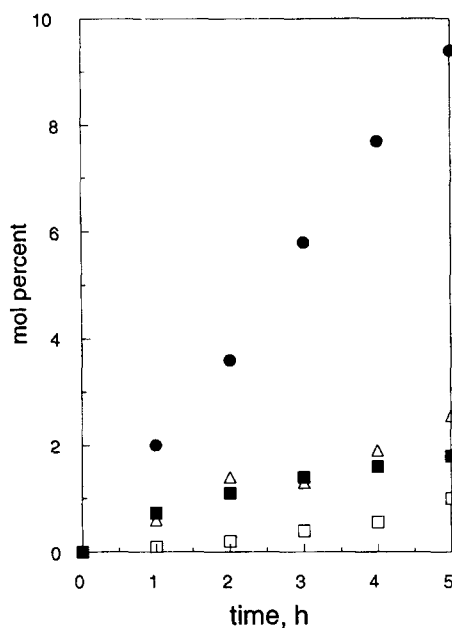
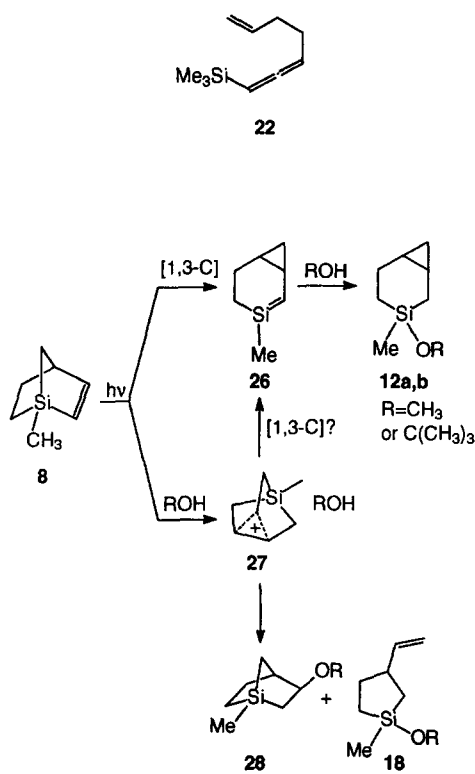


Fig. 1. Mole percent vs. time profile for products of 214 nm photolysis of **9**: nortricyclene **19** (●), methylenebicyclohexane **20** (▲), norcarene **21** (■), allene **22** (□).

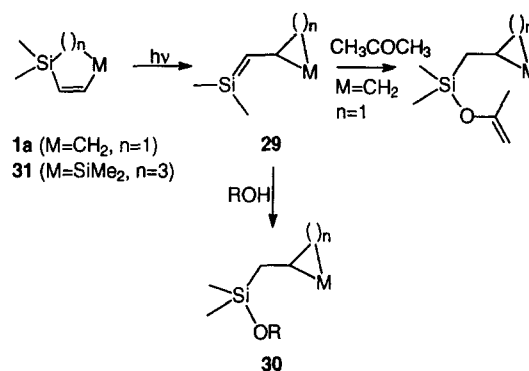
were isolated by preparative GC and further identified by comparison of ^1H NMR spectra with authentic samples. Trifluoroethanol adducts **24** were also isolated, but could not be separated by preparative GC. Thus, definitive structural assignments could not be made, although they appeared to be stereoisomeric 3-trifluoroethoxy-2-trimethylsilylnorbornanes **24** on the basis of combustion analysis, ^1H , ^{13}C NMR spectroscopy, and MS fragmentation patterns. The chemical yields and quantum yields are summarized in Tables 1 and 2; GC response factors for **24** were estimated from a standard prepared from the preparative GC isolated mixture of adducts.

2.4. Deuterium labeling

The deuterium labeling of photoproducts was studied for 214 nm photolyses of 2-trimethylsilylnorbornene **9** in MeOD and $\text{CF}_3\text{CD}_2\text{OD}$. GC-MS analyses of a low conversion run with MeOD as the solvent revealed that norbornane **23** was 100% monodeuterated. Isomers **19**–**21** were more than 97% undeuterated. With $\text{CF}_3\text{CD}_2\text{OD}$ as the solvent no deuterium was detected by GC-MS analyses in **19**, **20**, and **22**. The three isomeric adducts **24** ($\text{R} = \text{CD}_2\text{CF}_3$) exhibited a parent ion at m/z 269, consistent with trideuteration. Since the parent ion was very weak, the m/z 184 fragment ion (loss of CD_2CF_3) was used instead to calculate the extent of monodeuteration, which was found to be 100% for each adduct. Norbornene **25** was completely monodeuterated.



Scheme 5.



Scheme 6.

3. Discussion

3.1. Photochemistry of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**)

The formation of bicyclic ethers **12a,b** can be attributed to a mechanism involving excited state [1,3-C] shift of 1-silabicyclo[2.2.1]hept-2-ene **8** to silene **26**, followed by trapping of the silene intermediate by CH_3OH and $(\text{CH}_3)_3\text{COH}$ (Scheme 5). Such a mechanism was proposed for the formation of the analogous ring contracted alcohol adducts **30** upon 214 nm photolysis of silacyclopentene **1a** [1]. In the case of **1a** the silene intermediate **29** ($\text{M} = \text{CH}_2$, $n = 1$) was trapped, not only by alcohols (ROH) to form **30**, but also by silene traps such as methoxytrimethylsilane and acetone (Scheme 6). Thus, the alternate mechanism for formation of **30** involving [1,3-C] shift in carbonium ion **27** was considered unlikely. Excited state [1,3-C] photorearrangement to a silene has also been observed upon 214 nm irradiation of 1,1,4,4-tetramethyldisilacyclohept-2-ene (**31**, Scheme 6) [6]. The principal volatile product in the absence of added strong acid was the (silacyclopentylmethyl)silyl ether **30** ($\text{M} = \text{SiMe}_2$, $n = 3$) deriving from methanol addition to silene **29** ($\text{M} = \text{SiMe}_2$, $n = 3$). Since silyl ether **30** ($\text{M} = \text{SiMe}_2$, $n = 3$) was not a significant photoproduct upon photolysis of **31** in acidified methanol, its mechanism appeared to be independent of the carbocation mechanism proposed for the formation of photoalcoholysis products of *trans*-**31**.

The photoprotonation of rigid 1-silabicyclo[2.2.1]hept-2-ene **8** by CH_3OH and $(\text{CH}_3)_3\text{COH}$ must be considerably less efficient than the more flexible analog, silacyclopentene **1a**, which gives photoalcoholysis products **5a** plus **7a** (Scheme 1) with total quantum yields of 0.072 in MeOH, 0.030 in $(\text{CH}_3)_3\text{COH}$, and 0.086 in $\text{CF}_3\text{CH}_2\text{OH}$ [1]. Although photoalcoholysis of **8** would have been expected to give **18** ($\text{R} = \text{CH}_3$ or $\text{C}(\text{CH}_3)_3$) and/or **28** as products of carbonium ion **27**, only a very low yield of a potential photoalcoholysis product was observed in

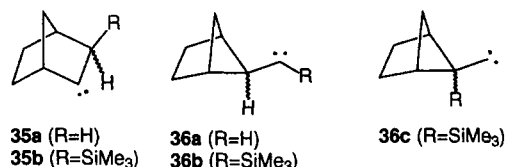
methanol, and **12b** was the sole product observed in $(\text{CH}_3)_3\text{COH}$ as the solvent. On the basis of the quantum yield data for **8**, we estimate $\Phi < 0.01$ for photoalcoholysis in methanol and $\Phi = 0$ for *tert*-butyl alcohol. With $\text{CF}_3\text{CH}_2\text{OH}$ a dark reaction produced a photoalcoholysis type of product, silyl ether **18** ($\text{R} = \text{CH}_2\text{CF}_3$).

The low reactivity of 1-silanorbornene **8** with respect to direct proton transfer in the excited state is not attributable to highly efficient excited state decay via [1,3-C] migration. Quantum yields for **12a,b** in methanol or *tert*-butyl alcohol are only four- to six-fold more efficient for **8** than for **1a**, which produces cyclopropylmethylsilyl ethers **30** ($\text{M} = \text{CH}_2$, $n = 1$) with quantum yields [1] of 0.013 ($\text{R} = \text{CH}_3$), 0.010 ($\text{R} = \text{C}(\text{CH}_3)_3$), and 0.019 ($\text{R} = \text{CH}_2\text{CF}_3$). The higher efficiency for [1,3-C] migration in **8** than in **1a** may be due to favorable overlap and the elimination of *Z,E* photoisomerization as a competing process of the excited state.

3.2. 2-Trimethylsilylbicyclo[2.2.1]hept-2-ene (**9**)

In pentane and *tert*-butyl alcohol as the solvents the photochemistry of 2-trimethylsilylnorbornene **9** resembles that of the parent compound, norbornene **25**. Photolysis of norbornene **25** ($\text{R} = \text{H}$ in Eq. (4)) at 185 nm in pentane [14,15] produces nortricyclene **32** ($\Phi \sim 0.02$) and 5-methylenebicyclo[2.1.1]hexane **33** ($\Phi \sim 0.02$) in addition to products of hydrogen abstraction from solvent, including norbornane, norbornyl dimer, pentane dimer, and a pentane adduct of **25**. The proposed intermediates, carbenes **35a** and **36a**, are considered as being produced via [1,2-H] and [1,2-C] migrations in the $\pi,3s$ (Rydberg) state of **25** ($\text{R} = \text{H}$) [7,9–12]. When the cation radical-like Rydberg state is destabilized relative to the π, π^* excited state by electron deficient 2-trifluoromethyl [16,17] or 2-cyano substituents [18], [1,3-C] migration to form C-1 substituted 2-norcaradienes **34** ($\text{R} = \text{CF}_3$ or CN) becomes the major photoprocess, and Rydberg-type products **32** and **33** are not observed.

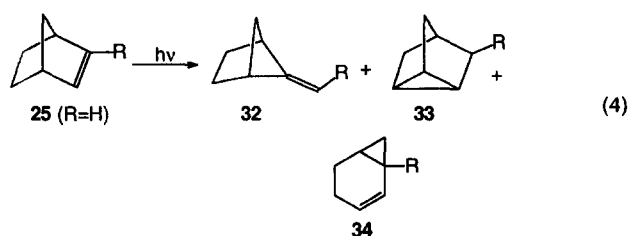
As with norbornene **25**, the formation of Rydberg-type photoisomers **19** and **20** (Eq. (2)) can be ascribed to the intermediacy of carbenes **35b** and **36b,c**. Whereas only carbene **35b** is required to account for the major photoisomer **19**, the minor photoisomer **20** can be

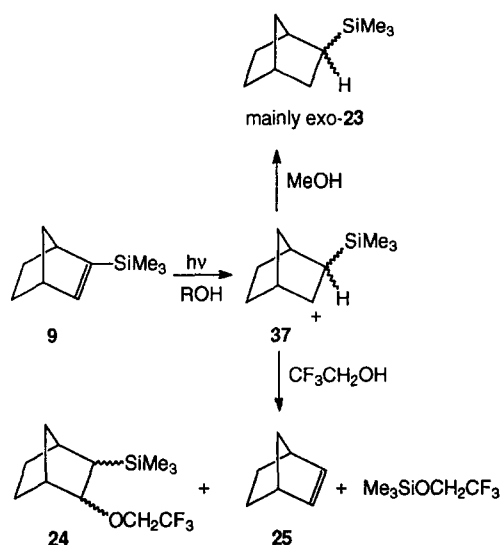


formed by [1,2-C] shift in carbene **35b** and [1,2-H] or [1,2-Si] shifts in carbenes **36b,c**. Product ratios and quantum yields with pentane as solvent indicate a three- to four-fold preference for formation of nortricyclene **19** over bicyclic product **20**. This preference implies that photoexcited **9** predominantly photorearranges to carbene **35b** by [1,2-Si] migration, since in norbornene **25** the competition between [1,2-H] and [1,2-C] migrations affords no preference for products **32** and **33** via carbenes **35a** and **36a** as intermediates. The low quantum yields for **19** and **20** further suggest that in carbene **35b** reverse [1,2-Si] migration [37] to regenerate reactant competes effectively with CH insertion or [1,2-C] shift. Little preference for **19** over **20** is expected based on the relative stabilities of the intermediates, since both **35b** and **36c** are potentially stabilized by a β -silyl substituent [37,38].

The onset of photoprotonation of **9** was observed in methanol, as evidenced by the formation of traces of **24** ($\text{R} = \text{CH}_3$) and desilylation product norbornene **25**, as well as the emergence of 2-trimethylsilylnorbornane **23** (mainly *exo*, $\Phi = 0.0035$) as a significant photoproduct. Since photolysis in methanol-*O-d* led to 100% incorporation of one deuterium into **23**, this product can be ascribed to a mechanism involving initial proton (deuteron) transfer to form silylnorbornyl cation **37** (Scheme 7) followed by a hydride transfer. Such a mechanism has been demonstrated previously for the formation of 2-phenylnorbornane from 2-phenylnorbornene [19]. Given the likelihood of silylnorbornyl cation **37** as the precursor to **23**, we considered the possibility that nortricyclene **19** could have been formed, at least in part, by a mechanism involving deprotonation from the C_6 position of this intermediate. This possibility was ruled out by the fact that **19** contained essentially no deuterium (97% d_0) upon irradiation of **9** in MeOD. Nortricyclene **19** thus appeared to derive solely from the aforementioned carbene mechanism. Since methylenebicyclohexane **20** and allene **22** were also undeuterated, the total quantum yield for photoprotonation was estimated to be $\Phi \geq 0.0035$ on the basis of data for **23**.

The formation of the mixture of adducts **24** upon photolysis of **9** in $\text{CF}_3\text{CH}_2\text{OH}$ can be attributed to capture of silylnorbornyl cation **37** by alcohol, while desilylation through β -cleavage of this intermediate





accounts for formation of norbornene **25**. On the basis of these conclusions, the total efficiency of photoprotonation of **9** for these two products is estimated from the quantum yields in Table 2 as $\Phi > 0.014$. This value can be considered a lower limit, since the photoprotonation of **9** could be reversible.

As in the case of photolysis with CH_3OD , the absence of significant deuterium incorporation into nortricyclene **19** and methylenebicyclohexane **20** upon photolysis in $\text{CF}_3\text{CD}_2\text{OD}$ is consistent with these products being formed via a carbene mechanism. Since the quantum yields for **19** and **20** are undepressed in alcohols vs. pentane as solvent, carbene **35b** does not appear to be diverted to carbocation **37** by protonation by $\text{CF}_3\text{CH}_2\text{OH}$ or CH_3OH . If anything, the quantum yields for these carbene-derived products appear to increase with increasing polarity of the solvent. The efficiency for allene **22** increases monotonically with solvent polarity, and this increase appears to be at the expense of norcarene **21** (Table 2). Possibly the solvent affects the partitioning of an excited state zwitterionic intermediate between closure and cleavage pathways to **21** and **22**, in which case allene **22** may not entirely derive from secondary photolysis of **21** (vide supra). Such an excited state zwitterionic intermediate has been proposed previously for the [1,3]-photorearrangement of 2-cyanonorcarene to 2-cyanonorbornene [17].

4. Conclusion

The inefficiency of 1-silanorbornene **8** and 2-silylnorbornene **9** towards photoalcoholysis indicates that a significant degree of twisting about the double bond is a prerequisite for protonation and formation of alcohol adducts by a carbocation mechanism. Photoalcoholysis

is most efficient in flexible medium ring systems such as 1-silacyclohex-2-ene, where total quantum yields as high as 0.34 have been observed in $\text{CF}_3\text{CH}_2\text{OH}$. Increased constraint to twisting in 1-silacyclopent-2-ene results in decreased efficiency ($\Phi_{\text{tot}} = 0.10$ in $\text{CF}_3\text{CH}_2\text{OH}$), but photoalcoholysis nonetheless remains a relatively efficient channel for reaction with less acidic alcohols such as methanol and *tert*-butyl alcohol. In contrast, 1-silanorbornene **8** undergoes almost exclusive [1,3-C] migration in CH_3OH and $(\text{CH}_3)_3\text{COH}$, whereas Rydberg-type carbene chemistry dominates the photoreactivity of 2-silylnorbornene **9** until the acidity of the alcohol approaches that of $\text{CF}_3\text{CH}_2\text{OH}$. Excited state proton transfer then becomes the major photoprocess, but the efficiency is low.

5. Experimental

Spectra were recorded with the following spectrometers: GE GN-300 (300 MHz, ^1H ; 75 MHz, ^{13}C , chemical shift units δ relative to TMS), and Mattson 4020 Galaxy Series (FTIR). A Hewlett-Packard 5890 GC and HP-5970 mass selective detector were used for GC-MS analyses, which were performed at 70 eV with a 0.25 mm $\times$ 30 m DB-1 capillary column programmed at 40 $^\circ\text{C}$ for 4 min and then 250 $^\circ\text{C}$ at 10 $^\circ\text{C min}^{-1}$.

Preparative GC separations were performed on a Gow-Mac Series 580 gas chromatograph with He as carrier gas at 30 ml min^{-1} flow rate on the following columns: column A, 16 ft $\times$ 1/4 in 20% DC 550 on 80/100 mesh Chromosorb P AW; column B, 15 ft $\times$ 1/4 in 15% QF-1 on 60/80 mesh Supelcoport; column C, 16 ft $\times$ 1/4 in 10% Carbowax 20M on 80/100 mesh Chromosorb W AW DMCS; column D, 17 ft $\times$ 1/4 in 15% didecyl phthalate on 60/80-mesh Chromosorb W.

An HP 5710 gas chromatograph equipped with a flame ionization detector and a PE Nelson model 1020 Personal integrator were used for analytical separations. Nitrogen was the carrier gas at a flow rate of 30 ml min^{-1} . The following columns were used: column E, 0.547 mm $\times$ 30 m DB-1 Megabore capillary column; column F, 12 ft $\times$ 1/8 in 10% QF-1 on 80/100 mesh Supelcoport; column G, 20 ft $\times$ 1/8 in 10% Carbowax 20M on 80/100 mesh Chromosorb W AW DMCS; column H, 22 ft $\times$ 1/8 in 10% OV101 on 100/120 mesh Chromsorb W HP.

Methanol (EM Omnisolv) was freshly distilled from magnesium under nitrogen. *tert*-Butyl alcohol (Alfa 95%) was freshly distilled from CaH_2 .

5.1. 1-Chloro-1-silabicyclo[2.2.1]heptane

The literature procedure [23,24] was modified. To 7.8 g (0.33 mol) of magnesium was added a 2 g portion

of 1,5-dichloro-3-(trichlorosilylmethyl)pentane [24] in 50 ml anhydrous ether under nitrogen. After initiation with several drops of iodomethane, the remaining 30 g of 1,5-dichloro-3-(trichlorosilylmethyl)pentane (total 0.11 mol) in 180 ml anhydrous ether was added slowly over a period of 2 days with heating followed by an additional day of refluxing. Pentane was added, the precipitate was removed by suction filtration, and the supernatant was concentrated by distillation through a 6 in Vigreux column. Short-path distillation of the residue gave 9.0 g (56% yield) of bicyclic chlorosilane, b.p. 55–56 °C (5 mm) (Ref. [24] b.p. 53–54 °C (5 mm)).

5.2. 1-Methyl-1-silabicyclo[2.2.1]heptane (10) [39]

To a solution of 18 g (0.12 mol) of 1-chloro-1-silabicyclo[2.2.1]heptane in 100 ml anhydrous ether at –40 °C under nitrogen was added dropwise 127 ml (0.19 mol) of 1.5 M methyl lithium in diethyl ether. The mixture was stirred for 1 h, and then water was added dropwise, while maintaining the temperature at –35 to –45 °C. The aqueous layer was extracted three times with ether, and the combined extracts were dried over anhydrous magnesium sulfate followed by distillation of the ether through a 6 in Vigreux column. Short-path distillation of the residue gave 12.6 g (81% yield) of 1-methyl-1-silabicyclo[2.2.1]heptane (10), b.p. 45–48 °C (20 mm). The spectral data were as follows: ^1H NMR (CDCl_3) δ 0.37 (s, 3H, methyl), 0.34–0.42 (m, obscured, 6H, CH_2), 1.52–1.74 (m, 4H, methylene), 2.18–2.25 (br s, 1H, methine); ^{13}C NMR (CDCl_3) δ –7.23, 5.62, 17.38, 30.34, 33.70; GC-MS m/z (relative intensity) 128 ($\text{M} + 2^+$, 0.9), 127 ($\text{M} + 1^+$, 1), 126 (M^+ , 20), 111 (3), 97 (100), 95 (8), 83 (47), 70 (33), 55 (29), 43 (66).

5.3. 1-Methyl-2-phenylseleno-1-silabicyclo[2.2.1]heptane (11)

Five reactions were run simultaneously in magnetically-stirred Erlenmeyer flasks exposed to air. Each flask contained 250 mg (2.00 mmol) of 1-methyl-1-silabicyclo[2.2.1]heptane, 1.12 g (20.0 mmol) of iron powder, and 312 mg (1.00 mmol) of diphenyldiselenide in 29 ml of pyridine. After addition of 2.3 ml of water and 2.3 ml of acetic acid, the mixtures were heated to 40 °C in a water bath for a few minutes to initiate reaction and then stirred without heating for 2–3 h. To each mixture was added 20 ml ether followed by acidification to pH = 1 with 18 N sulfuric acid while cooling in dry ice. The ether and aqueous phases of the five reactions were separated. The combined aqueous phases were extracted three times with 100 ml of ether. The combined ether extracts were washed three times with 300 ml of water, saturated sodium chloride, and dried over MgSO_4 , followed by distillation of the ether

through a 6 in Vigreux column. Unreacted silanorbornane was recovered by short-path distillation at 20 mm. The residue was chromatographed on an 80 cm $\times$ 3 cm column of silica gel, eluting with hexane, to give fraction 1 (200 ml), pyridine adducts of the silanorbornane plus diphenyldiselenide, fraction 2 (250 ml), mostly diphenyldiselenide, fraction 3 (800 ml), diphenyldiselenide and phenylselenides 11, and fraction 4 (250 ml), 160 mg of phenylselenides 11. An additional 60 mg of phenylselenides 11 was obtained by rechromatography of fraction 3. The combined yield of NMR pure phenylselenides 11 was 220 mg (7.8% yield), as a mixture of four isomers in a ratio of 3:5:22:70 in order of elution with retention times of 17.2, 18.3, 19.6, 20.9 min according to GC-MS analysis. The spectral data of the isomeric mixture were as follows: ^1H NMR (CDCl_3) δ 0.30–0.57 (m, 4H, CH_2), 0.41 (s, 3H, CH_3), 0.95 (d, J 12.7 Hz, 1H, CH_2), 1.14 (dd, J 1.3, 8.3 Hz, 1H, CH_2), 1.67 (td, J 0.7, 3.2 Hz, 2H, CH_2), 2.31 (br s, 1H, CH), 3.72 (dd, J 1.4, 5.5 Hz, 1H, CH), 7.48–7.63 (m, 5H, Ph); ^{13}C NMR (CDCl_3) δ –6.68, 4.84, 14.67, 16.70, 31.37, 40.00, 45.68, 127.38, 129.57, 129.87, 132.15, 133.88; GC-MS retention time, m/z (relative intensity), minor isomer A, 9.8 min, 284 ($\text{M} + 2^+$, 5), 283 ($\text{M} + 1^+$, 4), 282 (M^+ , 22), 280 (11), 125 (25), 97 (100), 95 (20), 77 (12), 43 (19); minor isomer B, 9.9 min, 283 ($\text{M} + 1^+$, 3), 282 (M^+ , 18), 280 (9), 125 (30), 98 (12), 97 (100), 95 (18), 77 (16), 71 (14), 45 (13), 43 (20); major isomer C, 10.0 min, 284 ($\text{M} + 2^+$, 2), 283 ($\text{M} + 1^+$, 2), 282 (M^+ , 12), 125 (32), 124 (17), 97 (100), 95 (17), 77 (12), 45 (10), 43 (21); major isomer D, 10.1 min, 284 ($\text{M} + 2^+$, 4), 283 ($\text{M} + 1^+$, 3), 282 (M^+ , 16), 281 (2), 280 (9), 254 (4), 200 (4), 125 (32), 98 (10), 97 (100), 95 (16), 77 (17), 45 (14), 43 (22).

5.4. 1-Methyl-1-silabicyclo[2.2.1]hept-2-ene (8)

To a solution of 1.0 g (3.5 mmol) phenylselenides 11 in 50 ml anhydrous THF was added 2.8 g (11.0 mmol) of *N*-chloro-*p*-toluenesulfonamide sodium salt (chloramine-T, Aldrich). With vigorous stirring at room temperature the yellow color disappeared within 10 min. After an additional 10 min water was added, and the mixture was extracted with 50 ml of pentane. The pentane extract was washed 12 times with 50 ml of water, and the pentane was distilled through a 6 in Vigreux column. Preparative GC of the residue (column A, 130 °C) gave 120 mg (27% yield) of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene. The spectral data were as follows: ^1H NMR (CDCl_3) δ 0.08–0.18 (m, 1H, CH_2), 0.35–0.62 (m, 3H, CH_2), 0.48 (s, 3H, CH_3), 1.20–1.30 (m, 1H, CH_2), 1.61–1.72 (m, 1H, CH_2), 3.09 (br s, 1H, CH), 6.04 (d, J 10.5 Hz, 1H, $\text{CH}=\text{CH}$), 6.91 (dd, J 4.7, 10.5 Hz, 1H, $\text{CH}=\text{CH}$); ^{13}C NMR (CDCl_3) δ –7.93, 1.41, 24.79, 28.68, 39.18, 130.80, 153.66; GC-MS, retention time 6.5 min, m/z (relative intensity) 124

(M^+ , 3), 109 (1), 96 (100), 83 (2), 81 (10), 68 (6), 55 (13), 43 (19). UV (pentane) $\lambda_{\max}$ 198 nm (ϵ 2650) and 206 nm (ϵ 2040). Anal. Found: C, 67.50; H, 10.20. $C_7H_{12}Si$. Calc.: C, 67.66; H, 9.73%.

5.5. 1,1-Dimethoxy-1-silacyclohex-3-ene (14)

A solution of 10 g (0.052 mol) of 2-chloro- and 4-chloro-1,1-dimethoxy-1-silacyclohexanes **13** in a ratio of 1:4 [40] and 8.0 g (0.052 mol) of DBU was heated under nitrogen in a high temperature oil bath at 180 °C for 2 h. The reaction mixture was then distilled to give 6.7 g (82% yield) of a 1:4 mixture of 1,1-dimethoxy-1-silacyclohex-2-ene and -3-ene, b.p. 150–160 °C. The mixture of isomers was used in the next step without further purification. A portion was subjected to preparative GC (column B, 100 °C) to isolate the major isomer, 1,1-dimethoxy-1-silacyclohex-3-ene. The spectral data were as follows: 1H NMR ($CDCl_3$) δ 0.79 (t, J 7.1 Hz, 2H, CH_2), 1.33 (dd, J 1.8, 4.51 Hz, 2H, CH_2), 2.28–2.37 (m, 2H, CH_2), 3.54 (s, 6H, MeO), 5.63–5.71 (m, 1H, $CH=CH$), 5.72–5.78 (m, 1H, $CH=CH$); ^{13}C NMR ($CDCl_3$) δ 6.87, 10.33, 22.99, 50.31, 125.35, 130.54; GC-MS m/z (relative intensity) 160 ($M+2^+$, 1), 159 ($M+1^+$, 3), 158 (M^+ , 21), 130 (34), 117 (32), 104 (40), 91 (18), 74 (54), 59 (100), 45 (16). Several attempts to obtain a satisfactory analysis were unsuccessful.

5.6. 1-Methoxy-1-methyl-1-silacyclohex-3-ene (15)

To a solution of 8.0 g (0.050 mol) of a mixture of 1,1-dimethoxysilacyclohex-2-ene and -3-ene in 60 ml of anhydrous ether was added, dropwise, 20.0 ml (0.060 mol) of 3.0 M methylmagnesium bromide in ether with stirring under nitrogen. The mixture was refluxed for 4–5 h, pentane was added, the precipitate was removed by suction filtration, and the supernatant was concentrated by distillation. Short-path distillation of the residue gave 5.4 g (75% yield) of a 1:4 ratio of 1-methoxy-1-methyl-1-silacyclohex-2-ene and -3-ene, b.p. 145–150 °C. The isomeric mixture was used without further purification for the next step. A portion was subjected to preparative GC (column B, 90 °C) to isolate the major isomer, 1-methoxy-1-methyl-1-silacyclohex-3-ene. The spectroscopic data were as follows: 1H NMR ($CDCl_3$) δ 0.17 (s, 3H, CH_3), 0.66 (ddd, J 6.0, 8.1, 14.4 Hz, 1H, CH_2), 0.88 (ddd, J 6.3, 7.5, 14.4 Hz, 1H, CH_2), 1.24 (br d, J 17.7 Hz, 1H, CH_2), 1.41 (br d, J 17.7 Hz, 1H, CH_2), 2.14–2.40 (m, 2H, CH_2), 3.45 (s, 3H, MeO), 5.62–5.70 (m, 1H, $CH=CH$), 5.71–5.78 (m, 1H, $CH=CH$); ^{13}C NMR ($CDCl_3$) δ -3.41, 9.44, 12.60, 22.81, 50.54, 125.42, 130.44; GC-MS m/z (relative intensity) 143 ($M+1^+$, 3), 142 (M^+ , 22), 127 (19), 114 (46), 101 (17), 99 (21), 88 (59), 75 (31), 59

(100), 58 (52), 45 (31), 43 (30). Anal. Found: C, 59.46; H, 10.20. $C_7H_{14}OSi$. Calc.: C, 59.10; H, 9.92%.

5.7. 3-Methoxy-3-methyl-3-silabicyclo[4.1.0]heptane (12a)

A mixture of 1.8 g (0.028 mol) of zinc dust, 0.2 g (2.0 mmol) of cuprous chloride, and 30 ml of anhydrous ether was refluxed under nitrogen for 50 min, and then 2.0 g (0.014 mol) of 1:4 mixture of 1-methoxy-1-methylsilacyclohex-2-ene and -3-ene (vide supra) in 10 ml of ether was added dropwise, followed by 3.8 g (0.014 mol) of diiodomethane in 3 ml of ether while maintaining reflux. After 48 h reflux, 100 ml of pentane was added, the mixture was washed six times with 100 ml of water, dried over anhydrous Na_2SO_4 , and concentrated by distillation. The residue contained unreacted starting material and a 57:43 mixture of 3-methoxy-3-methyl-3-silabicyclo[4.1.0]heptane and 2-methoxy-2-methyl-2-silabicyclo[4.1.0]heptane. 3-Methoxy-3-methyl-3-silabicyclo[4.1.0]heptane was isolated as a mixture of epimers by preparative GC (column B, 85 °C). The spectral data were as follows: 1H NMR ($CDCl_3$) δ -0.075 (dd, J 5.1, 10.2 Hz, 1H, CH_2), 0.08–0.18 (m, 1H, CH_2), 0.10, 0.15 (two overlapping singlets, 6 H, CH_3), 0.35–1.25 (complex m, 14H, CH_2 and CH), 1.42–1.54 (m, 2H, CH_2), 2.02–2.20 (m, 2H, CH_2), 3.40, 3.45 (two overlapping singlets, 6H, MeO); ^{13}C NMR ($CDCl_3$) δ -1.68, -1.05, 8.15, 8.30, 9.90, 10.11, 10.40, 10.80, 11.61, 12.31, 13.86, 13.89, 21.87, 22.18, 50.85, 50.97; GC-MS m/z (relative intensity) 156 (M^+ , 4), 141 (8), 128 (61), 113 (53), 101 (11), 96 (31), 88 (27), 75 (34), 74 (26), 59 (100), 45 (30). Anal. Found: C, 66.40; H, 11.17. $C_{11}H_{22}OSi$. Calc.: C, 66.60; H, 11.18%.

5.8. 1-Chloro-1-methyl-1-silacyclohex-3-ene (16)

A solution of 7.0 g (0.049 mol) of a 1:4 mixture of 1-methoxy-1-methyl-1-silacyclohex-2-ene and -3-ene (vide supra) in 60 ml of acetyl chloride was refluxed for 2 days. After distillation of the acetyl chloride through a 6 in Vigreux column, further distillation of the residue gave 6.5 g (91% yield) of a 1:4 ratio of 1-chloro-1-methyl-silacyclohex-2-ene and 3-ene, b.p. 110–115 °C (200 mm). The isomeric mixture was used without further purification to synthesize 1-methyl-1-*tert*-butoxy-1-silacyclohex-3-ene. The spectral data for 1-chloro-1-methyl-1-silacyclohex-3-ene were as follows: 1H NMR ($CDCl_3$) δ 0.48 (s, 3H, CH_3), 1.06 (ddd, J 6.6, 8.5, 15.4 Hz, 1H, CH_2), 1.45–2.15 (m, 2H, CH_2), 2.26–2.42 (m, 2H, CH_2), 5.71 (t, J 2.4 Hz, 2H, $CH=CH$); ^{13}C NMR ($CDCl_3$) δ 0.89, 12.73, 15.82, 22.31, 124.08, 130.46; GC-MS m/z (relative intensity) 150 ($M+4^+$, 0.4), 149 ($M+3^+$, 1), 148 ($M+2^+$,

12), 147 ($M + I^+$, 4), 146 (M^+ , 32), 131 (17), 120 (34), 118 (92), 110 (22), 105 (41), 92 (57), 79 (38), 65 (47), 63 (100), 53 (21), 43 (29).

5.9. 1-Methyl-1-tert-butoxy-1-silacyclohex-3-ene (17)

To a solution of 4.4 g (0.034 mol) of freshly distilled quinoline, 4.8 g (0.064 mol) of *tert*-butyl alcohol, and 100 ml of pentane was added dropwise 5.0 g (0.034 mol) of a 1:4 mixture of 1-chloro-1-methyl-1-silacyclohex-2-ene and -3-ene. After refluxing overnight, the mixture was cooled, suction filtered, and concentrated by distillation of the pentane. Short-path distillation of the residue at 140–145 °C (170 mm) gave 3.5 g (56% yield) of a 1:4 ratio of 1-methyl-1-*tert*-butoxy-1-silacyclohex-2-ene and -3-ene. The major isomer, 1-methyl-1-*tert*-butoxy-1-silacyclohex-3-ene, was isolated by preparative GC (column B, 100 °C). The spectral data were as follows: ^1H NMR (CDCl_3) δ 0.17 (s, 3H, CH_3), 0.70 (ddd, J 6.1, 6.9, 13.5 Hz, 1H, CH_2), 0.83 (ddd, J 6.0, 8.6, 14.5 Hz, 1H, CH_2), 1.24–1.32 (m, 1H, partially obscured by 9H singlet of ^tBuO , CH_2), 1.26 (s, 9H, ^tBuO), 1.39 (br d, J 17.5 Hz, 1H, CH_2), 2.11–2.24 (m, 1H, CH_2), 2.29–2.42 (m, 1H, CH_2), 5.56–5.64 (m, 1H, $\text{CH}=\text{CH}$), 5.67–5.75 (m, 1H, $\text{CH}=\text{CH}$); ^{13}C NMR (CDCl_3) δ -0.13, 12.46, 15.98, 23.54, 32.07, 125.87, 130.04. Several attempts to obtain a satisfactory analysis were unsuccessful.

5.10. 3-Methyl-3-tert-butoxy-3-silabicyclo[4.1.0]heptane (12b)

A mixture of 0.46 g (7.0 mmol) of zinc dust, 0.1 g (1.0 mmol) of cuprous chloride, and 15 ml of anhydrous ether was refluxed under nitrogen for 50 min, and then a solution of 0.65 g (3.5 mmol) of isomerically pure 1-methyl-1-*tert*-butoxy-1-silacyclohex-3-ene, obtained by preparative GC (vide supra), in 5 ml of ether was added dropwise, followed by 0.92 g (3.4 mmol) of diiodomethane in 3 ml of ether while maintaining reflux. After 48 h, the reaction mixture was cooled, 50 ml of pentane was added, the mixture was washed six times with 50 ml of water, dried over anhydrous Na_2SO_4 , and concentrated by distillation. The epimers of 3-methyl-3-*tert*-butoxy-3-silabicyclo[4.1.0]heptanes were separated by preparative GC (column C, 100 °C) to obtain the pure minor epimer in early cuts and enriched major epimer in later cuts of the partially resolved GC peak. The spectral data of the major epimer were obtained by subtraction of the minor epimer. The spectral data of the pure minor epimer were as follows: ^1H NMR (300 MHz, CDCl_3) δ -0.09 (ddd, $J_{\text{gem}} = J_{\text{vic}}$ 4.9 Hz, 1H, cyclopropyl CH_2), 0.10 (s, 3H, CH_3), 0.42–0.72 (m, 4H, CH_2 , CH, and cyclopropyl CH_2), 0.78–0.94 (m, 2H, CH_2 and CH), 1.11–1.19 (m,

1H, CH_2), 1.26 (s, 9H, $\text{C}(\text{CH}_3)_3$), 1.28–1.40 (m, 1H, CH_2), 2.10–2.22 (m, 1H, CH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 2.33 (CH_3), 7.87 (CH), 11.33 (CH_2), 12.64 (CH_2), 13.27 (CH_2), 13.31 (CH), 21.57 (CH_2), 32.09 (CH_3), 72.09 (C); GC-MS (70 eV) m/z (relative intensity) 198 (M^+ , 6), 183 (7), 170 (34), 155 (17), 141 (12), 115 (11), 114 (73), 99 (100), 97 (50), 96 (58), 87 (20), 75 (50), 74 (71), 61 (86), 45 (98), 43 (44). Spectral data for the major epimer after subtraction of minor epimer were as follows: ^1H NMR δ 0.09 (ddd, $J_{\text{gem}} = J_{\text{vic}}$ 4.9 Hz, 1H), 0.17 (s, 3H), 0.56–1.15 (m, 7H), 1.23 (s, 9H), 1.38–1.50 (m, 1H), 1.98–2.09 (m, 1H); ^{13}C NMR δ 1.44, 8.00, 12.05, 12.77, 13.15, 13.23, 22.12, 32.09, 72.19. Anal. Found (epimeric mixture): C, 66.40; H, 11.17. $\text{C}_{11}\text{H}_{22}\text{OSi}$. Calc.: C, 66.60; H, 11.18%.

5.11. 2-Trimethylsilylbicyclo[2.2.1]hept-2-ene (9)

The 2-trimethylsilylnorbornene was prepared following the literature procedure [33]. The spectral data were as reported previously. UV λ_{max} (pentane) 206 nm (ϵ 6390).

5.12. *exo*-2-Trimethylsilylbicyclo[2.2.1]heptane (*exo*-23) [32]

The procedure differed from that reported in the literature [32]. To a solution of 10.5 g (0.045 mol) of *exo*-2-trichlorosilylbicyclo[2.2.1]heptane [41] in 100 ml anhydrous ether at -40 °C was added, dropwise under nitrogen, 100 ml (0.15 mol) of 1.5 M methyl lithium in ether. The mixture was warmed to room temperature and stirred overnight. After dropwise addition of water, the organic phase was separated, washed with water, dried over anhydrous magnesium sulfate, and concentrated in vacuo. Fractional distillation of the residue through a 6 in Vigreux column gave 4.7 g (62% yield) of *exo*-2-trimethylsilylbicyclo[2.2.1]heptane (*exo*-23), b.p. 75–80 °C (12 mm). The spectral data were as follows: ^1H NMR (300 MHz, CDCl_3) δ -0.08 (s, 9H, methyl), 0.50 (t, J 8.5 Hz, 1H, methine), 1.10–1.22 (m, 4H, methylene and methine), 1.34–1.40 (m, 2H, methylene), 1.50–1.56 (m, 2H, methylene), 2.20 (d, J 22 Hz, 2H, methylene); ^{13}C NMR (75 MHz, CDCl_3) δ -2.66, 28.90, 29.42, 32.49, 34.32, 36.89, 37.68, 37.81.

5.13. *endo*-2-Trimethylsilylbicyclo[2.2.1]heptane (*endo*-23) [32]

The procedure differed from that reported in the literature [32]. To a thick-walled hydrogenation vessel was added 1.0 g (6.0 mmol) of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (9) (vide supra), 20 mg of 30% palladium on carbon, and 50 ml of acetic acid. The vessel was fitted to a Parr-shaker apparatus and evacuated with

an aspirator three times after pressurizing each time with 25 lbf in⁻² of hydrogen gas. The reaction mixture was shaken for 20 h at room temperature under 50 lbf in⁻² of hydrogen. A 50 ml portion of pentane was added to the resulting solution and water was used to wash the organic layer several times until it turned neutral; the organic layer was dried over anhydrous magnesium sulfate, and concentrated in vacuo. GC-MS analyses of the residue showed complete reduction to *endo*-2-trimethylsilylbicyclo[2.2.1]heptane. The product was purified by preparative GC on column B (100 °C). The spectral data were as follows: ¹H NMR (300 MHz, CDCl₃) δ 0.86–0.95 (m, 1H, methine), 1.03–1.12 (m, 2H, methylene), 1.22–1.34 (m, 2H, methylene), 1.35–1.40 (m, 1H, methylene), 1.42–1.52 (m, 1H, methine), 1.64–1.75 (m, 1H, methine), 2.24–2.32 (m, 2H, methylene); ¹³C NMR (75 Hz, CDCl₃) δ -0.84, 27.99, 29.48, 30.53, 32.19, 37.82, 40.06, 42.42.

5.14. Synthesis of 2-trimethylsilylnortricyclene (**19**) [32]

The compound was prepared by the literature method [32]. The spectral data were as follows: ¹H NMR (CDCl₃) δ 1.95 (br s, 1H, methine), 1.05–1.28 (m, 4H, methylene), 1.08 (s, 1H, methine), 1.01 (s, 1H, methine), 0.99 (s, 1H, methine), 0.62 (s, 1H, methine), 0.02 (s, 9H, methyl); ¹³C NMR (CDCl₃) δ -1.40, 9.94, 10.50, 12.73, 31.49, 32.14, 33.06, 36.42; GC-MS *m/z* (relative intensity) 166 (*M*⁺, 4), 151 (7), 138 (16), 123 (8), 92 (19), 91 (11), 85 (16), 73 (100), 66 (22), 59 (12), 45 (22), 43 (17).

5.15. General procedure for preparative direct photolyses

Photolyses at 214 nm utilized an air-cooled Philips Model 93106 E zinc lamp (Ealing) fitted into a quartz immersion well apparatus of 40 ml volume. Runs with pentane or methanol as the solvents were conducted at 5 °C, with *tert*-butyl alcohol as solvent at 26 °C, and with 2,2,2-trifluoroethanol at 5 °C. Photolysates were purged with nitrogen or argon 1 h prior to and during photolyses. Photolyses utilized 40 mg (0.32 mmol) of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) or 0.2–1.0 g (1.2–6.0 mmol) of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (**9**). Photolyses were monitored by GC or GC-MS analyses of aliquots taken at time intervals. Each 0.25–0.5 ml aliquot was extracted by 0.5 ml of pentane, followed by washing with 0.5 ml of water to remove the alcohol. Aliquots were then dried over anhydrous sodium sulfate and analyzed by GC or GC-MS. Products were quantified using the product yield procedure described below. After photolysis to 30–60% conversion of reactant, pentane was added to those photolyses performed in alcohols, followed by washing several times with water

and drying over sodium sulfate. For all runs, distillation of the pentane through a 6 in Vigreux column gave a residue which was subjected to preparative GC to isolate the products and unreacted starting material. The products were identified by comparison of GC-MS retention times and spectroscopic data with independently synthesized samples, unless noted otherwise. Details for individual runs are given below.

5.16. Preparative direct photolyses of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) in methanol

A solution of 40 mg (0.32 mmol) of silabicycloheptene **8** in 40 ml of methanol was irradiated for 2.5 h following the general procedure. The photoproducts were isolated by preparative GC (column B, 85 °C). ¹H NMR analysis showed the major photoproduct to be a 57:43 mixture of epimers of 1-methyl-1-methoxy-1-silabicyclo[4.1.0]heptanes (**12a**). The silabicycloheptanes **12a** were further identified by comparison of GC retention times (column E, 80 °C), and ¹H, ¹³C NMR and GC-MS spectral data to an independently synthesized sample (*vide supra*). The epimeric mixture of **12a** proved inseparable by capillary GC-MS and by GC on columns A, C, D, F, G, H.

5.17. Preparative direct photolyses of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) in *tert*-butyl alcohol

A solution of 40 mg (0.32 mmol) of silacycloheptene **8** in 40 ml of *tert*-butyl alcohol was irradiated for 2 h following the general procedure described above. GC-MS analyses of aliquots after workup showed only two closely overlapping peaks besides starting material. One corresponded to the major epimer of 1-methyl-1-*tert*-butoxy-1-silabicyclo[4.1.0]heptane at retention time 12.79 min, 198 (*M*⁺, 1), 184 (1), 183 (5), 170 (31), 155 (15), 141 (12), 114 (68), 101 (24), 100 (12), 99 (100), 97 (48), 96 (56), 95 (12), 87 (18), 75 (47), 74 (71), 61 (81), 60 (22), 59 (10), 57 (22), 55 (15), 53 (11), 45 (92); the other corresponded to a minor epimer at retention time 13.05 min, no parent, 184 (1), 183 (6), 170 (37), 155 (17), 141 (12), 115 (11), 114 (75), 101 (22), 100 (12), 99 (100), 98 (11), 97 (51), 96 (56), 95 (11), 87 (18), 75 (44), 74 (71), 61 (74), 57 (20), 45 (87), 43 (34). The photolysate was diluted with 40 ml of pentane, washed eight times with 40 ml of water, and dried over anhydrous sodium sulfate. After distillation of the pentane through a 6 in Vigreux column, GC analysis (column G, 90 °C) of the residue showed the two epimers in a 2:3 ratio, eluting in reverse order compared with GC-MS analyses, which employed a nonpolar column. The minor epimer was isolated in pure form by preparative GC (column C at 100 °C) from an early cut of the two overlapping peaks. Later cuts were only

enriched in the major epimer. The pure epimer and the enriched epimer were identical to independently synthesized samples (vide supra).

5.18. Preparative direct photolyses of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (9) in pentane

Two photolyses were conducted at 214 nm utilizing the general procedure. The first photolysis of 980 mg (5.90 mmol) of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (9) in 40 ml of pentane was for 12 h and corresponded to a relatively low conversion, in order to minimize secondary photolysis of 1-trimethylsilylbicyclo[4.1.0]hept-2-ene (21), which was one of the products isolated by preparative GC (column D at 125 °C). A second major product, trimethylsilylnortricyclene 19, was also isolated from this run. The second photolysis was performed for a longer period of 48 h and employed 450 mg (2.71 mmol) of starting material in 40 ml pentane. The high conversion facilitated partial separation of trimethylsilylmethylenebicyclo[2.1.1]hexane (20) from the overlapping starting material by preparative GC (column D at 115 °C) and made possible the preparative GC isolation of a minor, isomeric product, 1-trimethylsilyl-1,2,6-heptatriene (22). Trimethylsilylnortricyclene 19 was identified by comparison of GC retention times and spectral data with an authentic sample (vide supra).

The ^1H NMR spectrum of 1-trimethylsilylbicyclo[4.1.0]hept-2-ene (21) was identical to that reported previously [35]. ^{13}C NMR (CDCl_3) δ -3.54, 15.72, 17.69, 19.83, 20.81, 124.03, 130.41; GC-MS retention time 11.99 min, m/z (relative intensity) 166 (M^+ , 2), 151 (2), 149 (4), 123 (3), 121 (5), 95 (2), 93 (2), 92 (10), 91 (7), 83 (2), 77 (4), 75 (4), 74 (9), 73 (100), 59 (15), 55 (4), 53 (4), 45 (20), 43 (15).

The spectral data for trimethylsilylmethylenebicyclo[2.1.1]hexane (20) after subtraction of residual starting material were as follows: ^1H NMR (CCl_4) δ 0.05 (s, 9H, methyl), 1.09 (d, J 5.7 Hz, 1H, methylene), 1.54–1.64 (m, 4H, methylene), 2.21–2.26 (t, J 7.2 Hz, 1H, methylene), 2.75–2.79 (m, 1H, methine), 2.92–2.98 (m, 1H, methine), 4.69 (s, 1H, vinyl); ^{13}C NMR (CDCl_3) δ 0.05, 25.09, 34.80, 34.83, 46.39, 49.37, 101.70; GC-MS retention time 10.99 min, m/z (relative intensity), no parent, 153 (0.5), 152 (1), 151 (10), 150 (1), 149 (5), 137 (2), 123 (10), 121 (5), 109 (6), 106 (9), 97 (7), 95 (6), 92 (10), 91 (9), 85 (7), 83 (12), 73 (100), 59 (33), 55 (12), 53 (10), 45 (25), 43 (31).

The spectral data for 1-trimethylsilyl-1,2,6-heptatriene (22) were as follows: ^1H NMR (CDCl_3) δ 0.09 (s, 9H, methyl), 2.03–2.10 (m, 2H, methylene), 2.11–2.17 (m, 2H, methylene), 4.79 (dd, J 6.6 Hz, 1H, vinyl), 4.92 (dt, J_d 7.2, J_t 3.6 Hz, 1H, vinyl), 4.94–5.08 (m, 2H, vinyl), 5.78–5.91 (m, 1H, vinyl); ^{13}C NMR (CDCl_3) δ -0.97, 27.26, 33.76, 82.76, 82.84, 114.76, 138.31, 209.82; GC-MS retention time 11.60 min, m/z

(relative intensity) 166 (M^+ , 0.1), 153 (0.2), 152 (0.7), 151 (5), 149 (2), 137 (1), 123 (3), 107 (3), 106 (6), 92 (5), 91 (4), 83 (4), 74 (9), 73 (10), 59 (14), 45 (25), 43 (19). Anal. Found: C, 72.05; H, 10.87. $\text{C}_{10}\text{H}_{18}\text{Si}$. Calc: C, 72.21, H, 10.91%.

5.19. Preparative direct photolyses of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (9) in *tert*-butyl alcohol

A solution of 220 mg (1.33 mmol) of 2-trimethylsilylbicyclo[2.2.1]heptene (9) in 40 ml of *tert*-butyl alcohol was irradiated for 24 h following the general procedure (vide supra). GC-MS analyses of aliquots after workup showed, in order of elution, the formation of trimethylsilylmethylenebicyclo[2.1.1]hexane (20), 1-trimethylsilyl-1,2,6-heptatriene (22), trimethylsilylnortricyclene 19, and trimethylsilylbicyclo[4.1.0]hept-2-ene (21) in addition to unreacted starting material. The residue obtained after workup (general procedure, vide supra) was subjected to preparative GC (column A at 90 °C) to isolate the major photoproduct, nortricyclene 19, which was further identified by comparison of the GC-MS fragmentation pattern and ^1H , ^{13}C NMR spectral data with an independently synthesized sample (vide supra). The three minor isomers 20, 21, and 22 had identical GC-MS retention times and fragmentation patterns to isomers isolated from the runs performed with pentane as the solvent.

5.20. Preparative direct photolyses of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (9) in methanol

A solution of 210 mg (1.27 mmol) of 2-trimethylsilylbicyclo[2.2.1]heptene in 40 ml of methanol was irradiated for 20 h following the general procedure (vide supra). GC-MS analyses of aliquots after workup showed, in order of elution, a trace amount of nortricyclene, unreacted starting material, trimethylsilylmethylenebicyclo[2.1.1]hexane (20) and 1-trimethylsilyl-1,2,6-heptatriene (22) as minor photoisomers, trimethylsilylnortricyclene 19 as the major photoisomer, a minor photoreduction product *exo*-2-trimethylsilylbicyclo[2.2.1]nortricyclene (*exo*-23), and barely detectable amounts of three minor methanol addition products of reactant 9. Trimethylsilylbicyclo[4.1.0]hept-2-ene 21 was not detected, owing to the proximity of photoreduction product 23. After workup (general procedure, vide supra) the major product, nortricyclene 19 and the minor photoreduction product, *exo*-2-trimethylsilylbicyclo[2.2.1]nortricyclene (*exo*-23), were isolated as a mixture by preparative GC (column A at 85 °C). Since 19 and 23 also could not be separated on columns B or C, the mixture was characterized by comparison of GC-MS retention times and fragmentation patterns and ^1H , ^{13}C NMR spectral data with authentic samples (vide

supra). The two minor isomers of the reactant, **20** and **22**, had identical GC-MS retention times and fragmentation patterns to the isomers isolated from the runs performed with pentane as the solvent.

5.21. Preparative direct photolyses of 2-trimethylsilylcyclo[2.2.1]hept-2-ene (**9**) in 2,2,2-trifluoroethanol

A solution of 110 mg (0.663 mmol) of 2-trimethylsilylbicyclo[2.2.1]heptene **9** in 40 ml of 2,2,2-trifluoroethanol was irradiated for 22 h following the general procedure described above. GC-MS analyses of the residue after workup (general procedure, vide supra) showed eight product peaks in addition to unreacted starting material: norbornene at 3.84 min, m/z (relative intensity) 94 (M^+ , 7), 91 (4), 79 (9), 77 (10), 67 (8), 66 (100), 65 (14), 51 (7), 50 (5), 41 (7); secondary photoisomer of norbornene at 4.45 min, m/z (relative intensity) 94 (M^+ , 30), 93 (10), 91 (15), 80 (8), 79 (100), 78 (13), 77 (40), 66 (93), 65 (21), 53 (10), 51 (17), 41 (27); unreacted starting material at 11.80 min; trimethylsilylmethylenebicyclo[2.1.1]hexane **20** at 11.97 min; 1-trimethylsilyl-1,2,6-heptatriene (**22**) at 12.33 min; trimethylsilylnortricyclene **19** at 12.71 min; trimethylsilylbicyclo[4.1.0]hept-2-ene (**21**) was not detected; alcohol adduct A at 15.33 min, m/z (relative intensity) 266 (M^+ , 0.6), 251 (0.3), 192 (2), 183 (3), 171 (4), 152 (9), 95 (13), 94 (21), 91 (11), 93 (12), 81 (22), 79 (23), 77 (62), 73 (100), 67 (26), 66 (90), 59 (12), 45 (35), 43 (18), 41 (22); alcohol adduct B at 15.51 min, m/z (relative intensity) 266 (M^+ , 0.3), 193 (0.2), 192 (1), 183 (4), 171 (5), 152 (11), 94 (17), 91 (11), 81 (23), 79 (21), 77 (54), 73 (100), 67 (25), 66 (71), 45 (34), 43 (19), 41 (23); alcohol adduct C at 15.60 min, m/z (relative intensity) 268 ($M + 2^+$, 0.1), 267 ($M + 1^+$, 0.3), 266 (M^+ , 2), 251 (1), 193 (1), 192 (7), 167 (2), 110 (10), 93 (14), 79 (16), 77 (25), 73 (100), 67 (18), 66 (61), 59 (18), 45 (27), 41 (14). The reaction mixture was separated into four components by preparative GC on column C. A mixture of norbornene and its secondary photoisomer eluted at 120 °C, and the norbornene in this mixture was identified by comparison of ^1H NMR and GC-MS with an authentic sample. The starting material and photoisomers **19**–**22** eluted together at 170 °C. Only trimethylsilylnortricyclene **19** was present in sufficient amounts for identification by ^1H NMR of this mixture. The mixture of alcohol adducts were collected at 200 °C and were tentatively identified as stereoisomeric 3-trifluoroethoxy-2-trimethylsilylnorbornanes **24** from ^1H NMR spectroscopy, GC-MS data, and elemental analysis. Anal. Found: C, 54.26; H, 7.95. $\text{C}_{12}\text{H}_{21}\text{F}_3\text{OSi}$. Calc.: C, 54.11; H, 7.95%.

5.22. Determination of product yields for photolyses of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**)

Solutions of 0.01–0.02 M silanorbornene **8** plus undecane as internal standard in methanol or *tert*-butyl

alcohol were irradiated following the general procedure for quantum yields (see below). Aliquots taken at low conversions were subjected to the standard workup procedure described above and analysed by GC (column E at 80 °C or 100 °C for the methanol or *tert*-butyl alcohol runs respectively) to determine the quantum yields of 3-alkoxy-3-methyl-3-silabicyclo[4.1.0]heptanes **12a** or **12b**. The photolyses were then continued for a total time of 150–200 min to determine product yields at high conversions. The high conversion run with methanol as solvent showed 37% yield of 3-methoxy-3-methyl-3-silabicyclo[4.1.0]heptane (**12a**) at a retention time of 33 min, ca. 4% of an isomeric, unidentified methanol adduct at 27 min, and 57% unreacted starting material at 15 min; the mixture of epimers **12a** was not separable. The high conversion run with *tert*-butyl alcohol as the solvent showed 24% yield of 3-*tert*-butoxy-3-methyl-3-silabicyclo[4.1.0]heptane (**12b**) as a 65:35 ratio of epimers at retention times of 65 min (major epimer) and 66 min (minor epimer) in addition to 73% unreacted starting material at 12 min.

5.23. Determination of product yields for photolyses of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (**9**)

The product yields for photolyses in pentane, *tert*-butanol, methanol, and 2,2,2-trifluoroethanol as solvents are collected in Table 1. High conversion runs with 0.0075 M trimethylsilylnorbornene **9** in pentane used the general procedure for preparative direct photolyses (vide supra). Runs conducted with 0.01–0.02 M trimethylsilylnorbornene in methanol, *tert*-butyl alcohol, and 2,2,2-trifluoroethanol as the solvents utilized the same procedure employed for quantum yield determinations (vide infra). Trimethylsilylnortricyclene **19** was quantified using a known standard solution with undecane serving as the internal standard, and the identical response factor was used for the isomeric photo-products trimethylsilylmethylenebicyclo[2.1.1]hexane **20**, 1-trimethylsilyl-1,2,6-heptatriene **22**, and trimethylsilylbicyclo[4.1.0]hept-2-ene **21**. In photolyses with methanol, norbornene and 2-trimethylsilylnorbornane were additional products that were quantified using standard mixtures. A standard mixture was also used to quantify the mixture of three solvent adducts observed in trifluoroethanol; the isomeric adducts were assumed to have identical response factors.

For photolyses in pentane and *tert*-butyl alcohol GC analyses (column E at 70 °C), the components eluted in the order **20**, **22**, **19**, **21** with respective retention times of 47 min, 54 min, 59 min, and 62 min. For photolyses in methanol GC analyses (column H at 70 °C), the components eluted in the order **25**, **20**, **22**, **19**, **23**, **24** with retention times of 10 min, 27 min, 31 min, 32 min, 35 min, and 69 min. The order of elution for the trifluoroethanol runs was **25**, **20**, **22**, **19** at 12 min, 54 min, 57 min, and 61 min (column E at 70 °C) and three

solvent adducts at 55, 59, and 63 min (column H at 100 °C).

5.24. Quantum yields for direct photolyses

A jacketed aluminum cell holder and lamp enclosure was used [1,30] with a 15 W Philips Model 93106E zinc lamp (Ealing) and a 25 mm diameter Acton 214-B-1D filter. The lamp enclosure, including filter and sample cell, was flushed at a constant, metered flow of air during photolyses to maintain constant light intensity from run to run. A 10 mm path quartz cylindrical cell containing 3.0 ml of photolysate was maintained at 27 °C for *tert*-butyl alcohol as solvent and at 10 °C for methanol by circulating methanol water from a constant temperature bath. Solutions of 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) and 2-trimethylsilanorbornene **9** in 3.0 ml of alcohol were purged with nitrogen 45 min prior to and during the photolyses. The photolysates were diluted by an equal volume of pentane, washed repeatedly with water, and dried over anhydrous Na₂SO₄ prior to GC analyses. The procedures for product analyses are described above.

Uranyl oxalate actinometry [1,30,31] was performed before and after each photolysis. The quantum yield of all photoproducts are the average of pairwise runs. The quantum yields for 1-methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) are summarized below. Quantum yields for 2-trimethylsilylnorbornene **9** are collected in Table 2.

5.25. 1-Methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) in methanol as solvent

Run 1: reactant, 0.0118 M, 0.0204 mEinstein, product **12a**, 1.11×10^{-3} mmol, $\Phi = 0.055$; percent conversion 3.14%.

Run 2: reactant, 0.0118 M, 0.0204 mEinstein, product **12a**, 1.03×10^{-3} mmol, $\Phi = 0.051$, percent conversion 2.90%.

5.26. 1-Methyl-1-silabicyclo[2.2.1]hept-2-ene (**8**) in *tert*-butyl alcohol as solvent

Run 1: reactant, 0.0215 M, 0.012 mEinstein, product **12b**, 7.61×10^{-4} mmol, $\Phi = 0.063$, percent conversion 1.18%.

Run 2: reactant, 0.0215 M, 0.015 mEinstein, product **12b**, 9.35×10^{-4} mmol, $\Phi = 0.062$, percent conversion 1.45%.

5.27. Photolyses of 2-trimethylsilylbicyclo[2.2.1]hept-2-ene (**9**) in deuterated alcohols

The direct photolyses in pure methanol-*O-d* and 2,2,2-trifluoroethanol-*d*₃ were performed as described for quantum yields determinations. Two photolyses of

0.01 M trimethylsilylnorbornene **9** in alcohol or deuterated alcohol were taken to less than 5% conversion, and then aliquots were diluted with pentane and washed with water. GC-MS data obtained under identical experimental conditions for the two runs were compared to determine the extent of deuterium incorporation in products and reactants [42].

With methanol-*O-d* (99.5 + at.% D) as solvent, compounds **9**, **19**, **20**, **22**, **23** and trace amounts of **24** and **25** were detected. Isomers **9**, **19**, **20** and **22** were more than 97% undeuterated. Compound **23** was 100% monodeuterated, **24** was 93% deuterated, and **25** was 100% deuterated. The parent ion at *m/z* 199 of the monodeuterated compound **24** was weak, so the calculation of isotopic distribution used the M-15 (loss of methyl) fragment ion.

With 2,2,2-trifluoroethanol-*d*₃ (CF₃CD₂OD, Cambridge, 99 at.% D) as the solvent, compounds **9**, **19**, **20**, **22**, **24**, and **25** were detected. Compounds **9**, **19**, **20**, and **22** were undeuterated and **25** was 100% monodeuterated. The parent ion at *m/z* 269 indicated compound **24** was trideuterated. As it was weak, the *m/z* 184 fragment ion (loss of CD₂CF₃) was used to calculate the extent of monodeuteration, which was 100%.

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